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LOW-RANK COAL RESEARCH
FINAL TECHNICAL REPORT
APRIL 1, 1988 - JUNE 30, 1989
INCLUDING QUARTERLY REPORT FOR APRIL TO JUNE 1989
COOPERATIVE AGREEMENT DE-FC21-86MC10637

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U.S. Department of Energy
Morgantown Energy Technology Center
Morgantown, West Virginia

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1.0 TABLE OF CONTENTS

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TABLE OF CONTENTS

1.0 TABLE OF CONTENTS

2.0 CONTROL TECHNOLOGY AND COAL PREPARATION RESEARCH

- 2.1 SO_x/NO_x Control
- 2.2 Waste Management

3.0 ADVANCED RESEARCH AND TECHNOLOGY DEVELOPMENT

- 3.1 Turbine Combustion Phenomena
- 3.2 Combustion Inorganic Transformation
- 3.3 Coal/Char Reactivity
- 3.4 Liquefaction Reactivity of Low-Rank Coals
- 3.5 Gasification Ash and Slag Characterization
- 3.6 Fine Particulate Emissions (Completed 3/88)

4.0 COMBUSTION RESEARCH

- 4.1 Fluidized Bed Combustion
- 4.2 Beneficiation of Low-Rank Coals
- 4.3 Combustion Characterization of Low-Rank Coal Fuels
- 4.4 Diesel Utilization of Low-Rank Coals

5.0 LIQUEFACTION RESEARCH

- 5.1 Low-Rank Coal Direct Liquefaction

6.0 GASIFICATION RESEARCH

- 6.1 Hydrogen Production from Low-Rank Coals
- 6.2 Advanced Wastewater Treatment
- 6.3 Mild Gasification (Completed 3/89)
- 6.4 Color and Residual COD Removal from Synfuel
Wastewaters (Completed 3/88)
- 6.5 Great Plains Gasification Plant (Completed 6/87)
- 6.6 Gasifier Optimization (Completed 2/89)

2.0 CONTROL TECHNOLOGY AND COAL PREPARATION RESEARCH

2.1 SO_x/NO_x Control

SO_x/NO_x CONTROL - CATALYTIC FABRIC FILTRATION FOR
SIMULTANEOUS NO_x AND PARTICULATE CONTROL

FINAL TECHNICAL REPORT FOR THE PERIOD APRIL 1, 1988 - JUNE 30, 1989
INCLUDING THE QUARTERLY TECHNICAL
PROGRESS REPORT FOR THE PERIOD APRIL THROUGH JUNE, 1989

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TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT.....	1
1.0 INTRODUCTION.....	3
1.1 Background.....	4
1.1.1 OCF Laboratory Results.....	4
1.1.2 Slipstream Sample Trials at EMRC.....	7
1.1.3 Bag Trial at EMRC.....	9
2.0 GOALS AND OBJECTIVES.....	11
2.1 Three-Year Objectives.....	12
2.1.1 Task A. Catalyst/Fabric Development.....	12
2.1.2 Task B. Fabric Screening Tests.....	13
2.1.3 Task C. Bag Evaluation and Parametric Tests.....	13
2.1.4 Task D. Bag Durability and Process Assessment.....	13
2.2 Changes to the Third-Year Project Plan.....	14
3.0 ACCOMPLISHMENTS.....	15
3.1 Task A. Catalyst/Fabric Development.....	15
3.1.1 Description of Facilities and Procedures.....	16
3.1.2 Results and Discussion.....	17
4.0 CONCLUSIONS.....	38
4.1 Bench-Scale Fabric Screening Tests.....	38
4.2 Bench-Scale Parametric Tests.....	38
5.0 RECOMMENDATIONS.....	39
6.0 REFERENCES.....	39

LIST OF TABLES

<u>Table</u>	<u>Page</u>
1. Flue Gas Compositions.....	6
2. Slipstream Sampler Test Conditions.....	8
3. NO _x Reduction Efficiencies for Catalytic Fabric Samples.....	9
4. MIT Flex Data for Catalytic and Nextel Cloths.....	11
5. Summary of Results from Bench-Scale Catalytic Fabric Filter Experiments.....	18
6. Surface Area Data for Catalyst-Coated Fabric Samples.....	21
7. Full Factorial Experimental Design for Parametric Tests.....	23
8. Experimental Data Resulting from Parametric Tests.....	24
9. Operating Conditions Used During Fabric Screening Tests.....	27
10. Description of Catalytic Fabric Samples Evaluated During Screening Tests.....	28
11. Experimental Data Resulting from Fabric Screening Tests.....	29
12. Surface Area Data for Catalyst-Coated Fabric Samples Evaluated During Screening Tests.....	33
13. Experimental Design Parameters.....	35
14. Results from Second Series of Parametric Tests.....	35

LIST OF FIGURES

<u>Figure</u>	<u>Page</u>
1. Block Diagram of OCF Laboratory Apparatus Used to Evaluate Catalytic Fabric Activity.....	5
2. Fractional Decreases in NO _x Concentration As a Function of Temperature and Face Velocity.....	6
3. Schematic of Slipstream Sampler.....	8
4. Schematic of Fabric Filter Folder and Slipstream Sample System..	16
5. Scanning Electron Micrographs of Unexposed and Exposed Catalytic Fabric.....	20
6. Percent NO _x Removal Versus Air-To-Cloth Ratio and Ammonia/NO _x Molar Ratio.....	25
7. Percent NO _x Removal and Ammonia-Slip Data For Fabric Samples 4, 8 through 13, and 16.....	29
8. Percent NO _x Removal and Ammonia-Slip Data for Fabric Samples 1, 2, 3, 5, 6, 7, 14 and 15.....	30
9. BET Surface Area Versus Ammonia-Slip for Fabric Samples After Exposure to Flue Gas.....	34
10. Percent NO _x Removal Versus Air-To-Cloth Ratio and Ammonia/NO _x Molar Ratio.....	37

ABSTRACT

The objective of the University of North Dakota Energy and Mineral Research Center (EMRC) SO_x/NO_x Control Project is to develop a catalytic fabric filter for NO_x and particulate control that will provide high removal efficiency of NO_x and particulate matter, acceptably long bag and catalyst life, and an economic savings over a conventional SCR system and baghouse. Specific goals of the proposed work include development of a catalytic fabric that will provide:

1. 90% NO_x removal efficiency with <25 ppm ammonia-slip.
2. Particulate removal efficiency of >99.5%.
3. Bag/catalyst life of >1 year.
4. 20% cost savings over a conventional baghouse and SCR control technology.
5. Compatibility with SO_2 removal systems.
6. A nonhazardous waste product.

The experimental approach to meeting the stated project objectives involves further fabric and catalyst development, testing of the product at three levels, and selection of the best fabric for longer-term durability testing. The work is divided into four tasks: Task A - Catalyst/Fabric Development, Task B - Fabric Screening Tests, Task C - Bag Evaluation and Parametric Tests, and Task D - Bag Durability and Process Assessment. This report documents activities and results for Task A from April, 1988 through June, 1989.

Even though promising results were obtained previously, a continued bench-scale effort was determined to be necessary to develop the product that will give the best combination of high NO_x removal efficiency, low ammonia-slip, high particulate removal efficiency, and long catalyst/bag life. Specific parametric tests were conducted in which the fabric weave, coating composition, and coating process were adjusted to develop acceptable fabrics for further testing. Task A, the first level of screening, was employed to test the catalytic activity of the fabric in a simulated flue gas environment using a bench-scale fabric filter holder. Two series of parametric experiments were completed along with screening tests evaluating 16 catalytic fabric samples. The fabric samples used during all phases of the experimental effort were prepared by Owens-Corning Fiberglass Inc. and provided as a cost share to the project.

The completed parametric experiments involved two full factorial designs with four factors and two levels. Independent variables included NO_x concentration, SO_2 concentration, ammonia/ NO_x molar ratio, and air-to-cloth ratio. Dependent variables included NO_x removal efficiency, ammonia-slip, and SO_3 production. Statistical analysis of the results of the experiments showed that NO_x concentration, air-to-cloth ratio, and the interaction between NO_x concentration and air-to-cloth ratio had the greatest effect on NO_x removal efficiency. To a lesser degree, the ammonia/ NO_x molar ratio, the SO_2 concentration, and the interaction between NO_x and SO_2 concentration also were

observed to effect NO_x removal efficiency. Depending on experimental conditions, NO_x removal efficiency ranged from 53% to 96% and ammonia-slip values ranged from 2 to 580 ppm.

Sixteen catalytic fabric samples were evaluated using the bench-scale fabric filter holder and simulated flue gas system. The fabric samples were prepared to evaluate the effect of modifying the catalyst composition, applying the catalyst using a single coat of concentrated solution or multiple coats of a dilute solution, using a refractory undercoat, and using a textured or nontextured weave. NO_x removal efficiency and ammonia-slip values ranged from 3% to 93% and 2 to 341 ppm, respectively.

Modification of the catalyst composition by adding small amounts of alumina or zirconium to the original catalyst substantially reduced the catalytic reactivity of the fabrics tested. The purpose for adding the refractory components was to determine if the operating temperature range could be expanded.

NO_x removal efficiency and ammonia-slip data did not indicate an advantage one way or another for fabric samples prepared using multiple coats of a low concentration solution versus a single coat of a high concentration solution. Increases in NO_x removal efficiency and decreased ammonia-slip was observed when the quantity of catalyst placed on the fabric was increased through the use of multiple coatings of the catalytic solution.

The purpose for applying an undercoat to the glass fabric prior to the catalyst is to improve the abrasion resistance of the glass fibers and potentially develop more surface area. Data from the fabric screening tests indicated that the use of a refractory undercoat had no effect on NO_x removal or ammonia-slip.

The use of a textured fabric improved the catalytic performance of the catalyst-coated fabrics tested. Fabric comparisons in one case showed an increase in NO_x removal efficiency from 82% to 93% and a decrease in ammonia-slip from 56 ppm to 35 ppm. In a second case, comparison of two fabric samples that provided essentially identical NO_x removal values (84% versus 85%), showed that ammonia-slip was substantially less for the textured fabric (2 ppm versus 53 ppm).

Although the Task A effort was a preliminary step in the overall approach to development of the catalytic fabric filter, the positive results warrant proceeding with Task B - Fabric Screening Tests. Task B will be initiated and completed during a twelve month period beginning July 1, 1989 and ending June 30, 1990. Catalytic fabric samples will be selected for additional screening tests based on Task A results. The purpose of Task B will be to further evaluate the impact of air-to-cloth ratio, NO_x concentration, SO_2 concentration, coal type, and their interactions on NO_x removal efficiency, ammonia-slip, SO_3 production, and particulate control. Four coals will be used, two bituminous coals, a subbituminous coal, and a lignite. The coals will be fired in a pilot-scale pc-fired combustor and the fabrics will be tested using a slipstream of flue gas and the bench-scale fabric filter holder and oven used to perform Task A experiments.

1.0 INTRODUCTION

In 1983 the Grand Forks Energy Technology Center of the U.S. Department of Energy was transferred to the University of North Dakota. From April 1, 1983, through June, 1987, the facility had been operating as a nonprofit contract research organization called the University of North Dakota Energy Research Center (UNDERC). In June, 1987, the name was changed to the Energy and Mineral Research Center (EMRC), University of North Dakota. Department of Energy programs ongoing at the time of the 1983 transfer were continued under a three-year Cooperative Agreement with the Department of Energy. In 1986 a second multiyear Cooperative Agreement (Contract No. DE-FC21-86MC10637) was signed by the Department of Energy. This report documents the results for the SO_x/NO_x Control Project for the period April 1, 1988, through June 30, 1989. The highlights of previous work, current program goals and objectives, third-year accomplishments on a task basis, and conclusions based on the work completed are summarized.

Acid rain and the passage of legislation to reduce emissions of acid rain precursors continue to be prominent issues in the United States, Canada, Europe and Japan. Although SO_2 emissions are still the primary focus of acid rain control legislation in the United States, the role of NO_x in acid rain has become more prominent as a result of recent studies that have linked nitrate deposition to vegetation damage. In Europe, substantial reductions in NO_x emissions have been mandated, requiring local utilities to apply both staged combustion and post-combustion technologies to existing and new fossil fuel-fired systems. Selective catalytic reduction (SCR), an NO_x control technology originally developed in Japan, has been installed on more than 6,400 MW of full-scale utility boiler capacity as a post-combustion NO_x control technique in the Federal Republic of Germany (1), with a total of over 20,000 MW planned by 1990. The purpose of the initial full-scale demonstration projects is to evaluate and modify a technology originally designed for use on oil- and gas-fired systems. Application of conventional SCR technology to coal-fired systems presents several potential problems including catalyst plugging/deactivation due to fly ash and SO_3 , deposition on, and corrosion of air heater surfaces due to sulfur/ammonia by-products, solid waste handling/reuse/disposal problems, and general compatibility problems with existing coal-fired systems.

The overall project objective during the first and second years of the Cooperative Agreement was to expand the scientific and engineering data base necessary for the development of innovative processes to control SO_x emissions during coal combustion. Dry sorbent injection for SO_x control and methods of enhancing SO_x sorbent reactivity/utilization were investigated. The study addressed factors impacting both sorbent reactivity and operability of the combustion system for new and retrofit applications. Specific factors addressed included: 1) sorbent properties, 2) sorbent processing conditions, 3) the impact of sorbent injection on boiler performance, and 4) operability of the particulate control device.

Results from furnace injection work completed in the first and second years have not shown potential for substantial improvement in the levels of SO_2 control or sorbent utilization beyond those already demonstrated (2,3). Based on these results, EMRC believes that further pilot-scale work in the area of furnace sorbent injection is not necessary under the UND/DOE

Cooperative Agreement and would only be useful in support of site-specific utility evaluations of the technology. The future of furnace sorbent injection really rests with the demonstration projects being funded by EPA, EPRI, and the DOE Clean Coal Technology Program, as well as with the passage and implementation of acid rain legislation.

Therefore, plans were implemented to redirect the SO_x/NO_x Control Project. The focus of the project is now on advanced NO_x control with application to new and retrofit utility systems, as well as control of NO_x emissions from industrial-scale combustors. The overall objective of the project is to evaluate the potential of a catalytic fabric filter for simultaneous NO_x and particulate control.

1.1 Background

Initial development activities were carried out and funded exclusively by Owens-Corning Fiberglas Inc. (OCF). Following several years of in-house development, OCF contracted with the University of North Dakota Energy & Mineral Research Center (EMRC) to assist with the development effort. Due to funding constraints, the development work was discontinued in the fall of 1986.

In April of 1988 the development effort was resumed by OCF and EMRC. OCF activities are funded in-house and primarily involve preparation of catalytic fabrics for bench-scale experiments that are performed at EMRC. EMRC activities in the past fifteen months, funded within the Cooperative Agreement with the U.S. Department of Energy (DOE), have focused on bench-scale experiments designed to show continuity with previous work and screen several samples of catalytic fabric.

The general concept of a filter bag with catalytic properties is mentioned in a recent patent (4), though without details or supporting data. Within the last eight years, OCF has undertaken an extensive research effort to develop a catalytic fabric to be used in filter bags for simultaneous NO_x and particulate control. The key to this research effort has been the development of novel methods for producing highly active catalysts on glass fibers. The properties of the materials developed are summarized in the following discussion.

1.1.1 OCF Laboratory Results

A block diagram of the OCF laboratory apparatus used to evaluate catalytic activity is shown in Figure 1. The flow rates of the gases used were individually controlled by mass flow controllers (Matheson Model 10) to achieve the desired simulated flue gas composition and velocity. The gas mixture was passed through a Pyrex glass heat exchanger, then through a single thickness of the test cloth contained in a glass filter holder, and held within an oven. An all-glass filter holder was required because other materials such as 316 stainless steel, nickel, and copper, are slightly catalytic at elevated temperatures (5,6), and interfere with the measurement. After passing through the test fabric, the simulated flue gas entered a sample conditioner (Thermoelectron Model 90) and finally, a

Figure 1. Block diagram of OCF laboratory apparatus used to evaluate catalytic fabric activity.

chemiluminescent NO analyzer (Thermoelectron Model 10A). NO_x and ammonia concentrations were also measured using catalytic converters that converted these species to NO.

The steady state catalytic activity of a fabric sample was typically measured at seven different temperatures, each at four different face velocities. The composition of the simulated flue gas chosen for the laboratory tests is listed in the third column of Table 1. Although the simulated flue gas did not contain water, particulates, and minor flue gas components, it did contain ammonia, which is the reducing agent required for catalytic NO_x reduction. Catalyzed NO_x reduction reactions include:

Typical results for the OCF catalytic fabric are shown in Figure 2. The fractional decreases in NO_x concentration are plotted as a function of temperature and face velocity. For example, at a temperature of 350°C (662°F) and a face velocity of 0.6 m/min (2 ft/min), the fabric eliminated 90% of the NO_x in the gas stream. It should be noted that the OCF catalytic fabric exhibits an extraordinary degree of catalytic activity. If the fabric is 1 millimeter thick, a face velocity of 0.6 m/min (2 ft/min) is equivalent to a

TABLE 1
FLUE GAS COMPOSITIONS

Component	Typical Flue Gas, Vol%	Simulated Flue Gas, Vol%
N ₂	73.76	78.1
O ₂	4.83	6.0
CO ₂	12.31	15.7
SO ₂	0.24	0.0
SO ₃	0.0024	0.0
NO	0.06	0.1
NH ₃	0.0	0.1
HCl	0.01	0.0
H ₂ O	8.79	0.0
Particulates	15 g/m ³	0.0

Figure 2. Fractional decreases in NO_x concentration as a function of temperature and face velocity (7).

space velocity of 40,000/hour. Typical SCR catalysts operate at much lower space velocities ranging from 2,000 to 10,000/hour. The high degree of catalytic activity was expected, and is attributed to the mass transfer advantages inherent in using a high external-surface-area fiber, and in the exploitation of novel materials and processing techniques developed at OCF for producing catalytic materials.

The primary difference between the catalytic filter bag and conventional SCR technology is the catalyst support. Conventional SCR technology uses a honeycomb support structure. The catalytic fabric is prepared by coating the surface of an S-glass (high-temperature) cloth, resulting in a catalyst bonded to the surface of the fabric. The catalytic coating consists of a combination of titanium isopropoxide and vanadium tri-n-propoxide oxide, sometimes called "sol-gel" materials. After the fabric has been coated, the sol-gels hydrolyze during air-drying, resulting in a highly porous layer. The fabric is then cured at low temperature to drive off any residual organics and partially densify the coating. The final product is a highly porous catalytic coating strongly bonded to the surface of the glass fabric.

1.1.2 Slipstream Sample Trials at EMRC

While early in-house conversion efficiency results were promising, several critical flue gas conditions could not be duplicated in the OCF laboratory. For example, the effects of fly ash, sulfur, water vapor, and trace constituents on the catalytic cloth remained unknown. For these reasons, OCF contracted with EMRC to evaluate the NO_x reduction capability of the fabric while filtering fly ash from a pulverized coal-fired furnace. Velva, North Dakota lignite was fired in EMRC's Particulate Test Combustor (PTC) to produce fly ash and a source of flue gas. A description of the PTC has been presented in previous publications (2,3).

Since full bag samples of the test fabrics were not immediately available, a special slipstream sampler was designed and constructed by EMRC to test fabric samples of about 0.5 ft² in size prepared by OCF. The fabric sample was housed in an oven maintained at $650 \pm 25^\circ\text{F}$, and flue gas was drawn through the filter sample at an air-to-cloth ratio of 2.0 ft/min. After passing through the filter, the flow was split, with about 10 scfh going to a sample conditioner and flue gas analyzers, and the balance of about 20 scfh going to a gas pump and dry gas meter for control of the total flow. A drawing of the sampling scheme is shown in Figure 3. For these tests, ammonia was injected into the system well upstream of the sample point to insure sufficient mixing with the flue gas stream prior to sampling with the slipstream sampler.

In all, fifteen different catalytic fabric samples were tested in 8- to 11-hour runs (8). The samples represented variations in cloth composition, weave, and coating procedure. Average experimental conditions under which the samples were run are listed in Table 2. Conversion efficiencies, or percent NO_x removal for the fifteen samples are presented in Table 3. Overall, NO_x removal efficiencies ranged from 70% to 93% at an ammonia/ NO_x molar ratio of <1.0 . The non-catalytic blank was included to eliminate the possibility of NO_x removal due to: 1) reaction with ammonia, or 2) interaction with the fly ash or dust cake. Conversion efficiencies did not decrease with time as was thought possible due to catalyst blinding or fly ash build-up on the fabric;

Figure 3. Schematic of slipstream sampler.

TABLE 2
SLIPSTREAM SAMPLER TEST CONDITIONS

Temperature	650°F
NO _x inlet concentration	800 ppm
SO ₂ inlet concentration	300 ppm
Vol. % O ₂	5%
Vol. % CO ₂	15.5%
Air-to-cloth ratio	2 ft/min
Ammonia/NO _x molar ratio	<1.0
Test duration	11 hours

TABLE 3
NO_x REMOVAL EFFICIENCIES FOR CATALYTIC FABRIC SAMPLES

<u>Sample</u>	<u>% NO_x Reduction</u>
EMRC 1	83
EMRC 2	93
EMRC 3 ^a	4
EMRC 4	87
EMRC 5	92
EMRC 6	77
EMRC 7	85
EMRC 8	82
EMRC 9	85
EMRC 10	86
EMRC 11	76
EMRC 12	80
EMRC 13	82
EMRC 14	81
EMRC 16	70

^a Blank; non-catalytic glass cloth.

if anything, NO_x removal efficiency increased during the first few hours of testing, then stabilized. Cloth durability also appeared to be good for all catalytic samples.

1.1.3 Bag Trial at EMRC

The next logical step for proof-of-concept of the catalytic filter bags was construction and testing of bags. Nine bags approximately 4 feet long and 7 inches in diameter were constructed and placed in operation. Experimental conditions were similar to those used for the slipstream sampler (see Table 2). Test duration was planned to be approximately 100 hours and the primary objective was to demonstrate NO_x reduction and bag durability with time (8).

Low NO_x removal efficiency (roughly 50 percent) was observed early in the test, caused, at least in part by an air leak in the baghouse. It was also noted that the conversion efficiency dropped each time the bags were cooled and reheated; the cooling/reheating cycle occurred three times during the test period when the baghouse was taken off-line to seal air leaks. SEM analyses of a used bag revealed the presence of fibrils on the cloth surface that were not observed on the surface of fabrics with good activity. Further analysis using x-ray diffraction (XRD) indicated the presence of sodium sulfite, which probably condensed on the cloth as the flue gas cooled. Speculation at that time was that the sodium sulfite covered the catalyst surface, reducing activity. Both alkaline metal poisoning and deposition of ammonium bisulfate have been reported to reduce the activity of SCR catalysts when rapid cooling occurred in the presence of flue gas or ammonia and SO_x (9,10). However, this can be avoided by purging the catalyst prior to cooling. Recent work by EMRC

personnel has shown that silicone gasket material may have contributed to the cause of reduced catalyst activity. This issue is discussed in more detail in section 3.0, Accomplishments.

Later in the test, the original bags were removed and three new bags were installed. The temperature was not changed during the course of this run. Even though the air-to-cloth ratio was higher than in earlier tests (approximately 4 rather than 2 ft/min) and the baghouse temperature lower, NO_x reduction averaged about 77 percent. After two days of operation, NO_x removal efficiency had not decreased, and equally important, no holes or tears were found in the bags. These results indicate that good NO_x removal and bag durability were obtained, at least in a short test period. In addition, temperature cycling in the presence of ammonia should be avoided, although it is not expected to be a major obstacle, since conventional baghouses cannot tolerate excessive temperature cycling without damaging the bags.

While NO_x removal is of major importance for the successful development of the catalytic filter bag, also critical is the durability of the bag. Because of the higher (650°F) operating temperature of the bags, conventional Teflon® coatings for abrasion resistance cannot be utilized. Therefore, other high-temperature abrasion-resistant coatings had to be developed.

Nextel 312, manufactured by 3M Company, has been used in high-temperature filtration applications, and its abrasion resistance appears acceptable (11,12). Nextel was used as a standard against which OCF candidates for abrasion-resistant cloth were compared. The method of comparison was the room-temperature MIT flex test, in which a cloth is repeatedly folded until failure occurs. Results are reported as the number of cycles to failure. For comparison, Table 4 presents the MIT flex numbers for Nextel and a catalytic cloth. Results are reported for both as-received samples and heat-treated (8 hours at 650°F) cloths. For both cases, the catalytic fabric appeared to perform better than Nextel.

In an ongoing program at EMRC, Nextel fabric has been tested for over 16,000 hours in a nine-bag slipstream baghouse without a bag failure (13). This shows that a high-temperature fabric can sustain long-term operation when filtering coal fly ash. Since the catalyst-coated cloth performed better than the Nextel fabric in the MIT flex tests, it is expected that the catalytic fabric life would be at least as good as the Nextel fabric.

The initial work demonstrated the following with respect to the catalytic filter bag concept:

1. Good economic potential.
2. Over 90% reduction of NO_x in a flue gas stream.
3. Promising self abrasion characteristics.

Further study was determined to be needed in the following areas:

1. Although ammonia-slip does not appear to be a problem, it is anticipated that excess ammonia levels can be reduced by lowering the ammonia/ NO_x molar ratio and by altering the catalyst composition.

TABLE 4

MIT FLEX DATA FOR CATALYTIC AND NEXTEL CLOTHS
(Reported as Number of Cycles to Failure)

<u>Sample</u>	<u>As-Received</u>	<u>Heat-Treated (8 hrs at 650°F)</u>
Catalytic Cloth	140	135
Nxtel	32	25

All tests were run at ammonia/NO_x molar ratios of ≤ 1.0 , with ammonia-slip values ranging from 2 to 25 ppm. Continuous monitoring techniques for ammonia would be very useful in the development and commercialization of the technology.

2. Earlier tests showed that SO₂-to-SO₃ conversion due to the catalyst was not a problem, but changes in coal type, catalyst composition, temperature, and use of a better measurement technique could reveal a potential problem.
3. Although the MIT flex data indicated good abrasive characteristics, and no degradation in catalytic activity has been measured in a 24-hour period while filtering fly ash from flue gas emitted from a coal-fired furnace, an acceptable bag life has yet to be demonstrated.
4. Parameters such as fabric weave style, air-to-cloth ratio, and ammonia/NO_x molar ratio have not been optimized with respect to filtration efficiency and NO_x removal. The catalyst morphology, composition, and operating temperature have been optimized in the laboratory, but may need to be altered in response to catalyst or filtration problems.
5. Pilot-scale development efforts will have to address the effects of coal type (sulfur content and ash characteristics), ammonia/NO_x molar ratio, air-to-cloth ratio (1.5 to 6.0 ft/min), temperature cycling (250°-750°F), and fabric cleaning mode (reverse-gas and pulse-jet) on catalytic fabric performance. Performance will be based on NO_x removal, ammonia-slip, SO₃ production, particulate control efficiency, operating pressure drop, and catalyst/bag durability.
6. Based on the results of the pilot-scale effort, a technical and economic assessment of the technology will be necessary prior to performance of a demonstration test. The demonstration test should be at least one year in duration and at a scale of 1 to 10 MW.

2.0 GOALS AND OBJECTIVES

The U.S. Department of Energy, Pittsburgh Energy Technology Center (DOE-PETC) Combined SO_x/NO_x Control Program, initiated as part of the Flue Gas

Cleanup Program, has emphasized the development of novel approaches. The objective of the program is to develop a combined SO_x/NO_x flue gas cleanup technology through the proof-of-concept stage by October 1992, at which time the technology should be ready for private-sector commercialization. The technology must be capable of reducing both SO_2 and NO_x emissions by 90% at a levelized cost of at least 20% less than the costs of conventional limestone scrubbing and selective catalytic reduction (SCR). Process by-products must be saleable or classified as nonhazardous wastes suitable for landfill disposal.

The objective of the University of North Dakota Energy and Mineral Research Center (EMRC) SO_x/NO_x Control Project is to develop a catalytic fabric filter for NO_x and particulate control that will provide high removal efficiency of NO_x and particulate matter, acceptably long bag and catalyst life, and an economic savings over a conventional SCR system and baghouse. Specific goals of the proposed work include development of a catalytic fabric that will provide:

1. 90% NO_x removal efficiency with <25 ppm ammonia slip.
2. Particulate removal efficiency of >99.5%.
3. Bag/catalyst life of >1 year.
4. 20% cost savings over a conventional baghouse and SCR control technology.
5. Compatibility with SO_2 removal systems.
6. A nonhazardous waste product.

2.1 Three-year Objectives

The experimental approach to meeting the stated project objectives involves further fabric and catalyst development, testing of the product at three levels, and selection of the best fabric for longer-term durability testing. The work is divided into four tasks. Owens-Corning Fiberglas Inc. will prepare and provide, at no cost to the program, catalytic fabric samples and filter bags for use in the testing.

2.1.1 Task A, Catalyst/Fabric Development

Even though promising results have been obtained previously, a continued effort was needed to develop the product that will give the best combination of high NO_x removal capability, low ammonia-slip, high particulate removal efficiency, and long bag life. Specific parametric tests were conducted in which the fabric weave, coating composition, and coating process were adjusted to develop acceptable fabrics for further testing. Task A, the first level of screening, was employed to test the catalytic activity of the fabric in a simulated flue gas environment using a slipstream sampler. Data generated from the system included NO_x removal efficiency, ammonia-slip, SO_3 production, and particulate collection efficiency. Several fabric samples from this development effort have been chosen for further evaluation in Task B. Task A was essentially complete at the end of the past program year (April 1988-June 1989), but a small effort is planned for each of the next three years to support larger-scale development activities.

2.1.2 Task B, Fabric Screening Tests

Task B is designed to further evaluate samples developed in Task A while filtering fly ash from a pulverized coal-fired combustion facility. Fabric samples will be tested under actual flue gas conditions (e.g., 650°F, fly ash and SO_x present) to determine the effect of coal type/fly ash on catalytic activity. It is critical that the fabric be tested in an actual flue gas stream produced from the combustion of coal since submicron particles, volatile species, and trace elements are present which may affect the catalyst. Testing in a simulated flue gas stream with reentrained fly ash would not produce the same effect, since volatile species would not be present, and submicron fly ash particles are not easily reentrained as separate particles. Task B testing will include the use of four different coals and measurement of NO_x removal efficiency, ammonia-slip, and particulate removal efficiency. Task B will allow testing of a maximum number of fabric samples in an actual flue gas environment at a minimum cost. Since the slipstream sampler will test fabric swatches of <1.0 ft² in area, the cost of making multiple sets of full bags is avoided. The best-performing fabric samples will be selected from Task B results for further evaluation in full bag tests. Task B will be initiated and completed in the program year beginning July 1, 1989.

2.1.3 Task C, Bag Evaluation and Parametric Tests

Task C is the second level of fabric testing in the proposed work. Approximately five of the best fabrics developed in Tasks A and B will be made into bags and tested in a baghouse. The baghouse will filter fly ash from a pilot-scale pulverized coal-fired combustor during 100-hour tests. Test parameters will include ammonia/NO_x molar ratio, air-to-cloth ratio, temperature, cleaning mode, and coal type. Four coals will be selected for Tasks B and C at the beginning of the proposed work. It is important that several coals with different properties are included in the evaluation process, since the level of submicron particles, volatile trace elements, and SO₂/SO₃ ratio are highly dependent on coal type and may have varying effects on the catalytic fabric (14,15,16). In addition, particulate removal efficiency in a fabric filter is coal specific; therefore, tests of particulate penetration must include several coals (17,18,19). At the completion of Task C, an assessment of the technology will be made to determine if longer-term durability testing of the fabric will proceed or if further fabric development is needed. Task C will start in the program year beginning July 1, 1989, and will be completed as an add-on to the Cooperative Agreement, or under a separate contract. Additional cost share on the part of OCF and other commercial sources is likely for Task C.

2.1.4 Task D, Bag Durability and Process Assessment

Task D will proceed if Task C results are satisfactory. Two fabrics, based on results of Tasks A, B, and C, will be selected for 500-hour durability tests. The primary purpose of these tests is to evaluate the durability of the fabric and catalyst in longer-term testing with multiple cleaning cycles and dust cake build-up on the fabric. Following the 500-hour tests, an economic and technical assessment of the process, along with recommendations for further development, will be completed as part of Task D.

Task D will be performed as an add-on to the Cooperative Agreement, or under a separate contract. Additional cost share on the part of OCF and other commercial sources is likely for Task D.

EMRC has prepared and submitted a proposal entitled "Catalytic Fabric Filtration for Simultaneous NO_x and particulate Control," in response to a DOE/PETC solicitation for proposals entitled, "Development of Advanced NO_x Control Concepts for Coal-Fired Utility Boilers." The proposal outlined a three-year pilot-scale project that entailed the development activities discussed briefly in Tasks C and D above. The proposed project includes a 46% commercial cost share and, if selected for funding, should begin in late 1989 or early 1990.

2.2 Changes to the Third-Year Project Plan

Several modifications and one significant change were made to the third-year project plan. The first modification made to the SO_x/NO_x Control Project in the third year involved the carryover of funds from the second to the third year of the Cooperative Agreement. This carryover totaled \$14,500 and was distributed between the personnel (\$8,200), operating (\$4,600), and indirect (\$1,700) cost budget categories. The change was approved by Modification A012 to the Cooperative Agreement, DE-FC21-86MC10637.

The most significant change made to the project in the third-year was the extension of the project year by three months. Originally, the project year began April 1, 1988, and was scheduled to end March 31, 1989. The purpose for the proposed change was to match the Cooperative Agreement project year with the University of North Dakota fiscal year. By making this adjustment, changes in staff salaries and rates for fringe benefits and indirect costs would be encountered at the beginning of the project year rather than after the first quarter. This should simplify project planning and preparation of budgets.

During the second and third quarters (July through December, 1988) of the past year, poor NO_x reduction results were observed during bench-scale tests with several samples of catalytic fabric. These results were documented in monthly and quarterly reports. In December, 1988, the reason for the poor performance of the catalytic fabric during bench-scale tests was identified. The catalytic reduction capability of the fabric was destroyed by thermal decomposition products evolving from a silicone gasket material. As a result of the problems encountered with the catalytic fabric and the proposed extension of the Cooperative Agreement project year by three months, the EMRC proposed to reschedule Milestones a.2, a.3, and a.4 and add Milestone b.1. Milestone b.1 involved modification and relocation of bench-scale equipment to permit catalytic fabric screening tests to be performed using an actual flue gas stream resulting from the combustion of coal in a pilot-scale pulverized coal-fired combustion system. These changes were approved by Modification 88-007B to the Cooperative Agreement, DE-FC21-86MC10637.

To accommodate the three-month extension of the project year and the expanded work plan, EMRC requested that \$50,000 be added to the project budget for the third year. This additional funding increased the project budget from \$238,600 to \$288,600. The additional funding was placed in personnel

(\$27,100), operating (\$16,900), and indirect (\$6,000) cost budget categories. The budget change was also approved by Modification 88-007B to the Cooperative Agreement, DE-FC21-86MC10637.

Other less significant technical modifications made to the project plan were discussed with the project COTR and implemented as necessary. Specific technical modifications made to the project work plan will be presented in section 3.0, Accomplishments.

3.0 ACCOMPLISHMENTS

3.1 Task A - Catalyst/Fabric Development

The purpose of Task A, Catalyst/Fabric Development, was two-fold. First, limited experimental work was to be completed to establish continuity between the proposed project and previous work completed by OCF and EMRC. Second, further development of the catalyst-coated fabric was deemed necessary to achieve the best combination of high NO_x removal efficiency, low ammonia-slip, high particulate removal efficiency, and long catalyst/bag life. To accomplish these goals, Task A was divided into three subtasks.

Task A.1, Project Planning and Equipment Acquisition/Assembly, began with the preparation of the Annual Project Plan (APP-3) for the third year of the Cooperative Agreement in January, 1988. In April, 1988, more detailed planning was initiated to facilitate preparation of a project test plan and permit the design, assembly, and shakedown of the bench-scale test apparatus to be used to evaluate catalytic fabric samples in Tasks A.2 and A.3. The project test plan documented experimental activities that were to be completed during the period April, 1988 through March, 1989.

The purpose of Task A.2, Bench-Scale Catalytic Fabric Screening, was first, to verify that the operating conditions selected to evaluate the catalytic fabric samples were appropriate, and second, to conduct screening tests with up to 18 catalytic fabric samples. Initially, five independent variables (NO_x and SO_2 concentration, ammonia/ NO_x molar ratio, air-to-cloth ratio, and temperature) were to be evaluated using a fractional factorial experimental design and a catalytic fabric sample that had previously demonstrated NO_x reduction in excess of 80%. After further consideration, temperature was removed from the list of independent variables to be evaluated, since previous work by OCF and EMRC had already determined that temperature had a significant effect on catalytic fabric performance. This change resulted in a full factorial experimental design with four factors and two levels.

Following completion of the experimental effort to verify operating conditions, 16 separate catalytic fabric samples were evaluated during screening tests using the bench-scale fabric filter sample holder, simulated flue gas, and reinjected fly ash. Independent variables evaluated included cloth type (textured versus nontextured), fabric undercoat (silica/titanium versus silica/zirconium versus no undercoat), quantity of catalyst (one versus two coats of 1.0 M 25% V + 75% Ti), and catalyst composition (V/Ti versus V/Ti/Al versus V/Ti/Zr versus CuO).

Task A.3, Bench-Scale Operating Parameter Evaluation, was performed following completion of Task A.2. One catalytic fabric sample was selected from the 16 catalytic fabric samples screened to verify the impact of operating conditions (NO_x and SO_2 concentration, ammonia/ NO_x molar ratio, and air-to-cloth ratio) on catalytic fabric performance. The full factorial (four factors and two levels) experimental design was repeated with center points and replicate experiments to evaluate curvature and increase degrees of freedom, respectively.

In all cases catalytic fabric performance was based on overall NO_x removal efficiency and ammonia-slip. Other dependent variables measured included SO_3 production and particulate collection efficiency. Analytical techniques used to interpret catalytic fabric performance included BET surface area and scanning electron microscopy (SEM).

3.1.1 Description of Facilities and Procedures

Construction of components and final assembly of the bench-scale fabric filter holder/slipstream sample system was completed in August 1988. Figure 4 presents a schematic of the final system configuration. As a result of initial shakedown tests, several minor changes were made to the system prior to initiating the planned experimental effort. First, nitric oxide (NO) was introduced to the simulated flue gas stream at a different location than the

Figure 4. Schematic of fabric filter holder and slipstream sample system.

other flue gas components to prevent excessive conversion of NO to nitrogen dioxide (NO₂) when coming in contact with pure oxygen (O₂) at ambient temperatures. Secondly, a 1% sulfur dioxide/99% nitrogen calibration gas was used instead of anhydrous sulfur dioxide (SO₂) to increase overall system flow rate and improve control of the simulated flue gas flow rate. Finally, heat tape was used to preheat the simulated flue gas entering the oven housing the fabric filter holder rather than the tube furnace that had been originally proposed.

After passing through the filter, the simulated flue gas was split into two streams. Approximately 10 l/min (20 scfh) was pumped to the sample conditioner and the gas analyzers, with the remainder entering a condenser for moisture content reduction prior to being dumped into an exhaust hood system. By shutting off the flue gas flow to the sample conditioner and analyzers, the total flue gas flow was measured using a dry gas meter in the exit stream.

The operating procedure for the bench-scale system involved heating the oven to 650°F with nitrogen flowing through the flue gas lines and the fabric filter holder. Once the oven was heated, concentrations of simulated flue gas components were adjusted using precision rotameters. The carbon dioxide (CO₂) and O₂ concentrations were set at 15% and 5% by volume, respectively. The SO₂ and NO flow rates were then adjusted to achieve specific concentrations (300 to 3700 ppm and 300 to 1000 ppm, respectively) depending on the specific test condition required. Once all the flue gas constituent concentrations had been stabilized, the ammonia was added at the desired stoichiometric ratio. Flue gas constituent concentrations (O₂, CO₂, NO, NO₂, and SO₂) were then recorded every two minutes using a Kaye Data Logger. Each test condition was maintained for a minimum of four hours to assure stability in the bench-scale system and data quality. Ammonia-slip and SO₃ values were determined using wet chemistry techniques.

3.1.2 Results and Discussion

Task A.1 - Project Planning and Equipment Acquisition/Assembly

Following completion of the initial project planning and assembly of experimental equipment, a series of shakedown tests was completed to determine operability of the experimental equipment and if NO_x reduction results previously observed by OCF and EMRC could be duplicated. Initial shakedown tests with the bench-scale fabric filter holder/slipstream apparatus and gas sampling system were completed in September, 1988. Following completion of these system tests and the minor modifications required, tests with a catalytic fabric sample were initiated.

The first catalytic fabric sample tested (HS #1) had not been previously exposed to flue gas and had been originally prepared by OCF in 1985. The purpose of this effort was to determine if results previously observed with the catalytic fabric could be duplicated in the new bench-scale system. Actual results with the historic catalytic fabric sample were poor, with 10% to 32% catalytic NO_x reduction observed during three separate test periods. A summary of the test conditions and results for all the bench-scale experiments completed through December, 1988, are presented in Table 5. A careful review

TABLE 5

SUMMARY OF RESULTS FROM BEHIGH-SCALE CATALYTIC FABRIC FILTER EXPERIMENTS^{a,b}

Date	Fabric No.	O ₂ Vol. %	CO ₂ Vol. %	H ₂ O Vol. %	SO ₂ ppm	NO _x in ppm	NO _x Out ppm	Ammonia/NO _x Molar Ratio	A/C Ratio ft/min	NO _x Reduction %
09-07-88	HS #1	3.9	13.7	--	1003	613	465	0.82	1.8	24.1
09-12-88	HS #1	5.1	14.9	--	986	601	408	0.81	1.9	32.1
09-27-88	HS #2	4.9	17.3	--	317	637	472	0.76	2.0	25.9
09-28-88	HS #2	5.1	14.8	--	1002	681	566	0.68	2.3	16.9
09-30-88	HS #1	5.1	16.1	--	1055	604	542	0.75	2.1	10.3
10-13-88	TS #7	5.1	19.2	--	951	595	440	0.73	2.1	26.1
10-25-88	TS #7	5.0	14.0	--	--	607	445	0.81	2.1	26.7
11-22-88	HS #3	3.7	8.2	5.3	995	575	476	1.16	1.2	17.2
11-29-88	HS #3	4.8	15.1	3.1	990	626	106	0.62	3.5	83.1
	HS #3	4.8	15.1	3.1	921	607	20	0.90	3.5	96.7
11-30-88	HS #3	5.1	15.3	5.4	951	638	171	0.69	2.0	73.2
	HS #3	5.1	15.3	5.4	951	638	60	0.75	2.0	90.6
	HS #3	5.1	15.3	5.4	951	638	29	1.00	2.0	95.5
12-06-88	HS #3	5.2	15.4	5.5	1103	626	542	1.22	2.0	13.3

^a Catalytic filter temperature was 650 $\pm$ 10°F for each test.^b Each fabric sample tested was roughly 0.8 ft² in size.

of the new bench-scale system was completed to make sure that the poor results were not caused by some characteristic of the new system. Once the bench-scale system was checked out, the apparently unreactive (exposed) sample of catalytic fabric and a sample of catalytic fabric that had not been exposed to flue gas were submitted for SEM and BET surface area analysis.

Analysis by SEM showed that the morphology of the coated fabric surface had changed, possibly as a result of overheating. SEM microprobe analysis showed that the catalyst components (vanadium and titanium) were present and did not indicate the presence of any material which could have caused catalyst poisoning. Figure 5 presents four SEM micrographs that clearly show a change in the surface morphology of the coated fabric that appears to have occurred uniformly on and between the glass fibers. The catalytic coating on the exposed fabric sample appears to have been shattered or crushed when compared to the unexposed fabric sample.

The SEM results were discussed with OCF personnel to obtain their input and suggestions. OCF personnel felt the change in fabric surface morphology resulted from overheating the fabric. Similar results were observed in previous work by OCF, although an inconsistency exists with respect to the temperature at which the morphological change had been previously observed. Early work by OCF showed that a sintering effect occurred at temperatures of $>800^{\circ}\text{F}$. The morphological change resulting from the first bench-scale experiment would have had to have occurred at less than 700°F .

Surface area analysis of the unexposed ($4.18 \text{ m}^2/\text{g}$) and exposed ($1.13 \text{ m}^2/\text{g}$) catalytic fabric showed a significant reduction in fabric surface area as a result of heating and exposure to a simulated flue gas. Again, OCF personnel felt that the reduced surface area was a result of sintering due to overheating. Table 6 presents surface area data for all fabric samples analyzed through December, 1988.

A second unused historic catalytic fabric sample, HS #2, was tested on two separate occasions with similar results (26% and 17% NO_x reduction). Analytical results (SEM and BET surface area) for the second fabric sample were found to be similar to the first fabric sample. SEM analysis showed the same morphological change to the fabric surface, and surface area analysis showed that the fabric surface area was reduced to $<1.0 \text{ m}^2/\text{g}$.

Since the historic fabric samples had been in storage for three years, catalyst aging was considered a possible explanation. OCF prepared a new catalytic fabric sample, TS #7, which was tested in early October. Fabric sample TS #7 was heavily coated and expected to provide $>90\%$ NO_x reduction. In this case, the observed NO_x reduction was only 26% with 950 ppm SO_2 in the simulated flue gas, and 27% without SO_2 in the simulated flue gas. As with the two previous fabric samples, SEM analysis showed a change in the morphology of the fabric surface and a surface area reduction from 4.03 to $0.64 \text{ m}^2/\text{g}$.

Previous work by OCF had shown that reductions in catalytic fabric surface area were a result of sintering at temperatures exceeding 800°F . To determine if temperature alone was responsible for the reduction in catalytic fabric surface area, a piece of catalytic fabric was placed in the oven

a.) unexposed catalytic fabric

b.) exposed catalytic fabric

c.) unexposed catalytic fabric

d.) exposed catalytic fabric

Figure 5. Scanning electron micrographs of unexposed and exposed catalytic fabric.

TABLE 6
SURFACE AREA DATA FOR CATALYST-COATED FABRIC SAMPLES

<u>Fabric</u>	<u>Surface Area Unexposed (m²/g)</u>	<u>Surface Area Exposed (m²/g)</u>
Blank	0.33	---
HS #1	4.18	1.13
HS #2	---	0.85
HS #3	5.58	2.28
TS #7	4.03	0.64
Heat treated TS #7	---	5.41

housing the fabric filter holder during a 6-hour test period. The fabric sample was not exposed to the simulated flue gas. Analysis showed that no change in catalytic fabric surface area occurred due to simply heating the fabric to 650°F. This demonstrated that sintering due to temperature alone was not the cause of reduced catalytic fabric surface area or poor catalytic fabric reactivity.

Fabric samples were analyzed using electron spectroscopy for chemical analysis (ESCA) to determine if the catalyst was being physically removed from the catalytic fabric. Results indicated that a small loss of catalyst may have occurred in the exposed catalytic fabric samples that showed poor NO_x reduction capability when compared with unexposed catalytic fabric. However, this loss of catalyst was insufficient to explain the poor NO_x reduction observed.

At this point the effort to identify the cause of poor catalytic fabric reactivity focused on the simulated flue gas, the slipstream system, and the fabric filter holder. In November, six separate experiments were performed to identify or eliminate possible contributors to the poor results. Each test was performed using material from a third historic catalytic fabric sample, HS #3, which had not been previously exposed to flue gas.

All of the original catalytic fabric characterization efforts performed by EMRC for OCF had involved the use of actual flue gas from a pilot-scale combustion system. Therefore, a test was completed using a slipstream sample of flue gas from the particulate test combustor. The purpose of this test was to address the issue of simulated versus actual flue gas. The pilot-scale combustor was fired using natural gas. Anhydrous SO₂ was added in the combustion air to generate 1000 ppm SO₂ in the flue gas. The complete

composition of the flue gas stream is presented in Table 5 (November 22, 1988 HS #3). Again, NO_x reduction was poor (<20%), indicating that the simulated flue gas prepared using relatively pure components was not the cause of poor catalytic fabric reactivity. Also, the fact that the flue gas from the combustor contained moisture (5.3% by volume), unlike previous tests with the simulated flue gas, appears to have had no effect on NO_x reduction.

From observations made during previous tests, the silicone gasket material was known to off-gas acetic acid as it cured and during initial heating. Therefore, EMRC speculated that the off-gassing of acetic acid or possibly another component (at 650°F) may have been responsible for the poor NO_x reduction observed. Results from two tests, using a high temperature gasket material as a replacement for the silicone gasket material, were extremely positive with respect to NO_x reduction. For ammonia/ NO_x molar ratios ranging from 0.62 to 0.90, NO_x reduction ranged from 83% to 97%. Although these data strongly indicated that the silicone gasket material was responsible for the poor results observed, several additional experiments were performed to verify the results.

Three additional experiments were performed using the simulated flue gas system, equipment configuration, and operating conditions that had resulted in poor NO_x reduction during previous tests. The silicon gasket material was again replaced with a gasket material typically used to seal high-temperature pipe flanges. Results from these tests showed NO_x removal ranging from 73% to 96% for ammonia/ NO_x molar ratios ranging from 0.7 to 1.0. A summary of the data is presented in Table 5.

A single test (December 26, 1983, HS #3) was then performed using the same catalytic fabric sample, equipment configuration, and operating conditions. The only change was the addition of silicone gasket material to a small area of the catalytic fabric. In this case, NO_x reduction was about 13%, as shown in Table 5.

In an effort to identify the component of the silicone gasket material responsible for destroying the reactivity of the catalytic fabric, EMRC staff contacted the manufacturer, Loctite Corporation. The manufacturer confirmed that acetic acid is off-gassed when the gasket material is cured and that extended use at 650°F could cause thermal decomposition. The decomposition products are silicon dioxide and D3 and D4 siloxanes. Further discussions and review of available references confirmed that siloxanes will react under acidic conditions with vanadium to form a loose crystalline structure. This structure develops stress points that result in considerable cleavage of the crystals. The morphological changes seen on the surface of the catalytic fabric using SEM were consistent with this phenomena.

Further discussions with OCF personnel revealed that silicon dioxide was a component of the catalytic coating applied to the fabric. In addition, OCF and EMRC staff speculated that poor NO_x reduction results observed during a pilot-scale test performed in 1985 may have been caused by the same silicone gasket material. Only 50% NO_x reduction was observed during a pilot-scale test performed using bags made from catalytic fabric that had demonstrated >80% NO_x reduction during bench-scale tests. Early speculation by OCF was that the bags had been overheated even though baghouse temperature data did not show any temperature excursions. Unfortunately, the issue was not pursued

due to funding limitations. Based on present information and the knowledge that the same silicone gasket material had been used to seal access doors on the pilot-scale baghouse, it is very likely that the poor NO_x reduction experienced in the 1985 tests was caused by thermal decomposition products of the silicone gasket material.

Task A.2 - Initial Bench-Scale Parametric Tests

Prior to initiating the Task A.2 experimental effort, the bench-scale fabric filter holder was modified such that the silicone gasket material would no longer be needed to obtain a good seal. During the fourth quarter (January through March, 1989), the full factorial experimental design shown in Table 7 was completed and a statistical analysis was performed on the resulting data presented in Table 8.

During this experimental effort the simulated flue gas O_2 and water concentrations were approximately 5% by volume, the CO_2 concentration was about 15% by volume, and the temperature at the filter was held constant at 650°F. Fly ash was not injected into the bench-scale experimental system during these tests. A single catalytic fabric sample, designated as Sample No. 1 by OCF, was used to perform all sixteen experiments. The fabric sample

TABLE 7
FULL FACTORIAL EXPERIMENTAL DESIGN FOR PARAMETRIC TESTS

Run	NO_x Concentration (ppm)	SO_2 Concentration (ppm)	Ammonia/ NO_x Molar Ratio	Air-to-Cloth Ratio (ft/min)
1	300	300	0.8	1.5
2	1000	300	0.8	1.5
3	300	3000	0.8	1.5
4	1000	3000	0.8	1.5
5	300	300	1.1	1.5
6	1000	300	1.1	1.5
7	300	3000	1.1	1.5
8	1000	3000	1.1	1.5
9	300	300	0.8	4.0
10	1000	300	0.8	4.0
11	300	3000	0.8	4.0
12	1000	3000	0.8	4.0
13	300	300	1.1	4.0
14	1000	300	1.1	4.0
15	300	3000	1.1	4.0
16	1000	3000	1.1	4.0

TABLE 8
EXPERIMENTAL DATA RESULTING FROM PARAMETRIC TESTS

Test ^a	SO ₂ Conc. (ppm)	NO _x Conc. In (ppm)	NO _x Conc. Out (ppm)	Ammonia/NO _x Molar Ratio	Air-to-Cloth Ratio (ft/min)	NO _x Removal (%)	Ammonia Slip (ppm)
1	351	328	136	0.70	1.45	58.5	5
2	417	1037	151	0.78	1.48	85.4	71
3	2904	332	101	0.78	1.54	69.6	<1
4	3075	1042	226	0.82	1.52	78.3	88
5	331	316	44	1.01	1.72	86.1	65
6	340	1044	85	0.95	1.61	91.9	500
7	3074	300	43	1.38	1.32	85.7	114
8	3065	1019	164	0.98	1.62	83.9	361
9	311	328	104	0.81	3.90	68.3	151
10	328	1052	363	0.78	4.11	65.5	100
11	3063	325	117	0.80	3.89	64.0	108
12	3075	1045	445	1.04	4.09	57.4	451
13	318	315	74	1.05	4.15	76.5	329
14	329	1020	339	0.89	3.95	66.8	376
15	3028	310	92	1.26	4.04	70.3	198
16	3048	1055	429	1.02	4.10	59.3	495

^a Fabric Sample 1 was used for all of the parametric tests in this series.

had properties similar to fabric samples used during the original OCF tests. This same fabric type was tested again during the Task A.2 fabric screening experiments.

Based on the statistical analysis of the data in Table 8; the concentration of NO_x in the flue gas, the air-to-cloth ratio, and the interaction between these two parameters produce the greatest effect on NO_x removal. To a lesser degree, the ammonia/NO_x molar ratio, the SO₂ concentration, and the interaction between the NO_x and SO₂ also affect the ability of the catalytic fabric to reduce NO_x. Figure 6 graphically presents the results of the parametric tests in terms of NO_x removal efficiency versus air-to-cloth ratio and ammonia/NO_x molar ratio. The data presented in Figure 6 shows NO_x removal efficiency generally increasing as the ammonia/NO_x molar ratio increased. When air-to-cloth ratio was increased from about 1.5 to 4.0 ft/min, NO_x removal efficiency appears to have decreased.

The dependence of NO_x removal on NO_x concentration in the flue gas, air-to-cloth ratio, and the interaction of the two was expected. The concentration of NO_x in the flue gas would be expected to play a role in the rate of gas phase mass transfer to the catalyst site. Air-to-cloth ratio was expected to be important since it determines the contact time between the catalyst, NO_x, and ammonia. Therefore, the effect of the interaction of the NO_x concentration and air-to-cloth ratio is not surprising.

Figure 6. Percent NO_x removal versus air-to-cloth ratio and ammonia/NO_x molar ratio.

Ammonia/NO_x molar ratio would be expected to have a substantial impact on NO_x removal for values ranging from 0.0 to 0.9 simply because the free ammonia would be the limiting factor, assuming a reactive catalyst and sufficient contact time. For the range of ammonia/NO_x molar ratios studied (0.7 to 1.38) a small effect would be expected since the primary limiting factors would be catalyst reactivity and theoretical NO_x reduction.

The fact that SO₂ concentration in the flue gas was observed to have an effect on NO_x removal was not surprising, but the mechanism by which it affects NO_x removal efficiency is unclear. A direct reaction between SO₂ and ammonia would not be expected at a flue gas temperature of 650°F. However, the simulated flue gas temperature prior to the oven-housed fabric filter holder was <430°F. Another possible explanation would be that the concentration of SO₃ in the flue gas was proportional to the SO₂ concentration. Sulfur trioxide may have interfered with the catalytic reduction of NO_x by limiting the available catalytic sites or competing for available sites. The oxidation of SO₂ to SO₃ is a concern with SCR catalysts in general, and may increase with increasing flue gas SO₂ concentration. Whether the effect of SO₂/SO₃ concentration was real or an artifact of the bench-scale system will be determined in subsequent experiments using actual flue gas from pulverized coal firing during Task B.

Statistical analysis of the data also showed an effect due to the interaction of NO_x and SO_2 in the flue gas, indicating the possibility of competing reactions. For this series of parametric tests, the same fabric sample was used throughout the test matrix. Toward the end of the test series, NO_x removal efficiency appeared to be decreasing. The oxidation of SO_2 to SO_3 may have resulted in the deterioration of the catalyst. This may also explain the correlation observed between the NO_x and SO_2 concentrations. At the conclusion of the test matrix a BET surface area analysis determined that the catalytic fabric had undergone a reduction in surface area from 5.83 to 3.37 m^2/g . Based on previous experience with the catalytic fabric, a decrease in surface area comparable to that observed, always results in a decrease of catalytic fabric reactivity and observed NO_x reduction.

Due to the low ammonia concentrations required for these tests, ammonia/ NO_x molar ratio was a difficult parameter to control. The small precision flow meters that were used did not provide the stable/accurate flow rates originally expected. Therefore, the flue gas constituent concentrations and resulting data presented in Table 8 and Figure 6 were more variable than was expected/desired. For the fabric screening tests and the second series of parametric tests performed for Task A.3, mass flow meters were acquired and used to achieve more accurate control of flue gas constituent flow rates. Further discussion of the results from the first set of parametric tests is presented later in this report in combination with results from the second set of parametric tests.

Task A.2 - Bench-Scale Fabric Screening Tests

Results of the initial parametric tests tend to support an optimal ammonia/ NO_x molar ratio of 0.9. At the low value of 0.8, 85% NO_x reduction was not achieved except for one test at a low air-to-cloth ratio (1.5 ft/min). At the high ammonia/ NO_x molar ratios (>0.95), ammonia-slip was observed to be unacceptably high (>50 ppm) in all cases.

With the catalytic fabric used for the initial parametric tests, 90% NO_x reduction was not achieved at an air-to-cloth ratio of 4.0; however, >85% NO_x reduction was observed during several tests at an air-to-cloth ratio of 1.5. Therefore, an air-to-cloth ratio of 2.0 appeared to be a good baseline condition from which to evaluate other catalytic fabric samples. Table 9 presents the approximate conditions at which the sixteen catalytic fabric samples prepared by OCF were evaluated.

The catalytic fabric samples evaluated in the fabric screening tests are identified in Table 10. Table 10 identifies each catalytic fabric sample by number, the composition of the catalyst coating, the number of coating applications, whether or not a refractory undercoat was applied, and whether the weave had a textured or nontextured fill yarn. Fabric Samples 1 through 5 were all prepared using a 0.2-molar solution containing 25% vanadium and 75% titanium applied using seven duplicate coats. The differences in the first five fabric samples had to do with the application of a refractory undercoat (A or B), the application of no refractory undercoat, and the weave style (textured or nontextured). Fabric Samples 6 through 12 were all prepared

TABLE 9
OPERATING CONDITIONS USED DURING FABRIC SCREENING TESTS

Temperature	650°F
NO _x inlet concentration	600 ppm
SO ₂ inlet concentration	1000 ppm
Vol. % O ₂	5%
Vol. % CO ₂	15.0%
Vol. % H ₂ O	5%
Air-to-cloth ratio	2 ft/min
Ammonia/NO _x molar ratio	0.9

using fabric with a nontextured weave. Variations in these fabric samples were a result of changes in the catalyst composition, the number of coatings used to apply the catalyst, and the use or nonuse of a refractory undercoat. Fabric Samples 13 and 14 had the same catalyst composition, but 13 was prepared using a refractory undercoat and a weave with textured fill yarns. Fabric 14 did not have a refractory undercoat and used a nontextured fabric weave. Fabric 15 was similar to Fabric 14 except that the quantity of catalyst was increased by coating the fabric twice with the same solution. Fabric 16 was unique in that it was coated with a solution containing copper oxide rather than the vanadium/titanium catalyst. The fabric consisted of a textured weave but did not have a refractory undercoat.

Prior to initiating the tests, the simulated flue gas system was modified to include dust injection. The dry powder was injected during the fabric screening tests with a Model 3410 powder disperser manufactured by TSI, Inc. A calibrated piston pushes the dust onto a rotating brush, with a jet of air carrying the dust to the filter. Fly ash injection was not used continuously during all fabric screening tests, but was initiated at the beginning of each test to develop a differential pressure across the fabric sample of between 2 and 4 inches of water. Fly ash injection was discontinued when differential pressure reached 4 inches of water to prevent problems with the control of flue gas flowrate. The fly ash used during the fabric screening tests resulted from the combustion of a western subbituminous coal in a pc-fired utility boiler. Continuous measurement of flue gas constituent concentrations (NO_x, O₂, CO₂, and SO₂) were made during each test period along with periodic measurements of SO₃ and ammonia.

Table 11 summarizes the data and Figures 7 and 8 present NO_x removal and ammonia-slip data for each of the sixteen fabric samples tested. Figure 7 illustrates percent NO_x removal for eight catalytic fabric samples that demonstrated NO_x removal efficiencies and ammonia-slip values ranging from <5%

TABLE 10

DESCRIPTION OF CATALYTIC FABRIC SAMPLES EVALUATED DURING SCREENING TESTS

Fabric Sample	Catalyst Composition ^a					Refractory ^b			Weave ^c	
	A	B	C	D	E	A	B	C	A	B
1	X							X	X	
2	X							X		X
3	X					X			X	
4	X						X		X	
5	X					X				X
6		X				X			X	
7			X			X			X	
8				X				X	X	
9				X		X			X	
10					X			X	X	
11					X	X			X	
12					X		X		X	
13		X				X				X
14		X						X	X	
15			X					X	X	
16 ^d								X		X

^a Catalytic Composition:

- A -- 7 coats of 0.2 M 25% V + 75% Ti
 B -- 1 coat of 1.0 M 25% V + 75% Ti
 C -- 2 coats of 1.0 M 25% V + 75% Ti
 D -- 7 coats of 0.2 M 20% V + 5% Al + 75% Ti
 E -- 7 coats of 0.2 M 20% V + 5% Zr + 75% Ti

^b Refractory Undercoat:

- A -- 1 coat of 0.5 M 50% Si + 50% Ti
 B -- 1 coat of 0.5 M 50% Si + 50% Zr
 C -- No Refractory Undercoat

^c Weave:

- A -- 14 oz. Nontextured fill
 B -- 14 oz. Textured fill (Style 454)

^d Fabric Sample 16 was prepared using CuO instead of the V/Ti catalyst.

TABLE 11
EXPERIMENTAL DATA RESULTING FROM FABRIC SCREENING TESTS

Fabric Sample	Inlet SO ₂ Conc. (ppm)	Inlet NO _x Conc. (ppm)	Outlet NO _x Conc. (ppm)	Ammonia/NO _x Molar Ratio	Air-to-Cloth Ratio	NO _x Removal (%)	SO ₃ Conc. ^a		Ammonia Slip (ppm)
							W/O Dust (ppm)	With Dust (ppm)	
1	1060	625	113	0.90	1.95	81.9	38	64	56
2	1048	631	47	0.89	1.95	92.6	173	158	35
3	1040	642	94	0.88	1.92	85.4	133	116	53
4	1058	636	149	0.90	1.92	76.6	55	55	24
5	1026	624	101	0.77	1.95	83.8	---	79	2
6	1035	620	106	0.85	2.04	82.9	132	107	90
7	1051	603	74	0.91	1.97	87.7	183	207	9
8	1027	637	391	0.89	1.91	38.6	171	105	331
9	1058	647	420	0.84	1.96	35.1	217	46	341
10	1031	634	252	0.90	2.08	60.3	---	5	156
11	1028	632	229	0.90	2.10	63.8	---	121	104
12	1102	670	367	0.88	2.01	45.2	94	---	259
13	1030	603	231	0.95	1.91	61.7	115	163	8
14	1037	633	55	1.06	1.04	91.3	126	---	25
15	1053	630	63	0.91	1.98	90.0	---	4	44
16	1025	631	613	0.90	1.95	2.9	61	---	301

^a SO₃ measurements were made prior to fly ash injection (clean fabric) and during fly ash injection for several fabric samples. Ammonia injection was off during all SO₃ sampling periods.

Figure 7. Percent NO_x removal and ammonia-slip data for Fabric Samples 4, 8 through 13, and 16.

Figure 8. Percent NO_x removal and ammonia-slip data for Fabric Samples 1, 2, 3, 5, 6, 7, 14 and 15.

to about 77%, and 8 to 341 ppm, respectively. Fabric Sample 16, prepared using copper oxide as the catalyst, was observed to reduce NO_x by only 3%. This result should not have been surprising since the quantity of copper oxide in contact with the flue gas was small and the filter temperature (650°F) was lower than the temperature (750°F) at which copper oxide has been used to simultaneously remove SO₂ and NO_x (20).

Figure 8 presents NO_x removal and ammonia-slip data for eight additional fabrics. Values for NO_x removal and ammonia-slip ranged from 82% to 93%, and 3 to 90 ppm, respectively. Fabric Sample 2 demonstrated the highest NO_x removal efficiency (93%), but Fabric Samples 5 and 7 demonstrated the lowest ammonia-slip (3 ppm and 9 ppm, respectively).

Upon evaluation of the data resulting from the catalytic fabric screening tests, several general observations can be made with respect to the impact of catalyst composition, the quantity of catalyst, the use of a refractory undercoat, and the use of a weave with textured or nontextured fill yarns. First, the addition of refractory components, specifically alumina and zirconium, to the original catalyst substantially reduced the catalytic reactivity of the fabrics prepared using these materials. Fabric Samples 8 and 9 were prepared using seven coats of a catalytic composition with 5% alumina added. Removal of NO_x with the two fabrics ranged from 35% to 40%. Three fabric samples (10, 11, and 12) prepared using seven coats of a catalytic composition with 5% zirconium added, resulted in NO_x removal efficiencies ranging from 45% to 65%. In both cases, to accommodate the 5% alumina and zirconium additions, the vanadium content of the catalyst was

reduced from 25% to 20%. Since experiments performed by OCF using a 20% V/80% Ti catalyst did not show a decrease in NO_x removal, it appears that the addition of the refractory component (alumina or zirconium) to the catalyst was responsible for the reduced catalytic activity of the fabric samples.

The original objective of adding refractory components to the catalyst was to evaluate the impact of varying the V/Ti ratio and the potential for expanding the operating temperature range. A few additional experiments may be performed with temperature as the independent variable, although present data would not support expectations of increased NO_x removal as a result of an increase or decrease in operating temperature.

Fabric Samples 3 and 6, illustrated in Figure 8, were prepared by applying seven coats of a 0.2 M 25% V + 75% Ti solution and one coat of a 1.0 M 25% V + 75% Ti solution, respectively, to individual fabric samples. Both fabric samples had a refractory undercoat applied to a nontextured weave using a 0.5 M 50% Si + 50% Ti solution. Results show that NO_x removal was slightly higher for Fabric 3 (85% versus 83%) and that ammonia-slip was lower (53 versus 90 ppm). Although this data indicates that Fabric 3 performed better than Fabric 6, the small differences are not sufficient to draw a conclusion concerning the effect of multiple coats of low concentration catalytic solutions versus a single coat of a high concentration solution. OCF experience has shown that multiple coats of a low concentration catalyst solution results in a more uniform catalyst coating on the fabric when compared to a single coat of a high concentration catalyst solution. Theoretically, seven coats of the 0.2-molar solution should have resulted in a higher catalyst content per square foot of fabric than a single coat of the 1.0-molar solution. Analytical techniques are being considered to quantify the amount of catalyst (V/Ti) bonded to the surface of the fabric.

Similar results were observed for Fabrics 5 and 13. Fabrics 5 and 13 were similar to 3 and 6, respectively, except that a textured fabric was used. Although NO_x removal was significantly higher for Fabric 5 (84%) than 13 (62%), both fabrics showed low ammonia-slip values (3 and 8 ppm, respectively). Assuming the ammonia-slip data is accurate, NO_x removal for Fabric 13 may have been low due to a calculation or equipment error, resulting in a smaller actual ammonia/ NO_x molar ratio than the 0.95 value reported. One possible advantage of the multiple-versus single-coat approach may have to do with catalyst durability or loss from the fabric. This issue will have to be addressed during longer-term tests evaluating filter bags made from the catalytic fabric.

Comparison of Fabric Samples 6 and 7 is a direct evaluation of two fabric samples prepared using the same catalytic solution composition (1.0 M 25% V + 75% Ti), the same refractory undercoat (0.5 M 50% Si + 50% Ti), and the same fabric weave (nontextured fill yarns). The difference between the fabric samples is the number of coats of catalytic solution applied to each fabric. Fabric 6 was prepared using one coat and Fabric 7 was prepared using two coats, theoretically doubling the amount of catalyst on Fabric 7. Although Fabric 7 demonstrated greater NO_x removal than Fabric 6 (88% versus 83%), the difference was not as great as might have been expected. The real advantage observed for Fabric 7 when compared to Fabric 6 was the reduced ammonia-slip (9 versus 90 ppm). Although a quantitative determination has not been made as

to the amount of catalyst on each fabric, it would appear that coating Fabric 7 twice, increased the amount of catalyst on the fabric, which improved its overall catalytic performance in terms of NO_x removal and ammonia-slip.

The purpose for putting an undercoat on the glass fabric prior to the catalyst is to improve the abrasion resistance of the glass fibers and produce more surface area. Fabric samples were tested using one of two undercoats and no undercoat at all. The two undercoats tested were composed of silica/titanium (1 coat of 0.5 M 50% Si + 50% Ti) and silica/zirconium (1 coat of 0.5 M 50% Si + 50% Zr). The abrasion resistance of the two undercoats has been characterized as good and fair, respectively, for silica/titanium and silica/zirconium, based on MIT flex test data generated by OCF personnel. Bench-scale fabric screening tests focused on the impact of the undercoats on the reactivity of the catalytic fabric samples and measured surface area.

Comparing results for Fabric Samples 1, 3, and 4 does not indicate a substantial difference in catalytic performance. Each fabric sample was prepared using the same catalytic composition (7 coats of 0.2 M 25% V + 75% Ti) and fabric weave (nontextured fill yarns). Fabric 1 was prepared without an undercoat while 3 and 4 were prepared with undercoats (1 coat of 0.5 M 50% Si + 50% Ti and 1 coat of 0.5 M 50% Si + 50% Zr), respectively. The NO_x removal data does not show a significant difference between Fabric Samples 1 and 3 (82% versus 85%) and the ammonia-slip numbers were almost identical (56 versus 53 ppm). Fabric Sample 4 provided a slightly lower NO_x removal (77%) but its measured ammonia-slip was only 24 ppm. A similar observation can be made between Fabrics 2 and 5, where Fabric 2 resulted in higher NO_x removal than Fabric 5 (93% versus 84%), but ammonia-slip was less for Fabric 5 (2 ppm versus 35 ppm for Fabric 2). Therefore, the impact of using or not using a refractory undercoat on fabric performance in terms of catalytic reactivity does not appear to be significant. The use of a refractory undercoat would be preferable if the undercoat increases fabric durability.

The use of textured fabric definitely improved the catalytic performance of the catalyst-coated fabrics tested. Fabric Samples 1 and 2 were prepared without a refractory undercoat and the same catalytic composition (7 coats of 0.2 M 25% V + 75% Ti). The difference between the two fabric samples was that Fabric 1 was prepared with a nontextured fabric and Fabric 2 was prepared with a textured fabric. Fabric 2 resulted in higher NO_x removal (93% versus 82%) and lower ammonia-slip (35 versus 56 ppm). Fabric Samples 3 (nontextured) and 5 (textured) showed similar results. Although NO_x removal for Fabrics 5 and 3 were essentially identical (84% versus 85%), ammonia-slip was significantly less for Fabric 5, (2 ppm versus 53 ppm for Fabric 3). Based on these results, the use of a fabric with textured fill yarns definitely improves the catalytic performance of the catalyst-coated fabric.

Table 12 presents surface area data for all 16 fabric samples. BET surface area was measured for fabric samples prior to exposure to flue gas and after completion of reactivity tests. The use of a refractory undercoat did not increase the measured surface area of the catalytic fabric as had been hoped. When nontextured fabric samples were compared, the measured surface area of a fabric sample that had not been exposed to flue gas was about 6 to 7 m^2/g . Textured fabric samples had surface areas of about 9 to 10 m^2/g . In

TABLE 12
SURFACE AREA DATA FOR CATALYST-COATED FABRIC SAMPLES EVALUATED
DURING SCREENING TESTS^a

Fabric Sample	Unexposed (m ² /g)	Exposed (m ² /g)
1	6.67	4.21
2	9.58	4.41
3	6.15	4.35
4	2.60	5.76
5	9.01	7.93
6	9.73	4.01
7	5.91	4.98
8	4.40	3.64
9	4.38	2.95
10	5.80	2.28
11	5.27	3.53
12	3.94	2.52
13	10.73	8.64
14	3.88	1.21
15	6.47	4.58
16	1.01	0.48

^a Fabric samples were analyzed before and after exposure to hot (650°F) flue gas.

all cases but one, exposure of the fabric samples to flue gas resulted in a decrease in the measured surface area. The one exception, the unexposed Fabric 4 sample, is believed to be a data error.

Figure 9 presents BET surface area data for fabric samples exposed to flue gas as a function of ammonia-slip. Data is presented for 14 of the 16 fabric samples evaluated during bench-scale screening tests. Fabric 14 was excluded from the data set because the air-to-cloth ratio actually used was 1.0 ft/min rather than 2.0 ft/min. Fabric 16 was excluded because the fabric sample was prepared using CuO rather than the V/Ti catalyst. The data presented in Figure 9 indicates that fabric samples having a surface area of 8 to 9 m²/g after exposure to flue gas resulted in low ammonia-slip values (<10 ppm). Surface area values between 5 and 8 m²/g resulted in moderate ammonia-slip (10 to 30 ppm). Below 5 m²/g, ammonia-slip values increased exponentially.

Based on the results of the fabric screening tests, the only fabrics that will not be considered for additional testing at this time are Fabric Samples 8, 9, 10, 11, 12, and 16. One or more of these fabric samples may be tested again if questions arise concerning data consistency in future experiments.

Task A.3 - Bench-Scale Parametric Tests

A second full factorial parametric test matrix was completed using Fabric Sample 2. Fabric Sample 2 had performed well in the screening tests,

Figure 9. BET surface area versus ammonia-slip for fabric samples after exposure to flue gas.

resulting in 94% NO_x removal and 35 ppm ammonia-slip. The fabric sample was prepared using seven coats of a 0.2-molar solution of V/Ti catalyst. No undercoat was applied and the fabric was not textured. Table 13 presents the factors and levels that were tested in the experimental design.

The experimental design had four factors with two levels. In addition, three center point experiments were performed to test for curvature. One experimental condition (Test 15) was performed four times to increase the degrees of freedom. To determine any change in the fabric reactivity with time, one test condition (Test 9) was performed early in the matrix, repeated toward the middle, and performed again at the end of the experimental series. Table 14 summarizes the data and Figure 9 presents NO_x removal efficiency as a function of air-to-cloth ratio and ammonia/ NO_x molar ratio.

Test 15 was repeated four times to determine data variability. Data in Table 14 shows that NO_x removal efficiency for Test 15 ranged from 73% to 76% and averaged 75%. Ammonia-slip data for the four tests ranged from 106 to 144 ppm and averaged 122 ppm. NO_x removal efficiency did not vary significantly but ammonia-slip was variable, considering one of the process goals is to operate at an ammonia-slip value of <25 ppm and most probably <10 ppm. Based on the fabric screening tests, the catalytic fabric sample (Fabric 2) used for these experiments demonstrated a moderate level of ammonia-slip (35 ppm), and therefore may not be indicative of the ammonia-slip variability that will be observed when using a more reactive fabric.

TABLE 13
EXPERIMENTAL DESIGN PARAMETERS

Factors	Levels	Center Point
NO _x Concentration	300 ppm and 1000 ppm	600 ppm
SO ₂ Concentration	300 ppm and 3000 ppm	1000 ppm
Ammonia/NO _x Molar Ratio	0.8 and 1.1	0.9
Air-to-cloth Ratio	1.5 ft/min and 4.0 ft/min	3.0 ft/min

TABLE 14
RESULTS FROM SECOND SERIES OF PARAMETRIC TESTS

Test ^a	SO ₂ Conc. (ppm)	NO _x Conc. In (ppm)	NO _x Conc. Out (ppm)	Ammonia/NO _x Molar Ratio	Air-to-Cloth Ratio (ft/min)	NO _x Removal (%)	Ammonia Slip (ppm)
1	305	326	154	0.80	1.58	52.8	34
2	452	1031	185	0.80	1.52	82.1	24
3	3027	361	107	0.81	1.56	70.4	2
4	3035	1038	183	0.80	1.51	82.4	65
5	356	368	34	1.11	1.59	90.8	27
6	333	1038	46	1.12	1.51	95.6	263
7	3025	348	60	1.10	1.53	82.8	9
8	3046	1009	120	1.09	1.54	88.1	229
9	338	311	68	0.91	3.97	78.1	15
9	365	336	83	0.80	4.01	75.3	27
9	335	348	102	0.80	3.98	70.7	36
10	394	1018	239	0.80	4.06	76.5	109
11	3037	337	117	0.79	3.94	65.3	41
12	3029	1067	419	0.86	4.03	60.7	380
13	307	325	62	1.10	4.02	80.9	80
14	361	1007	195	1.10	4.01	80.6	401
15	2989	333	89	1.10	3.88	73.3	113
15	3011	352	83	1.10	3.96	76.4	106
15	3030	347	84	1.11	3.97	75.8	127
15	3041	340	90	1.10	4.03	73.5	144
16	3028	1003	336	1.10	4.02	66.5	580
C1	1036	617	112	0.90	3.07	81.8	245
C2	1065	603	114	0.90	3.01	81.1	92
C3	995	631	129	0.88	3.07	79.6	91

^a Fabric Sample 2 was used for all of the parametric tests in this series.

Test 9 was performed three times during the experimental series (beginning, middle, and end) to determine if the reactivity of the catalytic fabric sample decreased with use. Data presented in Table 14 shows that NO_x removal efficiency decreased from 78% to 75% and then to 71% for the three tests. Ammonia-slip values increased from 15 ppm to 27 ppm, then to 36 ppm for the three test periods, respectively. This data indicates that the reactivity of the fabric decreased with use. What caused the decrease in catalytic fabric reactivity is unknown. Assuming the data is correct and fabric reactivity was reduced, factors that may have had an effect include temperature cycling and flue gas SO_2/SO_3 concentration. Although temperature cycling did occur, the range was minimal (350° to 650°F) and the fabric was never cooled to room temperature between tests. The potential impact of SO_2/SO_3 in the flue gas has been previously discussed and is a possible explanation. Further investigation of this issue is under consideration with respect to analysis of the fabric sample used during the parametric tests and future experimental efforts.

Statistical analysis of the results agreed with those obtained from the first parametric test series. The factors resulting in the greatest degree of significance in determining NO_x removal efficiency were the air-to-cloth ratio, NO_x concentration, and the interaction between air-to-cloth ratio and NO_x concentration. To a lesser degree, the ammonia/ NO_x molar ratio, SO_2 concentration, and the interaction between NO_x concentration and SO_2 concentration were significant.

Data presented in Figure 10 indicates that NO_x removal efficiency decreased as air-to-cloth ratio increased from 1.5 to 4.0 ft/min. When the center point data are considered, the decrease in NO_x removal efficiency between air-to-cloth ratios of 1.5 and 3.0 appears to be small relative to the decrease between air-to-cloth ratios of 3.0 and 4.0 ft/min. The impact of air-to-cloth ratio on NO_x removal will be studied further in experiments planned for the next project year (July, 1989 through June, 1990).

At an air-to-cloth ratio of 1.5 ft/min, data in Table 14 shows that an increase in the NO_x concentration from 300 to 1000 ppm resulted in an increase in NO_x removal efficiency. However, at an air-to-cloth ratio of 4 ft/min, an increase in the NO_x concentration did not result in an increase in NO_x removal efficiency. This observation is consistent with the statistical analysis of the data that showed an interaction between the NO_x concentration and air-to-cloth ratio. Therefore, at low air-to-cloth ratios (2 ft/min or less) and all other conditions being constant, it appears that in this process scheme the NO_x removal efficiency is controlled to some degree by the concentration of NO_x in the flue gas due to gas phase mass transfer to the catalyst site. At the moderate to high air-to-cloth ratios (4 ft/min or greater), the NO_x removal efficiency appears to be controlled by the contact time at the catalyst site.

Again, the degree to which ammonia/ NO_x molar ratio affected NO_x removal was less than one might expect due to the limited range evaluated (0.8 to 1.1). However, the range of ammonia/ NO_x molar ratios evaluated is appropriate with respect to the level of NO_x removal desired.

The statistical significance of SO_2 concentration and the interaction of SO_2 and NO_x is consistent with the first series of parametric experiments.

Figure 10. Percent NO_x removal versus air-to-cloth ratio and ammonia/ NO_x molar ratio.

Although data presented in Table 14 indicates that in some cases NO_x removal efficiency decreased with increased SO_2 concentration, in other cases no effect was observed. This observation raises two questions. First, is the observed effect actually caused by SO_2 or is SO_3 responsible? Second, is the observed effect real or is the inconsistency in the data an indication that the effect of SO_2/SO_3 concentration is an artifact of the simulated flue gas and/or the bench-scale system used during the experimental effort.

Fabric Sample 2 produced significant levels of SO_3 (>100 ppm) during fabric screening tests. Therefore, SO_3 may actually be responsible for decreased NO_x removal rather than SO_2 . If the observation is real, the statistical significance observed for SO_2/SO_3 concentration and the interaction of SO_2/SO_3 and NO_x indicates the potential for competing reactions at the catalyst sites and may explain the apparent decrease in fabric reactivity with time observed in this series of experiments. This issue will also be investigated further in future experiments using actual flue gas from pulverized coal firing. Measurement of SO_3 concentration downstream of the catalyst-coated fabric will be necessary in future experimental plans to better address this issue.

Although the bench-scale fabric filter holder/simulated flue gas system was not amenable to routine particulate sampling, particulate measurements were made using Fabric 15. The calculated particulate control efficiency was 99.8% with a measured inlet dust loading of 2.05 gr/scf. Since this data does not represent performance as a result of long term operation or the impact of cleaning cycles, it should be considered qualitative in nature. The filter

cake generated on the outlet filter was not uniform indicating that the measured particulate emissions may have been high due to the release of material from tubing walls downstream of the fabric. Also Fabric 15 was prepared using a nontextured cloth. Textured fabric samples would be expected to perform better with respect to particulate emissions control. Particulate emissions measurements will be made during Task B, Fabric Screening Tests, planned for the period July, 1989 through June, 1990. Task C, Bag Evaluation and Parametric Tests, will specifically evaluate fabric performance in terms of particulate emissions control.

4.0 CONCLUSIONS

Based on the results of work completed during the period April 1, 1988 through June 30, 1989, on the SO_x/NO_x Control Project, sponsored by the U.S. Department of Energy under the Cooperative Agreement (Contract No. DE-FC21-86MC10637), several conclusions are presented.

4.1 Bench-Scale Fabric Screening Tests

Addition of a refractory component (Al or Zr) to the original V/Ti catalyst substantially reduced the catalytic reactivity of the fabric.

The reactivity of the catalytic fabric was improved by increasing the amount of catalyst on the fabric. Two approaches were tested with similar results. The first approach involved increasing the catalyst concentration in the coating solution and the second approach involved coating a fabric sample several times using the same coating solution.

Application of a refractory undercoat prior to applying the catalyst coating did not appear to significantly impact the performance of the catalytic fabric.

The use of a textured cloth improved the performance of the catalytic fabric in terms of higher NO_x removal efficiency and lower ammonia-slip.

4.2 Bench-Scale Parametric Tests

Statistical analysis of the data indicated that the flue gas NO_x concentration, the air-to-cloth ratio, and the interaction between these two parameters produced the greatest effect on NO_x removal efficiency. At a low air-to-cloth ratio (1.5 ft/min) an increase in NO_x concentration from 300 to 1000 ppm resulted in an increase in NO_x removal efficiency. When air-to-cloth ratio was increased to 4 ft/min, an increase in NO_x concentration had no effect on NO_x removal efficiency. Increasing air-to-cloth ratio from 1.5 to 4.0 ft/min resulted in a decrease in the NO_x removal efficiency.

To a lesser degree, the ammonia/ NO_x molar ratio, the SO_2 concentration, and the interaction between NO_x concentration and SO_2 concentration appear to impact NO_x removal efficiency. As expected, increasing the ammonia/ NO_x molar ratio from 0.8 to 1.1 increased the NO_x removal. But due to the limited range, the statistical significance of the effect was small.

Although there was inconsistency in the data, increasing SO_2 concentration from 300 to 3000 ppm decreased NO_x removal for most experimental conditions. Whether the effect of SO_2 concentration was real or an artifact of the bench-scale tests will be determined in future experiments. This will require routine measurement of SO_3 concentration downstream of the catalyst-coated fabric during future experiments.

5.0 RECOMMENDATIONS

Based on the results reported for Task A, Catalyst/Fabric Development, EMRC believes that sufficient success has been achieved to warrant the initiation of Task B, Fabric Screening Tests, as outlined in the Annual Project Plan (APP-4) for the fourth year of the Cooperative Agreement. EMRC will initiate Task B by preparing a detailed work plan and submitting the work plan for review by the project COTR. The work plan will document proposed activities for the time period of July, 1989 through June, 1990.

Although EMRC personnel are not aware of documented evidence in the literature showing the formation of N_2O to occur as a result of conventional SCR catalytic reactions, the reducing environment of an SCR system creates the potential for N_2O formation due to the role that N_2O may play as a greenhouse gas, concern with respect to its formation and emission from industrial and utility combustion systems is warranted. To address this issue with respect to the catalytic fabric filter concept, EMRC is evaluating two options that could be implemented during Task C, Bag Evaluation and Parametric Tests. The first option would involve purchasing a commercial instrument that would provide EMRC with the capability to monitor N_2O concentrations downstream of the catalyst-coated fabric during all phases of the proposed pilot-scale test program. The second option would involve paying a subcontractor to measure N_2O concentrations downstream of the catalyst-coated fabric during a one-week test period. The estimated cost of the first option is \$8,000 to \$10,000, versus \$3,000 to \$4,000 for the second option. A decision concerning this issue is expected to be made in December, 1989.

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U.S. DEPARTMENT OF ENERGY
FEDERAL ASSISTANCE MANAGEMENT SUMMARY REPORT

1. Program/Project Identification No.		2. Program/Project Title SO _x /NO _x Control		3. Reporting Period 04-01-88 through 06-30-89	
4. Name and Address University of North Dakota Energy & Mineral Research Center Box 8213, University Station Grand Forks, ND 58202				5. Program/Project Start Date 4/1/86	
				6. Completion Date 3/31/92	

Milestone ID. No.	Description	Planned Completion Date	Actual Completion Date	Comments
a.1	Complete detailed project plan for 4/88 - 3/89 including COTR review	05/15/88	06/15/88	
	Complete design and assembly of the bench-scale test apparatus	07/31/88	08/20/88	
a.2	Complete catalytic fabric screening experiments	02/28/89	06/10/89	
a.3	Complete operating parameter evaluation experiments	05/31/89	06/30/89	
a.4	Complete Annual Project Report	06/30/89	08/31/89	
b.1	Modify and relocate the bench-scale test apparatus to permit use of actual flue gas from a pilot-scale pc-fired combustion system	06/30/89		(Note)
Note: Milestone b.1 has been rescheduled for completion by 08/31/89 and has been included in the APP-4 work plan.				

2.2 Waste Management

WASTE MANAGEMENT

Final Technical Progress Report for the Period April 1, 1988 - June 30, 1989
Including the Quarterly Technical Progress Report
for the Period April through June 1989

by

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Prepared for
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Office of Fossil Energy
Morgantown Energy Technology Center
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TABLE OF CONTENTS

	<u>Page</u>
1.0 GOALS AND OBJECTIVES.....	1
2.0 ACCOMPLISHMENTS.....	1
2.1 Waste Characterization Studies.....	1
2.2 Fly Ash Liner Accomplishments.....	3
2.3 Fly Ash Carbon Reduction.....	5
3.0 WASTE CHARACTERIZATION STUDIES.....	6
3.1 Waste Characterization Test Methods.....	6
3.2 Waste Characterization Results.....	8
3.2.1 Pressure-Hydrated Lime Injection Wastes.....	8
3.2.2 Diesel Engine Waste.....	13
3.3 Waste Characterization Conclusions.....	15
4.0 FLY ASH LINER FIELD TESTS.....	15
4.1 Liner Construction Methods for the Field Tests.....	16
4.2 Problems Encountered During the Field Tests.....	17
4.3 Liner Physical Property Test Results.....	19
4.4 Liner In-Field Permeability Test Results.....	25
4.5 Fly Ash Liner Field-Test Site Inspections.....	26
4.5.1 SWEPCO Site Inspection.....	26
4.5.2 NIPSCO Site Inspection.....	28
4.5.3 NSP Site Inspection.....	28
4.6 Conclusions and Topics for Future Research.....	28
5.0 ELECTROSTATIC SEPARATION OF UNBURNED CARBON FROM FLY ASH.....	29
5.1 Introduction.....	29
5.2 Materials and Methods.....	30
5.3 Electrostatic Separator Test Results.....	33
5.3.1 Electrode Placement Tests.....	35
5.3.2 Additional Process Optimization Tests.....	36
5.3.3 Ash Collection Runs.....	36
5.4 Carbon Separation - Summary and Conclusions.....	38
6.0 REFERENCES.....	39
APPENDIX A	
APPENDIX B	

LIST OF TABLES

<u>Table</u>	<u>Page</u>
1 List of Samples Characterized by the Waste Management Project.....	1
2 Waste Characterization Test Protocol.....	3
3 Maximum Allowable Concentrations of Leachate Contaminants for RCRA Hazardous Waste Classification.....	8
4 EPA-EP Leaching Test Results for Fly Ashes From Pressure-Hydrated Lime Injection Tests Using Pittsburgh #8 Bituminous Coal.....	9
5 ASTM Leaching Test Results for Fly Ashes From Pressure-Hydrated Lime Injection Tests Using Pittsburgh #8 Bituminous Coal.....	9
6 Elemental Compositions of Fly Ashes From Pressure-Hydrated Lime Injection Tests Using Pittsburgh #8 Bituminous Coal.....	11
7 Mineral Compositions of Fly Ashes From Pressure-Hydrated Lime Injection Tests Using Pittsburgh #8 Bituminous Coal.....	11
8 Physical Properties of Fly Ashes From Hydrated-Lime Injection Tests Using Pittsburgh #8 Bituminous Coal.....	12
9 Elemental Composition of the Diesel Engine Ash.....	14
10 Leaching Test Results From Diesel Engine Ash.....	14
11 Physical Property Tests From the Diesel Engine Ash.....	15
12 Liner Physical Property Test Methods.....	20
13 Construction Dates and Sample Collection Dates for the Fly Ash Liner Field Tests.....	20
14 Laboratory Test Results for the SWEPCO Liner Samples Collected in the Field.....	21
15 Laboratory Test Results for the NIPSCO Liner Samples Collected in the Field.....	23
16 Laboratory Test Results for the NSP Liner Samples Collected in the Field.....	24
17 Infiltrometer Test Results.....	27
18 Elemental Composition of the King Fly Ash.....	34

LIST OF FIGURES

<u>Figure</u>	<u>Page</u>
1 Schematic Diagram of the Electrostatic Separator.....	31
2 Photograph of the Bench-Scale Separator Apparatus.....	32
3 Fly Ash Particle Size Distribution Curve.....	33
4 LOI of the Various Fly Ash Fractions Collected for the Particle Size Distributions.....	34
5 Diagram of the Various Electrode Positions Tested for the Separator.....	35
6 LOI of the Recovered Fly Ash Fraction as a Function of the Ash Loading Rate.....	37
7 Weight Percent Fly Ash Recovered in the Low-LOI Fraction as a Function of the Ash Loading Rate.....	37

1.0 GOALS AND OBJECTIVES

Waste Management Project personnel are conducting research to characterize waste materials from advanced coal utilization processes and to develop innovative management practices for coal utilization by-products.

The purpose of the waste characterization work is to predict the environmental impacts of wastes from several processes being developed at the University of North Dakota Energy and Mineral Research Center (EMRC). The project is currently evaluating the chemical and physical properties of combustion wastes after treatment with a pressure-hydrated lime injection process designed to reduce SO_2 emissions, and combustion wastes from a coal slurry fired diesel engine.

Project personnel are also developing innovative uses for coal combustion by-products. Current activities in this area include development of methods for constructing fly ash liners at waste disposal sites and for reducing the unburned carbon content of fly ash. The purpose of the liner study is to assist utility companies to implement new environmental regulations in a cost-effective manner, and the purpose of the carbon removal study is to increase the utilization of fly ash as a replacement for portland cement in concrete.

2.0 ACCOMPLISHMENTS

2.1 Waste Characterization Studies

Waste materials characterized during this reporting period included fly ashes produced from combustion tests performed at EMRC in which pressure-hydrated lime was injected into the flue gas for SO_2 control, and a solid waste from a diesel engine burning a coal-derived liquid fuel.

Three fly ash samples were obtained from combustion tests that used pressure-hydrated lime injection for SO_2 control. The fuel used for the combustion tests was a Pittsburgh #8 bituminous coal. The fly ash samples were collected in an electrostatic precipitator installed on a 500,000-BTU/hr pulverized coal combustion unit. The samples were obtained from baseline combustion runs during which no lime was injected, and from combustion runs with lime injection, which caused either a 50% or a 90% SO_2 content reduction in the flue gases.

The other waste material studied was a residual ash from a diesel engine designed to burn coal-derived liquid fuels. The fuel used was a light coal tar fraction obtained from the Great Plains Coal Gasification Plant. The diesel waste was basically a high-carbon-content soot collected from the engine exhaust gas.

Additional information about the wastes characterized is contained in Table 1.

The general test protocol used for the characterization studies consisted of waste analyses for elemental, mineral, and trace organic content; waste leachate analyses for trace metals and trace organic compounds; and tests of

TABLE 1
LIST OF SAMPLES CHARACTERIZED BY THE WASTE MANAGEMENT PROJECT

<u>Sample No.</u>	<u>Fuel Type</u>	<u>Process Modification</u>	<u>Sample Type</u>
<u>Hydrated-Lime Injection Test Samples:</u>			
1.	Pittsburgh #8 (Bit*)	No Lime Injection (Baseline Test)	ESP Fly Ash
2.	Pittsburgh #8 (Bit)	Lime Injection - 1.7:1 Ca-to-SO ₂ Ratio 50% SO ₂ Removal	ESP Fly Ash
3.	Pittsburgh #8 (Bit)	Lime Injection - 4.1:1 Ca-to-SO ₂ Ratio 90% SO ₂ Removal	ESP Fly Ash
<u>Diesel Engine Ash:</u>			
4.	Great Plains Coal Tar	Diesel Engine Modified to Burn Coal Liquids	Engine Ash

* Bituminous Coal

physical properties relevant to waste disposal. The waste characterization protocol is listed in Table 2.

It was not possible to perform the entire characterization protocol on the diesel engine waste since only about ten grams of waste was obtained from the combustion tests.

The results of the waste characterization activities are summarized as follows:

- * EPA-EP leachates produced from the combustion wastes ashes contained trace metal concentrations well below the maximum allowable contaminant levels specified by the regulations of the Resource Conservation and Recovery Act (RCRA) for hazardous waste classification.
- * No significant trace organic compounds were detected in leachates produced from the hydrated lime injection wastes. It appeared that some organic material was extracted from the diesel engine ash, but the materials could not be identified by routine GC/MC analysis.

TABLE 2
WASTE CHARACTERIZATION TEST PROTOCOL

A. Solid Waste Leachate Production

1. EPA-EP batch extraction and inorganic trace element analyses
2. ASTM D 3987-81 batch extraction and inorganic trace element analyses
3. Trace organic analyses of waste leachates

B. Solid Waste Chemical and Mineral Analyses

1. Major and trace inorganic elemental composition
2. Mineral composition
3. Trace organic content

C. Solid Waste Physical Properties

1. Bulk density
 2. Specific surface area
 3. Loss on ignition
 4. Hydraulic conductivity, as measured by permeability coefficient (on selected samples)
 5. Particle density (on selected samples)
 6. Compacted dry density (on selected samples)
-

* The hydraulic conductivities of the 50% and 90% SO₂ reduction flyashes were both well below the 10⁻⁷ cm/sec criteria generally required for clay liner materials.

* The fly ash obtained from the 90% SO₂ reduction test contained a significant amount of unhydrated calcium oxide that caused an extremely exothermal reaction when the material was wetted.

2.2 Fly Ash Liner Accomplishments

The objective of the fly ash liner study is to develop cost-effective liner technology for utility waste disposal sites. In the first year of the study, a series of laboratory tests was performed to develop liner formulas for six different types of fly ash wastes, and in the second and third years, three 40 by 40 by 2-foot liner test sections were constructed at field sites located in Texas, Indiana, and Minnesota.

The fly ash liner materials were produced by mixing coal combustion wastes with appropriate amounts of portland cement, hydrated lime and water. Each liner formula was selected so that the material would exhibit a hydraulic conductivity (as measured by the coefficient of permeability) of less than 10⁻⁷ cm/sec and sufficient strength to withstand the loading and weathering stresses encountered in the field.

During this reporting period, fly ash liner tests were completed at the Texas, Indiana, and Minnesota field sites. To monitor the performance of the fly ash liners, three sets of samples were collected from each field site over a one-year period and sent to EMRC for testing. The samples were tested for permeability coefficient, unconfined compressive strength, tensile strength, modulus of elasticity, Poisson's ratio, coefficient of thermal expansion, porosity, and dry density. In addition to the laboratory tests, a double-barrel infiltrometer test was conducted at each of the sites to estimate the permeability of the liner using an in-field method.

The Texas fly ash liner test was performed at the H. W. Pirkey Power Plant, owned by the Southwestern Electric Power Company (SWEPCO). The SWEPCO liner section was made with a Texas lignite fly ash. Approximately 5 wt% portland cement, 1.5 wt% hydrated lime, and 18 wt% (dry weight) water were added to the fly ash to produce the liner material.

The results of the SWEPCO field test generally indicated that the Texas lignite fly ash produced an acceptable liner material. Permeability coefficients measured in the laboratory for 12 liner samples varied from 1.4×10^{-9} cm/sec to 3.8×10^{-9} cm/sec, and the permeability coefficient measured in the field was estimated to be less than 10^{-7} cm/sec. The liner material developed an unconfined compressive strength of approximately 1000 psi after curing in the field for one year. The only visible deterioration of the SWEPCO liner section during the field test was the development of some cracks on the liner surface. The cracks appeared to be limited to the top six inches of the liner.

The Indiana fly ash liner test was performed at the R. M. Schahfer Plant, owned by the Northern Indiana Public Service Company (NIPSCO). The NIPSCO liner section was made with a 50/50 mixture of Illinois #6 fly ash and lime-based scrubber sludge. Approximately 5 wt% portland cement, 3 wt% percent hydrated lime, and 30 wt% (dry weight) water were added to the fly ash-scrubber sludge mix to produce the liner material.

The results of the NIPSCO field test indicated that this liner material did not meet the target permeability criteria. Permeability coefficients measured in the laboratory for 12 Indiana liner samples varied from 8.0×10^{-5} cm/sec to 2.0×10^{-5} cm/sec, and the permeability coefficient measured in the field was estimated to be 7.8×10^{-7} cm/sec. The liner material developed an unconfined compressive strength of approximately 700 psi after curing in the field for one year. The only visible deterioration of the liner section during the field test was some crumbling at the liner surface. The crumbling extended about two inches below the surface. Although the permeability of the NIPSCO liner did not meet the target level of less than 10^{-7} cm/sec, it may still be useable for some liner applications, since Indiana regulations only require that liners for coal combustion wastes have a permeability coefficient less than 10^{-6} cm/sec.

The Minnesota fly ash liner test was performed at the Sherburne County Power Plant, owned by the Northern States Power Company (NSP). The NSP liner section was made with a dry scrubber powder containing Sarpy Creek, Montana, subbituminous coal fly ash and a lime-based spray dryer residue. Approximately 23 wt% (dry weight) water was added to the scrubber powder to produce the liner material. No lime or cement addition was required for the NSP liner.

A problem occurred with the NSP liner material used for the field test when shrinkage cracks developed during the initial stage of curing. The shrinkage was reduced by decreasing the amount of water added to the liner mix from 23% to approximately 20% of dry weight. Unfortunately, decreasing the water content of the liner mix caused its permeability to increase. The log-mean permeability coefficient of the liner material placed with 23% water was 5.9×10^{-9} cm/sec, while the log-mean permeability coefficient of the liner material placed with 20% water was 3.7×10^{-6} cm/sec. The permeability coefficient estimated from the in-field test was 1.8×10^{-5} cm/sec. The unconfined compressive strength of the NSP liner material ranged between 1000 and 2000 psi.

It was not possible to determine from the results of the field test whether the shrinkage cracks in the NSP liner were continuous. If the cracks were continuous through the full depth of the liner, then, obviously, it is an unacceptable liner. If the cracks are not continuous, then the material may be useable as a liner.

Microscopic analysis of the liner materials indicated that the SWEPCO liner was cemented mainly by point bonds between the fly ash particles, while the NIPSCO and NSP liner materials, both of which contained scrubber residues, were cemented by a continuous interparticle matrix. The principal cementitious mineral phase identified in all three of the liners was ettringite.

Chemical analyses were done for both the fly ashes and the liner materials produced in the field. The results of the chemical analyses are contained in Appendix A.

2.3 Fly Ash Carbon Reduction

An "off-the-shelf" electrostatic separation process was modified for use to reduce the unburned carbon content of fly ash. A bench-scale separator apparatus was constructed at EMRC and a series of test runs was performed to optimize the process. After the process was optimized, a sufficient amount of low-LOI fly ash was collected to determine its air entrainment characteristics.

The fly ash used for the separation tests was obtained from the Allen S. King power plant owned by the Northern States Power Company. The King plant burns a mixture of Wyoming and Montana subbituminous coals and Illinois bituminous coal. A chemical analysis of the King ash is shown in Table 18.

The separator apparatus operates by dispensing fly ash from a vibrating pan through a slit onto a grounded, rotating steel drum. The high-LOI ash fraction falls off the drum due to gravity as it rotates. The low-LOI ash fraction sticks to the wheel due to electrostatic forces and is scraped off at a separate collection point. The off-the-shelf version of this separator uses a high-voltage electrode to induce a negative charge on the particles being classified. For the fly ash separator, the electrode did not improve the operation of the apparatus and so it was removed. It appeared that the fly ash had a sufficient electrostatic charge to stick to the drum without using the electrode.

The results of the separator tests showed that the apparatus was capable of splitting the bulk fly ash, which had an LOI of 7.3%, into two physically separate fractions. One fraction contained approximately 25 wt% of the ash and had an LOI of 3.6 percent, while the other fraction contained 75 wt% of the ash and had an LOI of 8.2 percent. Air entrainment tests performed on the two fly ash fractions indicated that the low-LOI fraction required 13.2% less air entraining agent than the bulk fly ash to produce an equivalent entrained air level.

The goal of the study was to produce fly ash with an LOI of less than three percent using the electrostatic separation process. It was not possible to achieve this level in the test runs performed. However, the ASTM C618 fly ash specification for cement replacement only requires that fly ash have an LOI of less than six percent, and the separation process easily achieved this level.

Based on the results of the bench-scale tests, it appears that the electrostatic carbon removal process has commercial development potential, since it is mechanically quite simple and produces significant carbon removal with a relatively low energy input. One drawback of the process is that only about 25% of the bulk fly ash is recovered in the low-LOI fraction. However, it may be possible to increase this recovery with further development of the process. Furthermore, some power plants may not be able to sell more than 25% of their fly ash for cement replacement due to market limitations.

3.0 WASTE CHARACTERIZATION STUDIES

The test protocol for waste characterization consisted of leaching tests, chemical and mineral analyses, and physical property tests. The characterization data was used to evaluate the waste disposal requirements for advanced combustion processes being developed at EMRC. The principal objective of the evaluation process was to identify any potential regulatory problems that may develop from the disposal of these wastes when advanced processes are implemented on a commercial scale.

3.1 Waste Characterization Test Methods

The methods used for the waste characterization studies are discussed in this section. Well-documented and standardized methods were selected for each of the characterization procedures.

Various leaching tests are used to evaluate the regulatory status of solid wastes. The purpose of the EPA-EP batch leaching test is to determine whether a solid waste could be classified as a hazardous waste under the RCRA regulations. Generally, a solid waste may be designated as a hazardous waste if its leachate trace metal levels exceed the maximum allowable contaminant concentrations listed in Table 3 (1). Although coal combustion wastes are exempted from hazardous waste classification under the current RCRA regulations, the EPA-EP leaching test was performed as part of the waste characterization protocol for possible future reference. The EPA-EP leaching test uses a 20:1 liquid-to-solids ratio and acetic acid addition to simulate representative municipal-waste landfill conditions. A detailed description of the procedure for the EPA-EP leaching test is contained in Reference 2.

The ASTM D 3987-81 batch leaching test was used for the waste characterization protocol to evaluate trace metal extraction from the wastes under alkaline leaching conditions. The ASTM procedure uses a 4:1 liquid-to-solids ratio and no acid is added to the leaching solution. Generally, ASTM-type leachates from western low-rank coal ashes have pH values ranging from 10 to 13. The data obtained from the ASTM leaching test is useful for estimating the impact of coal combustion waste disposal practices on groundwater. In this regard, the RCRA regulations specify that a disposal facility shall not contaminate an underground drinking water source beyond the boundary of the facility. To "contaminate" in this context means to cause trace metal concentrations in the groundwater to exceed their primary drinking water standards. The primary drinking water standards for regulated trace metals are equal to 1/100 of the concentrations listed in Table 3.

The presence of trace organic compounds in solid wastes is becoming more of a regulatory concern due to the 1984 amendments to the RCRA regulations. In response to these amendments, the EPA has proposed the addition of phenol, cresol, benzene, and toluene to the list of regulated leachate contaminants. For this reason, trace organic analyses were included in the waste characterization protocol. Trace organic compounds in the waste samples and their leachates were extracted and analyzed using methods developed at the Morgantown Energy Technology Center (3). To perform the test, the waste materials were extracted (a) directly from the waste solids with methylene chloride in a soxhlet apparatus, and (b) from ASTM waste leachates with methylene chloride to yield separate acid and base/neutral fractions.

The methylene chloride extracts were analyzed using a semi-quantitative gas chromatography/mass spectrometry (GC/MS) scanning procedure. If significant amounts of organics were detected in the samples by the GC/MS scan, additional analyses using gas chromatography were done to quantify the trace organics. The detection limit for organic compounds extracted directly from the waste was 1.0 µg/gram ash, and the detection limit for organic compounds extracted from the ASTM leachates was 20 mg/L in the leachate.

Information about the elemental and mineral compositions of a waste can be used to evaluate relevant disposal properties such as leaching behavior, exothermal hydration potential, abrasiveness, and self-hardening potential. Compositional data can also be used to evaluate the by-product utilization potential of the waste. Elemental analyses were performed on the waste samples using energy-dispersive X-ray fluorescence. The mineral composition of the waste samples were determined by powder X-ray diffraction.

The waste permeability coefficient, or hydraulic conductivity, is a measure of the rate at which water passes through the material under a specified hydraulic head, and thus indicates the amount of leachate that may be produced after waste disposal. The permeability coefficient was measured with a falling-head test apparatus (4).

The bulk density of a waste can be used to calculate volume requirements for future disposal facilities. Bulk density was measured by a conventional volume displacement technique.

TABLE 3
MAXIMUM ALLOWABLE CONCENTRATIONS OF LEACHATE CONTAMINANTS
FOR RCRA HAZARDOUS WASTE CLASSIFICATION

<u>Element</u>	<u>Maximum Concentration (mg/l)</u>
Arsenic	5.0
Barium	100.0
Cadmium	1.0
Chromium	5.0
Lead	5.0
Mercury	0.2
Selenium	1.0
Silver	5.0

The specific surface area of a waste may affect its leaching behavior. In general, the greater the specific surface area, the higher will be the rate at which soluble inorganic constituents leach from the waste. Specific surface area was measured with a Quantachrome, single-point, monosorb instrument, using the BET liquid nitrogen adsorption technique.

The loss-on-ignition test measures the unburned carbon content of a waste. A high unburned carbon content generally reduces the by-product utilization value of fly ash because it tends to adsorb the air-entrainment chemicals added to concrete mixtures. Loss-on-ignition was measured using the procedure specified in ASTM Method C 311-68.

3.2 Waste Characterization Results

3.2.1 Pressure-Hydrated Lime Injection Wastes

The results of the EPA-EP batch leaching tests performed on pressure-hydrated lime injection wastes are summarized in Table 4. The EPA-EP test is used to determine whether a solid waste may be classified as a hazardous waste under the regulations established by the Resource Conservation and Recovery Act (RCRA). The maximum allowable leachate trace element levels, as specified in the RCRA regulations, are shown in Table 3. Comparing Table 4 to Table 3 shows that the three fly ashes from the lime injection tests produced EP leachates with trace element concentrations well below the RCRA limits. Therefore, these wastes would not be classified as hazardous based on leachate trace element content.

ASTM D 3987 batch leaching tests were performed on the lime injection wastes to evaluate inorganic trace metal leaching behavior under alkaline pH conditions. This type of leaching behavior is important because wastes containing free lime generally produce alkaline leachates after disposal. Furthermore, some states use the ASTM test to determine whether wastes may eventually contaminate groundwater after disposal. A waste may be considered to have a low potential for contaminating groundwater if the trace element concentrations in its ASTM leachate are less than 10% of the RCRA limits shown in Table 3.

TABLE 4

EPA-EP LEACHING TEST RESULTS FOR FLY ASHES FROM PRESSURE-HYDRATED
LIME INJECTION TESTS USING PITTSBURGH #8 BITUMINOUS COAL

Element*	Baseline Ash (0% SO ₂ Removal)	Ash From 50% SO ₂ Removal Test	Ash From 90% SO ₂ Removal Test
Arsenic	0.9	0.0085	0.0023
Barium	0.06	0.38	0.32
Cadmium	<0.1	<0.1	<0.1
Chromium (Total)	<0.05	0.08	0.1
Lead	<0.6	<0.6	<0.6
Mercury	0.0018	0.0008	0.0012
Selenium	0.0044	0.0026	<0.002
Silver	<0.5	<0.5	<0.5

* All elemental concentrations measured for the EPA-EP leachates have units of mg/L.

TABLE 5

ASTM LEACHING TEST RESULTS FOR FLY ASHES FROM PRESSURE-HYDRATED
LIME INJECTION TESTS USING PITTSBURGH #8 BITUMINOUS COAL

Element*	Baseline Ash (0% SO ₂ Removal)	Ash From 50% SO ₂ Removal Test	Ash From 90% SO ₂ Removal Test
Aluminum	0.6	<0.5	<0.5
Arsenic	1.2	0.0046	0.0031
Barium	0.16	0.34	0.31
Boron	41.0	3.0	4.4
Cadmium	<0.1	<0.1	<0.1
Calcium	680.0	1700.0	2000.0
Chromium (Total)	<0.05	<0.05	0.22
Lead	<0.6	<0.6	<0.6
Mercury	0.001	0.0015	0.001
Selenium	0.0093	0.0096	0.0059
Sodium	39.0	8.4	8.1
Sulfate	2040.0	1720.0	1750.0
pH	5.9	12.5	12.5

* All elemental concentrations measured for the ASTM leachates have units of mg/L.

The results of the ASTM leaching tests are shown in Table 5. The only trace element that exceeded 10% of its RCRA limit was arsenic in fly ash from the baseline test. The arsenic concentration in the baseline leachate was 1.2 mg/L; the RCRA limit is 5.0 mg/L. It is interesting to note that the arsenic concentrations in the two fly ash leachates produced with lime injection were both much lower than the concentration in the baseline leachate. Some of the reduction in arsenic concentration is due to dilution of the fly ash with spent lime, but dilution does not account for all of the reduction.

We have seen similar arsenic immobilization behavior in leaching studies performed at EMRC. In these studies, 3.3 wt% lime added to an ash from a North Dakota lignite caused the arsenic concentration of the leachate to be reduced from 1.4 mg/L to 0.1 mg/L (5). However, the chemical mechanism responsible for the apparent arsenic immobilization was not clearly understood. Canadian researchers have also noted a reduction in the solubility of arsenic in the presence of lime, and they have postulated that the formation of a calcium arsenate-lime complex is the mechanism causing the observed arsenic immobilization. These researchers suggested that the complex may be represented by the formula $3\text{Ca}_3(\text{AsO}_4)_2 \cdot \text{Ca}(\text{OH})_2$ (6).

The lime injection fly ashes were tested for trace organic content using a procedure developed by the Morgantown Energy Technology Center. No significant amounts of trace organics were detected in any of the lime injection fly ashes. The minimum detection limit for the analysis of organics in the leachates was 20 mg/L. The minimum detection limit for organics extracted directly from the wastes was 2.0 $\mu\text{g/g}$.

The elemental and mineral analyses of the lime injection fly ashes are summarized in Tables 6 and 7. The baseline fly ash from the Pittsburgh #8 coal was composed almost entirely of oxides of silicon, aluminum, and iron. The environmentally significant trace element that were present in highest concentrations in the baseline ash were arsenic and barium. The most abundant elements in the ashes from the 50% and 90% SO_2 reduction tests, however, were calcium and sulfur. The altered compositions of the lime injection ashes is due to the reaction of $\text{Ca}(\text{OH})_2$ with SO_2 to form calcium sulfate. The effect of lime injection on the mineral compositions of the fly ashes is also apparent since the major mineral phases in the baseline ash are quartz (SiO_2) and spinels while the major mineral phases in the ashes produced with lime injection are anhydrite (CaSO_4) and lime (CaO). The fact that lime was a major mineral phase in both the 50% and 90% SO_2 reduction fly ashes indicated that a significant amount of unutilized lime was present in both of these wastes.

The elemental composition of the baseline Pittsburgh #8 fly ash indicates that this is an ASTM "Class F" material, and therefore it should exhibit good pozzolanic properties. Pozzolanic materials form strong interparticle bonds when they react chemically with free calcium and moisture. Since the mineral analyses detected the presence of lime in both the 50% and 90% SO_2 reduction ashes, extensive interparticle bonding can be expected to occur in both of these wastes after they have been deposited in a landfill. Interparticle bonding will generally cause a decrease in the permeability and an increase in the strength of a waste over a extended period of time.

TABLE 6

ELEMENTAL COMPOSITIONS OF FLY ASHES FROM PRESSURE-HYDRATED LIME
INJECTION TESTS USING PITTSBURGH #8 BITUMINOUS COAL

Element*	Baseline Ash (0% SO ₂ Removal)	Ash From 50% SO ₂ Removal Test	Ash From 90% SO ₂ Removal Test
Silicon	23.5%	8.4%	3.4%
Aluminum	11.6%	4.4%	1.8%
Iron	14.7%	7.3%	3.4%
Calcium	1.75%	29.0%	42.8%
Magnesium	0.8%	0.5%	0.3%
Sodium	<0.1%	<0.1%	<0.1%
Potassium	2.2%	0.7%	0.1%
Sulfur	0.6%	8.2%	7.1%
Phosphorus	0.1%	0.4%	0.3%
Titanium	0.7%	0.4%	0.2%
Arsenic	240.0	90.0	40.0
Barium	360.0	300.0	190.0
Copper	70.0	40.0	40.0
Chromium	140	60.0	20.0
Manganese	1300.0	150.0	80.0
Nickel	120.0	<10.0	<10.0
Strontium	200.0	170.0	150.0
Zinc	160.0	70.0	10.0

* Elemental concentrations for the waste materials are in units of either % of dry weight or micrograms/gram of waste. All analyses were done by X-ray Fluorescence.

TABLE 7

MINERAL COMPOSITIONS OF FLY ASHES FROM PRESSURE-HYDRATED LIME
INJECTION TESTS USING PITTSBURGH #8 BITUMINOUS COAL

Baseline Ash:
(0% SO₂ Removal)

Major Phases: Amorphous Phases, Quartz (SiO₂), Spinel (Fe₃O₄)

Minor Phases: Hematite (Fe₂O₃)

Ash From 50% SO₂ Reduction Test:

Major Phases: Anhydrite (CaSO₄) and Lime (CaO)

Minor Phases: Quartz (SiO₂) and Hematite (Fe₂O₃)

Ash From 90% SO₂ Reduction Test:

Major Phases: Anhydrite (CaSO₄) and Lime (CaO)

TABLE 8
PHYSICAL PROPERTIES OF FLY ASHES FROM HYDRATED-LIME INJECTION
TESTS USING PITTSBURGH #8 BITUMINOUS COAL

<u>Element</u>	<u>Baseline Ash (0% SO₂ Removal)</u>	<u>Ash From 50% SO₂ Removal Test</u>	<u>Ash From 90% SO₂ Removal Test</u>
Permeability Coefficient (cm/sec)	1.3×10^{-6}	2.5×10^{-8}	1.3×10^{-8}
Particle Density (g/ml)	1.87	1.82	2.58
Compacted Dry Density (lb/ft ³)	93.5	80.9	66.0
Optimum Moisture Content (% Dry Wt)	22.5	23.0	25.0
Specific Surface Area (m ² /g)	1.47	1.52	1.91
Loss On Ignition (Wt%)	3.2	1.0	1.8
Exothermal Hydration	None	Slight	Extreme

The physical properties of the lime injection fly ashes are listed in Table 8. The most important physical properties relating to the management of these wastes are compacted density, hydraulic conductivity, and exothermal hydration behavior.

The maximum compacted dry densities of the lime injection fly ashes ranged from 93.5 to 66 lb/ft³. The compacted densities were determined by preparing a moisture-density curve for each ash using standard proctor compaction. The compacted densities listed in Table 8 were measured at the optimum moisture addition levels which produced maximum dry densities.

Information about the compacted density of a waste is useful for predicting volume requirements for landfill design. Table 8 shows that the compacted densities of the lime injection fly ashes decreased as more lime was injected into the system. In practical terms, this means that a larger landfill will be needed to hold a given mass of waste material if lime injection is used to control SO₂ emissions. It should be noted, however, that there will not be a separate scrubber sludge stream requiring disposal when lime injection is used.

The hydraulic conductivities of the lime injection fly ashes were measured by compacting ash cylinders at approximately the optimum moisture content and then testing the cylinders using flexible membrane confinement in a triaxial cell. The hydraulic conductivities of the fly ashes ranged from 1.2×10^{-6} cm/sec to 1.3×10^{-8} cm/sec, and the lowest hydraulic conductivity was measured for the 90% SO₂ reduction ash. Comparing the hydraulic conductivities of the lime injection fly ashes to the common conductivity specification for clay soil liners of 10^{-7} cm/sec, indicates that both the 50 and 90% SO₂ reduction ashes had hydraulic conductivities similar to liner materials typically used for landfill construction.

An important feature of the lime injection fly ashes that was noticed during the moisture-density tests was that the materials from both the 50 and 90% SO₂ reduction tests gave off significant amounts of heat when they were initially mixed with water. The amount of heat released by the 50% SO₂ reduction ash was relatively small; the temperature of the waste increased by approximately 50°F after the water was added. The amount of heat released by the 90% SO₂ reduction ash, however, was quite large; in fact, a noticeable amount of steam was generated shortly after the water was added. This heat release is explained by the fact that both of these ashes contained lime, which hydrated when the water was added. This type of exothermal hydration behavior could make these waste materials difficult to handle during the disposal process. The heat generated with the 50% SO₂ reduction ash could probably be dealt with by some simple handling modifications, but the excessive heat from the 90% SO₂ reduction ash might require special handling procedures.

3.2.2 Diesel Engine Waste

A solid waste sample was collected from a diesel engine designed to burn coal-derived liquid fuels. The engine was operated at EMRC. The fuel used was a light coal tar fraction obtained from the Great Plains Coal Gasification Plant.

A relatively small amount of ash, approximately 10 grams, was generated from the diesel test, and this was basically a soot. Since there was only a small amount of material available for the characterization, the test protocol was modified to accommodate the small sample size.

A loss-on-ignition test performed on the diesel engine ash showed that the material was approximately 95% combustible. This means that the waste material has a high carbon content resulting from incomplete combustion of fuel in the engine. The material will be referred to as an ash, but technically it is more like a soot. The elemental composition of the inorganic fraction of the ash was analyzed by x-ray fluorescence spectroscopy, and the results of the analysis are summarized in Table 9.

A modified ASTM D3987 batch leaching test was performed on the diesel engine ash. Since there was only about ten grams of the ash available, five grams were leached with distilled-deionized water using a 4:1 liquid-to-solid ratio. The results of the leachate analysis are listed in Table 10. An insufficient volume of leachate was generated from the ash to analyze for either arsenic or selenium.

TABLE 9
ELEMENTAL COMPOSITION OF THE DIESEL ENGINE ASH

<u>Element</u>	<u>Wt% of Ash</u>
Silicon	0.4%
Aluminum	0.05%
Iron	1.4%
Titanium	0.2%
Phosphorous	0.2%
Calcium	2.0%
Magnesium	<0.1%
Sodium	<0.1%
Potassium	<0.1%
Sulfur	2.0%

TABLE 10
LEACHING TEST RESULTS FROM DIESEL ENGINE ASH

<u>Element</u>	<u>Leachate Concentration (mg/L)</u>
Barium	<5.0
Calcium	20.0
Chromium	0.12
Iron	0.5
Magnesium	3.8
Manganese	0.2
pH	6.0

It does not appear, based on the results in Table 10, that the diesel engine ash would create any significant trace element leaching problems when disposed of in a landfill.

The diesel engine ash was extracted with methylene chloride and the extract was analyzed by GC/MS for trace organics. Significant amounts of trace organics appeared to be extracted from the ash based on the dark color of the methylene chloride fraction, but the extracted materials could not be identified by the GC/MS analysis. It is probable that the organics in the ash extract were high molecular weight aromatic compounds produced from incomplete combustion of the gasifier tar. These types of compounds are difficult to identify because they cannot be separated by routine gas chromatographic analysis.

TABLE 11
PHYSICAL PROPERTY TESTS FROM THE DIESEL ENGINE ASH

Bulk Density	1.5 g/ml
Specific Surface Area	21.3 m ² /g
Loss On Ignition	99.5%

The diesel engine ash was analyzed by x-ray diffraction for mineral composition, but no significant mineral phases were identified.

The diesel engine ash was tested for bulk density, specific surface area, and loss-on-ignition. The results of the tests are listed in Table 11.

3.3 Waste Characterization Conclusions

The characterization data generated for the lime injection fly ashes indicates that no major regulatory problems should be encountered for the disposal of these materials. The results of the EPA-EP leaching tests clearly show that the wastes would not be classified as hazardous based on trace metal content under the existing RCRA regulations. The baseline Pittsburgh #8 fly ash did produce an ASTM leachate with an arsenic concentration that exceeded 10% of the RCRA limit, but both of the lime injection fly ashes had much lower arsenic concentrations.

The exothermal hydration behavior of the two fly ashes produced with lime injection could require implementation of special handling procedures if this SO₂ control process were implemented on a commercial scale. Facilities exist, however, which are disposing of similar wastes products without serious problems.

The diesel engine waste does not appear to pose any significant handling or disposal problems based on its inorganic trace element content. Although it was not possible to identify any specific trace organics, there did appear to be a significant amount of non-chromatographable material in the methylene chloride extract from the diesel engine waste.

4.0 FLY ASH LINER FIELD TESTS

Three fly ash liner test sections were constructed in the field using the SWEPCO, NIPSCO, and NSP fly ashes. For the field tests, liner sections having dimensions of 40 feet by 40 feet by 2 feet thick were constructed at power plants located in Texas (SWEPCO), Indiana (NIPSCO), and Minnesota (NSP). The physical properties of the liner sections were monitored for approximately one year to evaluate their performance.

The purpose of the field tests was to determine whether the liners could be constructed using in-field mixing and compaction methods and to evaluate their performance when exposed to outside weather conditions. The critical

weather related stresses of concern were expansion and contraction caused by freeze-thaw conditions and thermally induced warping.

Field tests were conducted at each of the power plants where the ashes were produced. The SWEPCO fly ash liner was placed at the H. W. Pirkey Power Plant, located near Hallsville, Texas. The Texas liner section was made with a Texas lignite fly ash. The NIPSCO fly ash liner was placed at the R. M. Schahfer Plant, located near Wheatfield, Indiana. The Indiana liner section was made with approximately a 50/50 mixture of Illinois #6 fly ash and lime-based scrubber sludge. The NSP fly ash liner was placed at the Sherburne County Power Plant, located near Becker, Minnesota. The Minnesota liner section was made with a dry scrubber powder containing Sarpy Creek, Montana, subbituminous coal fly ash and a lime-based spray dryer residue.

The three fly ashes for the field tests were selected so that one lignite ash, one subbituminous coal ash, and one bituminous coal ash would be represented in the study, and also so that the liner materials would be exposed to a wide range of different weather conditions at the various test sites.

Approximately 25% of the cost of the field tests was paid for by the three participating utility companies.

4.1 Liner Construction Methods for the Field Tests

Each of the liner sections was located in a low traffic area adjacent to the power plant's waste disposal landfill. The fly ashes used to construct the liners were freshly produced materials transported directly from the ash storage area to the test site.

The 40-foot lateral dimensions of the liner test sections were selected to be large enough to permit the use of representative in-field construction techniques and to permit maximum thermal warping stresses to develop at the liner surface. The test sections were made two feet thick because this is a typical design specification required by many states for clay liners.

The liner sections were installed so that the top surface was approximately flush with the surrounding soil surface. This type of placement exposed the test sections to ambient weather conditions throughout the test period and represented a "worst case" scenario in terms of the potential liner exposure.

The sections were installed in four vertical 6-inch lifts. Each lift was compacted using a vibratory steel drum roller. Three passes were made with the roller to obtain liner densities similar to those produced in the laboratory. The liner material was compacted within two hours after the water was added to ensure that it would set up properly.

At the SWEPCO and NIPSCO sites, each lift was placed by spreading approximately a 7-inch layer of fly ash and then tilling in the lime, cement, and water specified by the liner formulas. The SWEPCO fly ash was supplied to the test site with about a 5% moisture content, which was just enough to prevent a dusting problem. The NIPSCO fly ash was supplied to the test site already mixed with scrubber sludge, and it had about a 20% moisture content. At both sites, the lime and cement were added by laying the proper number of

bags of material in an evenly spaced pattern, spreading the material by hand, and then tilling it into the fly ash. A 5-foot tractor-mounted tiller was used to thoroughly mix the additives into the fly ash. After the lime and cement were mixed in, the required amount of water specified by the liner formula was added to the liner material using a water truck.

In-place mixing was used to construct the SWEPCO and NIPSCO liner sections because discussions with several contractors who had experience with fly ash pavement construction, indicated that in-place mixing would provide adequate control over the composition of the liner material and would cost about 50 percent less than batch mixing to use for a full-size project.

Batch mixing was used to construct the NSP liner section because the fly ash-scrubber powder is routinely conditioned in batch mixers at the plant, so the necessary batch mixing equipment was already available. Since no cementitious additives were required for the NSP liner material, the only modification needed to the normal ash conditioning operation was to increase the amount of water added. The NSP liner material was spread and compacted in the same manner as the SWEPCO and NIPSCO liners.

After each of the fly ash liner sections was completed, a double-ring infiltrometer apparatus was installed on the surface to perform an in-field permeability test.

4.2 Problems Encountered During the Field Tests

All three of the liner materials were fairly easy to work with during the field tests. The only problem encountered during the spreading and mixing steps was a slight dusting problem that occurred with the lime.

The most difficult part of the construction process was adding the proper amount of water to the liner material. In the field it was found that if a few percentage points of water were added over the level specified by the liner formula, it was impossible to compact the material because the roller bogged down. Further, the laboratory work had indicated that if the water addition level was more than a few percentage points below the specified level, the cured liner material would not be sufficiently impermeable to act as a liner. Based on these considerations, it was concluded that an acceptable moisture content for the liner materials ranged between about two percent above or below the level specified by the liner formula. Even when the moisture content was at the level specified by the liner formula, the liner was moderately difficult to compact because it tended to "pump" when the roller traveled over it, and the pumping action increased as more passes were made with the roller.

Based on the experience gained during the liner construction activities, a possible way to make the fly ash liner material workable over a wider range of moisture contents would be to add some aggregate to the mixture. The aggregate could be something as readily available as coarse bottom ash or boiler slag, which would not significantly increase the cost of the liner material. Adding aggregate would produce a stiffer liner mix to better support the roller during compaction, and the material could be handled more like a conventional roller-compacted concrete. The addition of aggregate to the fly ash liner mix would be a good topic for future research.

Both the SWEPCO and NIPSCO liners appeared to cure properly in the field without any significant shrinkage or expansion. The SWEPCO liner section was placed in August, and the afternoon temperatures were in the 90s. After the last lift of material was placed, half of the section was covered with plastic to retain the moisture. Both the covered and the uncovered portions of the liner seemed to cure properly, and it appeared that the plastic may not have been needed. It should be noted, however, that it rained soon after the liner section was completed and this additional moisture may have helped the uncovered section to cure properly. The rain was quite hard, but it did not appear to damage the freshly placed liner material.

The NIPSCO liner section was placed in September, and the afternoon temperatures were in the 70s. The finished NIPSCO section was not covered with plastic.

A serious problem occurred when the NSP liner material cured in the field. Shrinkage cracks developed overnight on the surface of the freshly placed lifts. Two lifts had been placed during the first day of construction. The cracks generally followed a three-foot-square grid pattern where the edge of the roller had traveled. Some of the cracks were about an eighth of an inch wide and one inch deep. This type of shrinkage behavior had not been observed in the preceding laboratory work.

The moisture content used for the first two lifts of the NSP liner averaged 24.5% of dry weight. The air temperature was about 95°F and the freshly mixed liner material was about 10 to 20 degrees warmer than the air temperature. The elevated temperature of the liner material was probably caused by exothermal hydration reactions that occurred when the water was added.

On the next day when the third and fourth lifts were placed, the moisture content was reduced to 23% of dry weight in an attempt to eliminate the shrinkage problem. At the lower moisture content, the liner material was easier to place and compact than it had been for the first two lifts. The weather conditions on the second day were similar to the day before. When the fourth lift was finished, a coat of clear acrylic concrete sealer was sprayed on the liner surface to prevent moisture loss.

After curing overnight, shrinkage cracks again developed on the surface of the fourth lift. The cracking was not as severe as had occurred on the second lift, however, and it appeared that reducing the moisture content had helped.

On the third day of the test, it was decided that a fifth lift should be constructed at a lower moisture content in a final attempt to overcome the cracking problem. The moisture content of the fifth lift was 21% of dry weight. At this moisture level, the liner material was noticeably dryer than it had been for the previous lifts and it tended to dust slightly. The material was easy to spread and compact, but it was so dry that some of the material on the surface tended to flake off because it had not bonded very well. A coat of acrylic sealer was applied to the surface of the fifth lift.

The fifth lift also cracked slightly after it had cured overnight. The cracking was less extensive than before but it was still significant.

Despite the cracking problem, the NSP liner material developed strength very rapidly as it cured in the field. After curing for only one night, the liner was so hard that it was not possible to dig into its surface with a small front-end loader.

Additional laboratory testing was done with the NSP liner material to determine whether the cracking would still occur if the material was placed at a lower ambient temperature. In early September, when the afternoon temperatures were in the 70s, two 4-foot by 4-foot by 3-inch-deep liner sections were placed in a yard beside the EMRC laboratory. One slab was covered with plastic and one was left uncovered. Both slabs cured for approximately two days without any cracks forming. On the third day, it started to rain lightly. The rain continued for two days. When the rain stopped, both liner slabs began to crack. These cracks however, appeared to be caused by swelling rather than shrinkage. Based on the results of follow-on laboratory-scale slab tests, it was decided that placing the liner material in cooler weather would not necessarily eliminate the cracking problem.

A microscopic examination of the liner material that had swelled showed that many large ettringite crystals had grown within the ash particle matrix. Apparently what had happened was that the additional moisture added to the liner material by the rain had caused more ettringite to form in the liner than normally occurred when the material was cured under controlled conditions. The results of these additional tests reinforced our belief that simply placing the liner material at a lower temperature would not necessarily eliminate the cracking problem.

4.3 Liner Physical Property Test Results

Samples of the fly ash liner sections from the three field test sites were collected and shipped to EMRC to study their physical properties. Each set of liner samples was tested for the properties listed in Table 12. The dates when the liner sections were constructed and the various samples were collected are shown in Table 13.

The results of the physical property tests performed in the laboratory on the liner samples collected at the SWEPCO field test site are summarized in Table 14. The first two sets of samples were cut from the liner with a core drill and the third set was collected by digging up two sections with a front-end loader. Since it was not practical to sample deeper than about six inches with the core drill, the first two sets of samples were taken from the top lift of the liner. For the third set however, care was taken to obtain representative samples from both the surface lift and the lower lifts.

The results of the laboratory tests indicated that the SWEPCO liner material generally exhibited permeability coefficients less than 10^{-7} cm/sec. A few of the liner samples exhibited permeabilities slightly higher than 10^{-7} cm/sec, but the log-mean permeability coefficients were all lower than the target value.

The strength data from the SWEPCO liner samples show that after the liner was placed in August of 1987, there was no significant increase in the strength of the material through the following winter. A substantial increase in the strength of the liner material did occur, however, between March and July of 1988. This behavior is normal for a cemented fly ash because the

TABLE 12
LINER PHYSICAL PROPERTY TEST METHODS

<u>Physical Property</u>	<u>Test Method</u>
Permeability Coefficient	Falling head test with sample confined in a triaxial cell
Unconfined Compressive Strength	ASTM D 1633 - 84
Modulus of Elasticity	ASTM C 469 - 83
Poisson's Ratio	ASTM C 469 - 83
Tensile Strength	Test done with direct loading of specimen to failure
Coefficient of Thermal Expansion	ASTM E 228 - 71
Dry Density	Ratio of dry weight to volume
Porosity	Ratio of volume of void moisture to total volume for a saturated sample

TABLE 13
CONSTRUCTION DATES AND SAMPLE COLLECTION DATES
FOR THE FLY ASH LINER FIELD TESTS

	<u>Constructed on</u>	<u>Sample Set 1 collected on</u>	<u>Sample Set 2 collected on</u>	<u>Sample Set 3 collected on</u>
SWPCO	8/22/87	10/05/87	3/01/88	7/26/88
NIPSCO	9/26/87	12/15/87	5/05/88	10/12/88
NSP	6/08/88	9/06/88	10/19/88	3/31/89

TABLE 14

LABORATORY TEST RESULTS FOR THE SWEPCO LINER SAMPLES COLLECTED IN THE FIELD

<u>Sample No.</u>	<u>Sample Set 1 Permeability Coefficients (cm/sec)</u>	<u>Sample Set 2 Permeability Coefficients (cm/sec)</u>	<u>Sample Set 3 Permeability Coefficients (cm/sec)</u>
1	7.6×10^{-8}	2.0×10^{-8}	1.4×10^{-7}
2	7.3×10^{-8}	1.1×10^{-8}	1.4×10^{-7}
3	1.1×10^{-7}	3.8×10^{-8}	4.5×10^{-8}
4	1.1×10^{-8}	6.7×10^{-8}	3.8×10^{-9}
Log-Mean Permeability Coefficient	5.1×10^{-8}	2.7×10^{-8}	3.9×10^{-8}

OTHER PHYSICAL PROPERTIES:

<u>Physical Property</u>	<u>Sample Set 1</u>	<u>Sample Set 2</u>	<u>Sample Set 3</u>
Unconfined Compressive Strength (psi)	346	360	915
Modulus of Elasticity (psi)	2.3×10^5	7.9×10^5	5.6×10^5
Poisson's Ratio	NR*	0.35	0.31
Tensile Strength (psi)	61	60	130
Coefficient of Thermal Expansion (in/°F)	3.5×10^{-6}	5.2×10^{-6}	6.9×10^{-6}
Dry Density (lb/ft ³)	112	113	112
Porosity (% of vol)	33.4	33.3	36.5

NR - Reproducible measurements of Poisson's ratio could not be obtained for this sample.

pozzolanic reactions that produce long-term strength-gain tend to proceed at a much lower rate when the temperature is below 60°F.

Generally, the permeability and compressive strength characteristics of the SWEPCO liner material produced in the field were similar to the characteristics observed in the laboratory development phase of the project. It should be noted, however, that it took almost a full year for the liner material placed in the field to achieve the same approximate level of strength that was observed in the laboratory tests.

The results of the physical property tests performed on the NIPSCO liner samples are listed in Table 15. The first and second sets of samples were obtained with a core drill, and the third set was obtained by digging into the liner with a backhoe. As was the case with the SWEPCO liner, it was difficult to obtain cores longer than about six inches using the core drill and so the first two sample sets came from the surface lift of the NIPSCO liner. Care was taken with the third set to obtain representative samples from both the surface lift and the lower lifts.

The results of the laboratory tests indicated that the first two sets of samples from the NIPSCO liner generally exhibited permeabilities less than the target value of 10^{-7} cm/sec, but the permeabilities measured for the third set were mostly above the target value. The observed difference in permeability between the first two sample sets and the third set was probably due to the manner in which they were collected. With the first two sets, the weaker samples tended to crumble during the coring procedure so that only the stronger samples could be tested in the laboratory. It is probable that if the samples that crumbled could have been tested, they would have exhibited higher permeabilities than the reported values. With the third sample set though, care was taken to obtain intact samples of the weaker liner materials as well as the stronger materials.

The strength of the NIPSCO liner material after curing for one year in the field was slightly higher than the strength measured in the liner-formulation phase of the study.

The results of the physical property tests performed on the liner samples collected at the NSP field test site are listed in Table 16. The first set of samples was taken from the surface lift using a core drill. The second and third sets were obtained from the lower lifts using a power chisel.

Comparing the results from the three sample sets shows that the surface lift of the NSP liner had a much higher permeability than the lower lifts. This difference occurred because the surface lift was placed with a lower moisture content (about 21% of dry weight) than the lower lifts to minimize the shrinkage and cracking. The laboratory study performed last year with the NSP ash indicated that when the moisture content of the liner material was reduced below about 22%, the permeability of the liner material tended to increase rapidly.

The unconfined compressive strength of the NSP liner material was higher than the strengths of either the SWEPCO or the NIPSCO liner materials, but its tensile strength was about the same.

The other physical properties measured for the liner materials are useful for designing full-scale liner systems for waste disposal sites. Tensile strength, Poisson's ratio, modulus of elasticity, and coefficient of thermal expansion can be used to estimate the ability of the material to withstand flexural stresses caused by point loading, subsurface settling, and thermally induced lateral warping of the liner materials. The values measured for these properties for the three liner materials are similar to other values reported in the literature for cemented fly ash materials (9).

TABLE 15
LABORATORY TEST RESULTS FOR THE NIPSCO LINER SAMPLES
COLLECTED IN THE FIELD

<u>PERMEABILITY COEFFICIENTS:</u>			
<u>Sample No.</u>	<u>Sample Set 1*</u> <u>Permeability</u> <u>Coefficients</u> <u>(cm/sec)</u>	<u>Sample Set 2</u> <u>Permeability</u> <u>Coefficients</u> <u>(cm/sec)</u>	<u>Sample Set 3</u> <u>Permeability</u> <u>Coefficients</u> <u>(cm/sec)</u>
1	1.8×10^{-7}	2.8×10^{-7}	1.5×10^{-6}
2	2.6×10^{-8}	2.0×10^{-9}	6.6×10^{-9}
3	1.7×10^{-7}	1.7×10^{-8}	8.0×10^{-5}
4	7.5×10^{-8}	2.3×10^{-7}	1.1×10^{-6}
Log-Mean Permeability Coefficient	8.8×10^{-8}	3.8×10^{-8}	9.7×10^{-7}

* Liner samples collected for the third sample set were more representative of the entire liner section than the samples collected for the first two sets.

<u>OTHER PHYSICAL PROPERTIES:</u>			
<u>Physical Property</u>	<u>Sample Set 1</u>	<u>Sample Set 2</u>	<u>Sample Set 3</u>
Unconfined Compressive Strength (psi)	200	336	489
Modulus of Elasticity (psi)	9.6×10^4	1.6×10^5	1.2×10^5
Poisson's Ratio	0.28	0.2	0.4
Tensile Strength (psi)	26	59	79
Coefficient of Thermal Expansion (in/°F)	1.3×10^{-5}	2.7×10^{-5}	1.5×10^{-5}
Dry Density (lbs/ft ³)	80	78	83
Porosity (% of Vol)	48.6	47.2	47.0

TABLE 16
LABORATORY TEST RESULTS FOR THE NSP LINER SAMPLES
COLLECTED IN THE FIELD

<u>Sample No.</u>	<u>Sample Set 1*</u> <u>Permeability</u> <u>Coefficients</u> <u>(cm/sec)</u>	<u>Sample Set 2</u> <u>Permeability</u> <u>Coefficients</u> <u>(cm/sec)</u>	<u>Sample Set 3</u> <u>Permeability</u> <u>Coefficients</u> <u>(cm/sec)</u>
1	1.4×10^{-6}	3.3×10^{-8}	8.5×10^{-8}
2	5.4×10^{-6}	2.2×10^{-9}	8.2×10^{-8}
3	3.6×10^{-6}	3.9×10^{-9}	5.4×10^{-8}
4	4.2×10^{-6}	3.9×10^{-9}	4.8×10^{-8}
Log-Mean Permeability Coefficient	3.7×10^{-6}	5.9×10^{-9}	6.5×10^{-8}

* Sample Set 1 was obtained from the surface of the liner section and Sample Sets 2 and 3 were obtained from the lower liner lifts.

OTHER PHYSICAL PROPERTIES:

<u>Physical Property</u>	<u>Sample Set 1</u>	<u>Sample Set 2</u>	<u>Sample Set 3</u>
Unconfined Compressive Strength (psi)	1045	2091	2860
Tensile Strength (psi)	48	59	90
Modulus of Elasticity (psi)	1.6×10^5	2.2×10^5	2.2×10^5
Poisson's Ratio	0.28	0.25	0.47
Coefficient of Thermal Expansion (in/in°F)	8.2×10^{-6}	9.7×10^{-6}	1.0×10^{-5}
Dry Density (lbs/ft ³)	85	99	99
Porosity (% of vol)	45	34.5	36.3

4.4 Liner In-Field Permeability Test Results

A double-barrel infiltrometer test was conducted on the liner sections at each of the three field test sites. The purpose of this test was to estimate the permeability coefficient of the liner sections using an in-field procedure.

The infiltrometer test was done by placing two barrels with their bottoms removed on the liner surface. A 30-gallon barrel was first inserted three inches into the liner, and a 55-gallon barrel was inserted six inches into the liner around the 30-gallon barrel. After the liner section had cured thoroughly, both barrels were filled with 18 inches of water, and the lid was placed on the 55-gallon barrel to limit evaporation.

The rate at which the water level in the 30-gallon barrel dropped was used to estimate the permeability coefficient of the liner. The purpose of the 55-gallon barrel was to saturate the liner around the inner 30-gallon barrel and thus direct the flow from the 30-gallon barrel vertically into the liner. A third barrel which did not have its bottom removed was also placed on the liner to serve as a control and measure how much water was being lost to evaporation during the course of the test. Each barrel had an aluminum yardstick mounted on the inside to measure the water levels. The water levels were checked every few weeks and readjusted to 18 inches. The permeability coefficient of the liner was calculated based on the infiltrometer test data using the following formula.

$$k = 2.3aL/At (\log h_1/h_2)$$

where:

k is the permeability coefficient with units of cm/sec.

a is the cross-sectional area of the 30-gallon barrel (cm²).

L is the length (cm) of the flowpath of water from the 30-gallon barrel moving through the liner.

A is the cross-sectional area (cm²) of the flowpath of water from the 30-gallon barrel moving through the liner.

h₁ is the hydraulic head (cm) in the 30-gallon barrel at the beginning of the test.

h₂ is the hydraulic head (cm) in the 30-gallon barrel after the test has proceeded for time t (sec).

For the double-barrel infiltrometer test, the cross-sectional area of the flowpath (A) is considered to be equal to the cross-sectional area of the 30-gallon barrel (a). Since it was not possible to determine the exact flowpath through the liner, it was assumed that the water from the 30-gallon barrel flowed directly down through the two-foot thickness of the liner. It was only possible to read the yardsticks in the barrels to the closest 1/16 inch, and

in the case of the SWEPCO liner, the water level dropped at a rate that was too small to measure. For this reason, the permeability could not be calculated as a discrete value but was estimated as a less-than value.

The water temperature in the infiltrometer apparatus influences the permeability measurement because it changes the viscosity of the water. Permeability coefficients are usually measured in the laboratory at 70°F; if the water temperature in the field deviates significantly from 70°F a correction factor must be applied.

The results of the infiltrometer tests are contained in Table 17. The permeabilities measured at the three liner test sites ranged from less than 10^{-7} cm/sec for the SWEPCO site to 1.8×10^{-5} cm/sec for the NSP site.

Since the initial target permeability for the fly ash liners was less than 10^{-7} cm/sec, the SWEPCO liner material displayed acceptable permeability characteristics. The permeability of the NIPSCO site was 8.5×10^{-7} cm/sec, and it did not meet the target criteria. Liner regulations for coal combustion waste disposal sites in Indiana, however, only require that the liner have a permeability less than 10^{-8} cm/sec. Therefore, a fly ash liner of the type tested at the NIPSCO site still could be useful for a coal combustion waste disposal site.

The permeability measured for the NSP field test site was clearly too high for a liner application. The high permeability measured in the field resulted because the infiltrometer apparatus was inserted into the top lift of the liner, and as was explained in Section 4.2, the top lift of the NSP liner was constructed with a low moisture content to minimize shrinkage cracking. Unfortunately, the low moisture content also increased the permeability of the liner material. The laboratory tests performed on the liner samples collected from the lower lifts confirmed that when the NSP liner material was prepared with the proper moisture content its permeability was well below 10^{-7} cm/sec.

4.5 Fly Ash Liner Field-Test Site Inspections

Each of the three field-test sites for the fly ash liners was inspected by project personnel approximately one year after the liners were constructed. The primary purpose of the inspection was to determine if the liners had been damaged as a result of their exposure to fluctuating temperatures, freeze-thaw cycles, and wet-dry cycles. When the site inspections were made, parts of the liners were broken up to collect samples, and this allowed the project personnel to examine the liners through their full depth.

4.5.1 SWEPCO Site Inspection

The SWEPCO liner was inspected in July of 1988. The test site was located in north-eastern Texas. The only noticeable damage observed was a network of thin cracks on the surface. The cracks were generally spaced several feet apart and extended over the entire liner surface.

The cracks were probably caused by thermally induced expansion and contraction of the liner surface. This can happen when the sun heats the liner surface, causing it to expand relative to the cooler subsurface. Cracks

TABLE 17
INFILTRMETER TEST RESULTS

SWEPCO LINER SECTION				
Date of Measurement	Time Interval (seconds)	Drop in Water Level (cm)	Water Temperature (°F)	Estimated Permeability Coefficient (cm/sec)
10/29/87	1.9×10^6	5.08	62	3.6×10^{-6}
11/11/87	1.2×10^6	0.64	61	7.1×10^{-7}
11/25/87	1.2×10^6	0.0	59	$<1.0 \times 10^{-7}$
12/09/87	1.2×10^6	0.0	58	$<1.0 \times 10^{-7}$
01/05/88	2.2×10^6	0.0	48	$<1.0 \times 10^{-7}$
NIPSCO LINER SECTION				
05/18/88	6.05×10^6	1.9	66	3.8×10^{-6}
06/13/88	1.7×10^6	1.1	90	8.5×10^{-7}
07/01/88	1.55×10^6	0.63	75	5.5×10^{-7}
09/16/88	6.7×10^6	4.3	72	8.5×10^{-7}
NSP LINER SECTION				
09/27/88	1.0×10^6	18.18	68	2.4×10^{-5}
10/04/88	6.1×10^5	8.10	61	1.8×10^{-5}

occur when the tensile stress brought about by the expansion exceeds the strength of the liner material.

When portions of the SWEPCO liner were dug up to collect samples, the lower lifts were examined. No cracks were observed in the exposed sections of the lower lifts. It appeared as though the surface lift had protected the lower lifts from the type of differential heating that may have caused the cracks in the surface lift. The lower lifts also had a noticeably higher moisture content than the surface lift.

4.5.2 NIPSCO Site Inspection

The NIPSCO field-test site was inspected in October of 1988. The only significant deterioration observed was some crumbling at the liner surface. The crumbling appeared to have been caused by freeze-thaw exposure during the winter months, and it extended a few inches below the surface.

Aside from the surface deterioration, the NIPSCO liner seemed to be well cemented. This was apparent when a backhoe was used to break up parts of the liner to collect samples for laboratory testing. To break up the liner, the backhoe operator first tried to dig directly into the liner surface, but found that the scoop could not penetrate more than a few inches. The operator finally broke up the liner by digging under the edge and pulling it up.

4.5.3 NSP Site Inspection

The NSP field-test site was inspected in March of 1989. The only observable deterioration was some crumbling at the liner surface. The crumbling appeared to have been caused by freeze-thaw exposure during the winter months, and it extended about a quarter of an inch below the surface.

Aside from the surface crumbling, the NSP liner seemed to be well cemented. A power chisel was used to break up a section of the liner to collect samples, and it was very difficult to cut through the material. The results of the laboratory tests indicated that the unconfined compressive strength of the liner material had not decreased over the winter months.

4.6 Conclusions and Topics for Future Research

This research project demonstrated that low-permeability liner materials could be made from fly ash by adding relatively small amounts of hydrated lime and portland cement and by carefully controlling the amount of water added to the mixture. Bench-scale laboratory tests were performed on six different fly ashes to determine the lowest total amounts of lime and cement required at a specific water addition level to produce materials with permeabilities less than 10^{-7} cm/sec and unconfined compressive strengths exceeding 400 psi. Additional tests were performed in the laboratory on large-scale fly ash liner specimens, which verified that their permeability and strength characteristics were acceptable for a liner application.

Three of the six fly ashes tested in the laboratory were selected for follow-on liner field tests. Texas lignite fly ash supplied by the Southwestern Electric Power Company was used to construct a two-foot-thick liner test section at the H. W. Pirkey Power Plant in Hallsville, Texas. Laboratory tests performed on liner samples collected at the SWEPCO test site over a one-year period indicated that the field-placed material had a permeability of less than 10^{-7} cm/sec and a relatively high unconfined compressive strength. The only notable deterioration of the liner section that occurred during one year of exposure to ambient weather conditions was some cracking of the liner surface. The cracks did not appear to extend beyond the top 6-inch lift of the liner. Overall, the results of the field test indicated that the lime and cement-amended SWEPCO fly ash was a potentially useful liner material.

A mixture of bituminous coal fly ash and lime-based scrubber sludge supplied by the Northern Indiana Public Service Company was used to construct a liner section at the R. M. Schahfer Power Plant located in Wheatfield, Indiana. Laboratory tests performed on liner samples collected at the NIPSCO test site over a one-year period indicated that the field-placed material had a permeability of less than 10^{-8} cm/sec and a moderately high unconfined compressive strength. The only notable deterioration of the liner section that occurred during one year of exposure to ambient weather conditions was some crumbling in the top two inches of the liner. The permeability of the field-placed liner did not meet the 10^{-7} cm/sec target criteria; however, the Indiana liner specifications for coal combustion waste disposal sites only require that the permeability be less than 10^{-8} cm/sec. Therefore, the results of the field test indicate that the lime and cement-amended NIPSCO fly ash may be a potentially useful liner material.

A mixture of subbituminous coal fly ash and lime-based dry scrubber powder supplied by the Northern States Power Company was used to construct a liner section at the Sherburne County Power Plant located in Becker, Minnesota. Laboratory tests performed on liner samples collected at the NSP test site over a one-year period indicated that the field-placed material had a permeability of less than 10^{-7} cm/sec and high unconfined compressive strength. The most serious problem with the NSP liner material was its tendency to shrink and crack when it was initially placed and cured in the field.

An important topic for future fly ash liner research is to evaluate cracking behavior and its impact on long-term durability. Cracks formed on both the NSP and the SWEPCO liners during the field tests, but in each case the cause of the cracks was different. The cracks in the NSP liner appeared to be caused by material shrinkage that occurred in the early stages of the curing process, while the cracks that occurred in the SWEPCO liner appeared to be caused by thermal expansion and contraction.

Further field testing of the fly ash liners should focus on commercial-scale construction methods, the structural properties of large liner sections, and the performance of a fully loaded landfill test cell.

5.0 ELECTROSTATIC SEPARATION OF UNBURNED CARBON FROM FLY ASH

5.1 Introduction

The addition of fly ash to concrete mixtures to replace some of the portland cement can exert a dramatic effect on the air-entraining properties of the mixture. There are two important reasons for this type of behavior. First, fly ash is normally finer than portland cement and the volume required for addition to a concrete mix is usually greater than the volume of the cement replaced. Thus, a larger amount of air entraining agent (AEA) is required to produce the same surface concentration of the active agent in a fly ash-containing mix. Secondly, the unburned carbon in the fly ash adsorbs some of the AEA, further reducing its surface concentration (8).

The amount of unburned carbon in a fly ash is usually determined by the loss-on-ignition test, which measures the amount of mass removed from the ash when it is heated from 103°C to 750°C. It must be recognized that for some

fly ashes, there is a significant difference between the measured loss-on-ignition and the actual unburned carbon content. The maximum loss-on-ignition of a fly ash to be used in an air-entraining concrete mix is 6.0% based on the ASTM C 618 specification, and 5.0% based on the AASHTO (The American Association of State Highway and Transportation Officials) M 295 specification (9,10). Additionally, a number of states have indicated that problems with erratic air entrainment have been experienced with fly ashes having carbon contents of less than 3.0%, and some states have specified loss-on-ignition limits in this range (8).

In practical terms, a fly ash with a high unburned carbon content may adversely effect the concrete mix to which it is added by requiring a higher AEA dosage to attain an equivalent entrained air content, and perhaps more importantly, by requiring that the AEA dosage be frequently changed to maintain a constant entrained air content due to variations in the carbon content. This type of behavior presents a major problem for both utility companies and ash brokers trying to sell high-carbon fly ash because market acceptance is greatly reduced.

In order to increase the marketability of high-carbon fly ash, a study was performed at EMRC to develop a cost-effective carbon separation process. The objective of the study was to test a bench scale process that could reduce the loss-on-ignition of the fly ash to less than 3.0 percent. Economic constraints on the separation process based on the market value of fly ash indicate that it must have relatively low equipment, operational, and maintenance costs. The chief technical constraint for the separation process is that it produce a dry separated fly ash fraction, since wetting the ash usually reduces its commercial value for cement replacement.

An electrostatic carbon separation process was selected for this study because of its mechanical simplicity and relatively low operational cost, and because it produced a dry fly ash product. The approach used was basically to take an "off the shelf" particle separation process and modify it to handle fly ash. The results of the study are presented in the following sections.

5.2 Materials and Methods

The basic configuration of the electrostatic separation process evaluated in this study is illustrated in Figure 1 (11). The operational principle of the process is to separate differentially conducting particles based on the rates at which they dissipate an induced charge. The process is performed by placing the material to be separated in a vibrating feeder box and dispensing it in a thin, even stream onto a rotating drum. The drum is a grounded conductor. An electrode induces a charge on the particles falling between the electrode and the drum. The particles thus obtain a charge opposite to that of the drum and so are attracted by the drum.

When a conducting particle contacts the drum, it loses its charge by conduction, becomes neutral, and drops off the drum. Nonconducting particles are also attracted to the drum; however, when a charged nonconducting particle contacts the drum, it retains its charge and sticks to the drum. The nonconducting particles can then be removed from the drum at a different point in its rotation and collected in a separate hopper. When the electrostatic

- 1 Combination 4-inch aluminum electrode with wire electrode
- 2 Vibratory feeder
- 3 Grounded rotating drum
- 4 Brush
- 5 Adjustable stream splitter

Figure 1. Schematic Diagram of the Electrostatic Separator.

separation process was selected for this study it was expected that the carbon particles would be better conductors than the fly ash particles and so the carbon particles would fall off of the drum first.

The actual bench scale separator apparatus constructed for this study is shown in Figure 2. The vibrating pan was made with a 1/16-inch-thick steel bottom with a magnetic vibrator attached below the pan. The drum was a 1/16-inch-thick stainless steel tube, seven inches long and six inches in diameter. The drum was grounded by a contact brush. The drum was turned by a geared-down electric motor that rotated at a rate of 0.55 revolutions per second. The electrode was a thin copper strip attached to adjustable positioning arms. The electrode was supplied with approximately a 45-kV charge from a high-performance automobile coil. A rubber padded scraper bar was attached across the length of the drum surface to remove the nonconducting fly ash from the drum. The scraper bar was located approximately 270° from the point where the fly ash was initially dropped onto the drum. The high- and low-carbon fly ash fractions were collected in a pan placed below the drum.

The experimental plan for evaluating the electrostatic separation process consisted of a) constructing the bench-scale separator, b) performing an initial series of separation runs to determine the best position for the electrode, c) performing a series of follow-on runs to optimize the process, and d) performing a final series of runs using the optimized conditions to collect enough separated fly ash to characterize its air-entrainment characteristics.

Figure 2. Photograph of the Bench-Scale Separator Apparatus

A separator run was performed in the following manner. The fly ash was heated to 100°C to be thoroughly dried, allowed to cool to room temperature, and put into the separator pan. Two hundred grams of fly ash was used for each run. The vibrator, electrode, and drum motor were then turned on to start delivering the fly ash to the drum. The time required to pass all of the ash over the drum was recorded and used to calculate the drum loading rate in units of grams of ash per square inch of drum surface. The high-carbon fly ash fraction was collected below the front of the drum and the low-carbon fraction was collected below the rear of the drum directly under the scraper bar. The weight, moisture content, and loss-on-ignition (LOI) of each of the collected fractions were measured to evaluate the performance of the separator. The carbon content of the fly ash was measured by its LOI. It is recognized that carbon content does not always correlate directly with LOI, but with most fly ashes LOI is a good representative carbon content parameter.

For the follow-on runs, a plate was attached to the front of the vibrating pan to form a thin slit through which the fly ash passed as it left the pan. The slit helped to dispense the fly ash onto the drum in a thin, even stream. The width of the slit was set between 0.015 and 0.063 inches to control the rate of delivery of the ash to the drum. The slit also served to break up the larger fly ash clumps present in the bulk ash.

For the first set of runs, the drum loading rate was kept approximately constant and the position of the electrode was changed to determine which configuration yielded the lowest LOI and the highest weight fraction of separated ash. In the follow-on runs, process variables such as loading rate

and temperature of the ash were changed to determine which combinations produced the best carbon removal. Once the process was optimized, a series of runs was performed to collect enough ash to characterize its air entrainment properties using the procedure specified in ASTM C311.

The fly ash used for the separation tests was obtained from the Allen S. King Power plant which burns a mixture of Wyoming and Montana subbituminous coals and Illinois bituminous coal. The fly ash was collected in an electrostatic precipitator.

The King fly ash had a grey-brown color and its loss-on-ignition was 7.34%. The fly ash particle size distribution is shown in Figure 3. A microscopic examination of the ash indicated that much of the carbon was present as relatively large particles compared to the fly ash particles, while the rest of the carbon was present as smaller particles of about the same order of magnitude as the fly ash particles. Most of the smaller particles were interspersed in small clumps of agglomerated fly ash. The LOI of the various fractions collected for the particle size distribution are shown in Figure 4. The figure illustrates the fact that most of the carbon was contained in the larger particle size fractions. An elemental analysis of the King fly ash is contained in Table 18.

5.3 Electrostatic Separator Test Results

The results of the test runs performed with the electrostatic separator are discussed in this section. The data collected from the various test runs is contained in Appendix B.

Figure 3. Fly Ash Particle Size Distribution Curve.

Figure 4. LOI of the Various Fly Ash Fractions Collected for the Particle Size Distributions

TABLE 18
ELEMENTAL COMPOSITION OF THE KING FLY ASH

Ash Component	Weight Percent of Ash
SiO ₂	22.4
Al ₂ O ₃	14.2
Fe ₂ O ₃	7.3
TiO ₂	2.1
P ₂ O ₅	1.4
CaO	27.3
MgO	5.7
Na ₂ O	1.4
K ₂	0.7
SO ₃	6.9

5.3.1 Electrode Placement Tests

The principal feature of the electrostatic separator apparatus is that the position of the electrode used to induce a charge on the fly ash particles can be readily adjusted. The basic electrode positions tested for this study were 1) directly under the edge of the ash delivery pan, so that the ash moved over the electrode before it fell on the rotating drum, 2) at an angle of 20 degrees from the top of the drum, 3) at an angle of 45 degrees from the top of the drum, 4) at an angle of 60 degrees from the top of the drum, and 5) removed from the apparatus (i.e., no electrode used). The various electrode positions are diagrammed in Figure 5.

Additionally, at each of the angular positions, the electrode was tested at two different heights above the surface of the drum (0.125 and 0.0625 inches), and with a rubber strip attached to part of the width of the electrode to smooth out the ash on the drum before it passed under the charged portion of the electrode. When the electrode was removed from the apparatus, all of the other operational features were kept the same as when the electrode was used.

The results of this first set of tests was surprising. The apparatus performed as well without the electrode as it did with the electrode in terms of the extent of LOI reduction and the relative percentage of fly ash recovered in the separated fraction. Further, any attempt to spread out the ash on the drum, with a rubber pad before it passed under the electrode tended to reduce the efficiency of the separator.

Figure 5. Diagram of the Various Electrode Positions Tested for the Separator.

It was concluded that the best mode in which to run the separator was with the electrode removed. Apparently the fly ash had a sufficiently large static electric charge to adhere to the grounded steel drum without inducing an additional charge. It was also concluded that no attempt should be made to disturb the ash after it falls on the drum, since this only tends to dislodge some of the ash.

During the tests it was noted that a major factor in determining how well the separator operated was the manner in which the ash was dispensed onto the drum from the vibrating pan. The separator worked best when the ash was sprinkled onto the drum in a thin even stream. It was also noted that running the vibrator too vigorously caused poor separation because it tended to cause the ash to ball-up in the pan and fall onto the drum in large clumps.

5.3.2 Additional Process Optimization Tests

Once it was decided to remove the electrode from the separator, several additional runs were made to determine the effect of fly ash temperature and loading rate on the performance of the process.

Two separator runs were performed with the ash heated to 100°C and cooled to room temperature to determine if the temperature difference affected the process. The results of these tests showed that the hot ash performed about the same as the cool ash in terms of both LOI reduction and the amount of ash recovered in the separated fraction.

Next, a series of tests were done using different loading rates to determine the effect on separator performance. The loading rates used ranged from 0.003 to 0.016 grams of ash/in² of drum surface. For this set of runs, an aluminum plate was attached to the front of the vibrating pan. The plate was attached to form a slit through which the fly ash passed before it fell onto the drum. (See Section 5.2 for a more complete description of the plate arrangement.) This arrangement made it easier to control the loading rate by either increasing or decreasing the width of the slit. The plate also helped to break up the fly ash clumps before they fell onto the drum and resulted in a finer stream of ash being delivered to the drum.

The results of the variable loading tests are shown in Figures 6 and 7. Figure 6 shows the LOI of the separated fly ash fraction as a function of the drum loading rate, and Figure 7 shows the weight percent of the total applied ash that was recovered in the low-LOI fraction as a function of the drum loading rate. The figures indicate that at the lowest loading rate, approximately 37.5% of the fly ash was recovered with an LOI of 3.6% and that at the highest loading rate, approximately 17% of the fly ash was recovered with LOI of 4.4%.

5.3.3 Ash Collection Runs

For the final phase of the process tests, twelve separator runs were done using similar loading conditions to collect enough fly ash to determine the air entrainment properties of the low-LOI fraction. An average loading rate of 0.009 grams/in² was used for the collection runs. A total of 625 grams of ash was collected from twelve runs (total applied bulk ash was 2400 grams) with an LOI of 3.6% (the LOI of the bulk fly ash was 7.3%). The air

Figure 6. LOI of the Recovered Fly Ash Fraction as a Function of the Ash Loading Rate.

Figure 7. Weight Percent Fly Ash Recovered in the Low-LOI Fraction as a Function of the Ash Loading Rate.

entrainment properties of both the bulk fly ash and the low-LOI fraction were tested with the procedure contained in ASTM C311 "Air-Entrainment of Mortar Test."

The air entrainment test is done by preparing several fly ash-cement mortar mixes using various doses of air entraining agent (a neutralized vinsol resin). The test data is analyzed by plotting the entrained air content of each mix as a function of the AEA dosage.

The results of the air entrainment tests showed that an AEA dose of 0.53% was required to produce an entrained air content of 18% in the bulk fly ash mortar mix. For the low-LOI fly ash mortar mix, an AEA dose of 0.46% was required to produce an entrained air content of 18%. Thus, the LOI removal achieved by the electrostatic separation process reduced the AEA dosage requirement of the low-LOI fly ash fraction by 13.2%.

In addition to removing carbon from the fly ash, the separation process appeared to produce a finer fly ash fraction than the bulk fly ash. A finer ash is generally more chemically active for the pozzolanic reactions involved in the cementing process than a coarser ash. Therefore, producing a finer ash would be an additional benefit of the separation process.

To evaluate the relative fineness of the separated fly ash, the percent ash retained on a #325 sieve was compared to the percent retained for the bulk ash. For the separated fraction of the king fly ash, 14.11% was retained on the #325 sieve, while for the bulk fly ash, 22.55% was retained on the #325 sieve. Thus, the separation process actually did produce a finer ash, since a lower percentage of the separated fly ash was retained on the #325 sieve.

5.4 Carbon Separation - Summary and Conclusions

An "off the shelf" electrostatic separation process was modified for use to reduce the unburned carbon content of fly ash. A bench-scale separator apparatus was constructed at EMRC and a series of test runs were performed to optimize the process. After the process was optimized, a sufficient amount of low-LOI fly ash was collected to determine its air entrainment characteristics.

The separator apparatus operates by dispensing fly ash from a vibrating pan through a slit onto a grounded, rotating steel drum. The high-LOI ash fraction falls off the drum due to gravity as it rotates. The low-LOI ash fraction sticks to the wheel due to electrostatic forces and is scraped off at a separate collection point. The "off the shelf" version of this separator uses a high-voltage electrode to induce a negative charge on the particles being classified. For the fly ash separator, the electrode did not improve the operation of the apparatus and so it was removed. It appeared that the fly ash had a sufficient electrostatic charge to stick to drum without using the electrode.

The results of the separator tests showed that the apparatus was capable of splitting the bulk fly ash, which had an LOI of 7.3%, into two physically separate fractions. One fraction contained approximately 25 weight percent of the ash and had an LOI of 3.6%, while the other fraction contained the other 75 weight percent of the ash. Air entrainment tests performed on the two fly

ash fractions indicated that the low-LOI fraction required 13.2% less air entraining agent than the bulk fly ash fraction to produce an equivalent entrained air level.

The goal of the study was to produce fly ash with an LOI of less than three percent using the electrostatic separation process. It was not possible to achieve this level in the test runs performed. However, the ASTM C618 fly ash specification for cement replacement only requires that fly ash have an LOI of less than six percent, and the separation process easily achieved this level.

Based on the results of the bench-scale tests, it appears that the electrostatic carbon removal process has some commercial development potential since it is mechanically quite simple and it produced significant carbon removal with a relatively low energy input. One drawback of the process is that only about 25% of the bulk fly ash is recovered in the low-LOI fraction. However, it may be possible to increase this recovery with further development of the process. Furthermore, some power plants may not be able to sell more than 25% of their fly ash for cement replacement due to market limitations.

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APPENDIX A
ELEMENTAL & MINERALOGICAL CHARACTERIZATION
OF FIELD-PLACED FLY ASH LINER MATERIAL

Test Site: SWEPCO

Elemental Composition

Element	Fly Ash*	Liner Material
SiO ₂	46.5	39.9
Al ₂ O ₃	16.4	14.4
Fe ₂ O ₃	15.4	23.4
TiO ₂	1.5	1.3
P ₂ O ₅	0.0	0.0
CaO	13.6	15.0
MgO	3.0	1.3
Na ₂ O	0.0	0.0
K ₂ O	0.8	1.1
SO ₃	2.1	3.6

Mineral Phases

<u>Fly Ash</u>	<u>Liner Material</u>
Quartz	Quartz
Mullite	Mullite
Ferrite Spinel	Ferrite Spinel
Hematite	Hematite
	Ettringite
	Calcite

*This is the composition of the fly ash used for the laboratory liner development tests.

Test Site: NSP

Elemental Composition

Element	Fly Ash-Scrubber Powder*	Liner Material
SiO ₂	24.2	25.3
Al ₂ O ₃	13.1	13.3
Fe ₂ O ₃	3.2	3.7
TiO ₂	0.9	1.0
P ₂ O ₅	1.0	0.9
CaO	32.3	27.9
MgO	3.0	3.3
Na ₂ O	1.3	1.4
K ₂ O	0.4	0.8
SO ₃	20.6	20.6

Mineral Phases

Fly Ash-Scrubber Powder

Quartz
Ferrite Spinel
Calcium Hydroxide
Calcium Sulfite hemihydrate
Gypsum
Lime
Anhydrate
Periclase
Tricalcium Aluminate

Liner Material

Quartz
Ferrite Spinel
Ettringite
Calcium Sulfite hemihydrate
Gypsum

*This is the composition of the fly ash used for the laboratory development tests.

Test Site: NIPSCO

Elemental Composition

Element	Fly Ash-Scrubber Mix*	Liner Material
SiO ₂	22.8	12.9
Al ₂ O ₃	10.8	4.2
Fe ₂ O ₃	10.0	4.9
TiO ₂	1.0	0.4
P ₂ O ₅	1.0	1.2
CaO	23.5	38.9
MgO	1.2	1.4
Na ₂ O	2.1	0.0
K ₂ O	0.8	0.6
SO ₃	26.7	35.6

Mineral Phases

<u>Fly Ash-Scrubber Mix</u>	<u>Liner Material</u>
Quartz	Quartz
Mullite	Mullite
Ferrite Spinel	Ferrite Spinel
Melilite	Calcium Hydroxide
Calcium Sulfite hemihydrate	Calcium Sulfite hemihydrate
Gypsum	Gypsum
Lime	Calcite
Anhydrate	Ettringite

*This is the composition of the fly ash-scrubber mix used for the laboratory development tests. Based on the CaO contents of the two materials, it appeared that the field-placed liner material contained a higher percentage of scrubber sludge than the material used for the laboratory work.

APPENDIX B

Run No.	Loading (gm/in ²)	Electrode Bar Position (angle, height above drum)	Weight of Low-LOI (gm)	LOI of Low-LOI (%)
1	0.02	45 ⁰ , 1/8 inch	89	5.93
2	0.02	60 ⁰ , 1/8 inch	100	5.64
3	0.018	90 ⁰ , 1/8 inch	58	4.7
4	0.017	20 ⁰ , 1/8 inch	83	5.0

Optimization Runs:

5	0.017	No electrode	74	4.1
6	0.008	Electrode attached to pan	109	6.25
7	0.013	20 ⁰ , 1/8 inch, rubber pad attached	88	6.23
8	0.002	20 ⁰ , 1/8 inch, rubber pad attached	62	3.68
9	0.016	Electrode placed directly under pan	54	4.78
10	0.008	No electrode, ash temperature = 100 ⁰ C	39	3.75
11	0.008	No electrode, ash temperature = 20 ⁰ C	39	3.8

Ash Collection Runs:

12	0.0065	No electrode	70	3.96
13	0.0158	No electrode	35	4.44
14	0.0038	No electrode	50	3.58
15	0.0089	No electrode	45	3.94
16	0.0051	No electrode	58	3.52
17	0.0083	No electrode	53	ND*
18	0.015	No electrode	39	ND
19	0.013	No electrode	40	ND
20	0.0067	No electrode	62	ND
21	0.0028	No electrode	75	ND
22	0.0036	No electrode	32	ND
23	0.0043	No electrode	35	ND

*ND--No LOI Data was taken for these runs.

U.S. DEPARTMENT OF ENERGY
FEDERAL ASSISTANCE MANAGEMENT SUMMARY REPORT

1. Program/Project Identification No. DE-FC21-86MC10637	2. Program/Project Title Waste Management	3. Reporting Period 4/1/88 through 6/30/89
4. Name and Address University of North Dakota Energy and Mineral Research Center Box 8213, University Station Grand Forks, North Dakota 58202		5. Program/Project Start Date 4/01/86
		6. Completion Date 3/31/92

11. Major Milestone Status	Units Planned	Units Complete
A. Waste Characterization Studies	P	2▲ 3▲
	C	
	P	
	C	
B. Fly Ash Liner Study	P	3▲
	C	
	P	
	C	
C. Year-2 Carryover	P	
	C	
	P	
	C	
D. LOI Reduction Testing	P	1▲
	C	
	P	
	C	
	P	
	C	
	P	
	C	
	P	
	C	
	P	
	C	
	P	
	C	
	P	
	C	
	P	
	C	

12. Remarks

13. Signature of Recipient and Date Charles J. Smith 8/29/89	14. Signature of DOE Reviewing Representative and Date
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FEDERAL ASSISTANCE MANAGEMENT SUMMARY REPORT

Page ____ of ____

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		6. Completion Date 3/31/92

Milestone ID. No.	Description	Planned Completion Date	Actual Completion Date	Comments
C.2 (From Year 2)	Fly Ash Liner Field Slab Construction	06/30/88	06/30/88	
C.3 (From Year 2)	Fly Ash Liner Slab Monitoring	09/30/88	10/30/88	
A.1	Characterization of Pressure Hydrated Lime Injection Wastes	07/30/88	08/30/88	
A.2	Characterization of Ash from Coal Slurry Fired Diesel	02/28/89	05/30/89	
A.3	Waste Characterization Report	03/30/89	06/30/89	
B.1	Evaluation of Fly Ash Liner Leachate Quality	09/30/88	09/30/88	
B.2	Liner Monitoring Visit	02/28/89	04/30/89	
B.3	Fly Ash Liner Study Report	03/30/89	06/30/89	
D.1	LOI Reduction Tests	06/30/89	06/30/89	

3.0 ADVANCED RESEARCH AND TECHNOLOGY DEVELOPMENT

3.1 Turbine Combustion Phenomena

TURBINE COMBUSTION PHENOMENA

Technical Report for the Period
April 1, 1988 - June 30, 1989

Submitted by:

Michael L. Swanson, Project Manager

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TABLE OF CONTENTS

	<u>Page</u>
1.0 INTRODUCTION.....	1
2.0 GOALS AND OBJECTIVES.....	2
2.1 Three-Year Objectives.....	2
2.2 Third-Year Objectives.....	3
3.0 REACTIVITY OF FUELS IN PRESSURIZED SYSTEMS - COMBUSTION BOMB STUDIES.....	4
4.0 CHARACTERISTICS OF BURNING COAL SLURRIES IN A TURBINE SYSTEM.....	4
4.1 Gas Turbine Simulator Description.....	4
4.2 Gas Turbine Test Matrix.....	10
4.3 Gas Turbine Simulator Results.....	11
4.3.1 Slurry Fuel Preparation.....	11
4.3.2 Combustion Test Results.....	18
4.3.2.1 Shakedown Tests 27 Through 42.....	18
4.3.2.2 Parametric Testing Runs 43 Through 47.....	32
4.3.2.3 Statistical Analysis of Parametric Tests 43 Through 47.....	46
4.3.3 Ash and Slag Deposit Analysis.....	49
4.4 Design and Construction of a Pressurized Atomization Spray Chamber.....	62
4.5 Design and Construction of a Pressurized Drop-Tube furnace...	62
5.0 CONCLUSIONS AND FUTURE PLANS.....	65
6.0 REFERENCES.....	65

LIST OF TABLES

<u>Table</u>	<u>Page</u>
1 Test Matrix for Combustion Tests on the Gas Turbine Simulator.....	11
2 Test Matrix for Long Residence Time Combustion Tests Using 4.6-Micron Otisca Taggart Seam Bituminous Coal/Water Fuel.....	11
3 Test Matrix for Short Residence Time Combustion Tests Using 4.6-Micron Otisca Taggart Seam Bituminous Coal/Water Fuel.....	12
4 Test Matrix for Short Residence Time Combustion Tests Using 10.1-Micron Kemmerer Subbituminous Coal/Water Fuel.....	12
5 Test Matrix for Short Residence Time Combustion Tests Using 20.1-Micron Kemmerer Subbituminous Coal/Water Fuel.....	13
6 Test Matrix for Short Residence Time Combustion Tests Using 15.9-Micron Beulah-Zap Lignite Coal/Water Fuel.....	13
7 Analysis of Coal/Water Fuels Used in Gas Turbine Simulator Shakedown Tests.....	16
8 Analysis of Coal/Water Fuels Used in Parametric Tests on the 1MM Btu/hr Gas Turbine Simulator.....	19
9 X-Ray Fluorescence Analysis of Coal/Water Fuels Used in Parametric Tests on the 1MM Btu/hr Gas Turbine Simulator.....	20
10 Various Operating Conditions Achieved in Gas Turbine Simulator Combustion Tests 27 and 28 Using Beulah-Zap Lignite Coal/Water Fuel.....	21
11 Various Operating Conditions Achieved in Gas Turbine Simulator Combustion Test 31 Using Otisca Taggart Seam Bituminous Coal/Water Fuel.....	22
12 Various Operating Conditions Achieved in Gas Turbine Simulator Combustion Test 32 Using Otisca Taggart Seam Bituminous Coal/Water Fuel.....	23
13 Operating Conditions from Gas Turbine Simulator Combustion Test 34 Using Otisca Bituminous Coal/Water Fuel.....	24
14 Operating Conditions from Gas Turbine Simulator Combustion Tests 35 and 36 Using a Beulah-Zap Lignite Coal/Water Fuel.....	25
15 Operating Conditions from Gas Turbine Combustion Test 37 Using Otisca Bituminous Coal/Water Fuel.....	26

16	Operating Conditions from Gas Turbine Combustion Test 38 and 39 Using Kemmerer Subbituminous Coal/Water Fuel.....	27
17	Operating Conditions from Gas Turbine Combustion Tests 40 and 42 Using Kemmerer Subbituminous and Otisca Bituminous Coal/Water Fuel.....	28
18	Comparison of Beulah-Zap and Otisca Combustion Test Fly Ashes.....	30
19	Comparison of Beulah-Zap and Otisca Combustion Test Fly Ashes.....	31
20	Comparison of Otisca and Kemmerer Combustion Test Fly Ashes.....	31
21	Comparison of Cyclone Fly Ashes for Combustion Test 43 Using Otisca Bituminous Coal/Water Fuel.....	32
22	Comparison of Cyclone Fly Ashes for Combustion Test 44 Using Otisca Bituminous Coal/Water Fuel.....	33
23	Comparison of Cyclone Fly Ashes for Combustion Test 45 Using 10- Micron Particle Size Kemmerer Subbituminous Coal/Water Fuel.....	33
24	Comparison of Cyclone Fly Ashes for Combustion Test 46 Using 20- Micron Particle Size Kemmerer Subbituminous Coal/Water Fuel.....	34
25	Comparison of Cyclone Fly Ashes for Combustion Test 47 Using Beulah-Zap Lignite Coal/Water Fuel.....	34
26	Average Operating Conditions from Long Residence Time Combustion Test 43 Using Otisca Taggart Seam Bituminous Coal/Water Fuel.....	35
27	Average Operating Conditions from Short Residence Time Combustion Test 44 Using Otisca Taggart Seam Bituminous Coal/Water Fuel.....	36
28	Average Operating Conditions from Short Residence Time Combustion Test 45 Using 10-Micron Kemmerer Subbituminous Coal/Water Fuel.....	38
29	Average Operating Conditions from Short Residence Time Combustion Test 46 Using 20-Micron Kemmerer Subbituminous Coal/Water Fuel....	39
30	Average Operating Conditions from Short Residence Time Combustion Test 47 Using 15-Micron Beulah-Zap Lignite Coal/Water Fuel.....	40
31	Normalized Gas Chromatograph Analyses of Rich Zone Gas Samples from Similar Test Conditions.....	46
32	Two Way Interactions for Parametric Tests 44 and 46	47
33	Two Way Interactions for Parametric Tests 43 Through 47.....	48

34	Chemical Composition of Otisca Coal Ash and Selected Ash Samples for Combustion Test 34.....	50
35	Chemical Composition of Beulah-Zap Coal Ash and Selected Ash Samples for Combustion Test 35.....	51
36	Chemical Composition of Beulah-Zap Coal Ash and Selected Ash Samples for Combustion Test 36.....	52
37	Chemical Composition of Otisca Coal Ash and Selected Ash Samples for Combustion Test 37.....	52
38	Chemical Composition of Kemmerer Coal Ash and Selected Ash Samples for Combustion Test 38.....	53
39	Chemical Composition of Kemmerer Coal Ash and Selected Ash Samples for Combustion Test 39.....	53
40	Chemical Composition of Kemmerer Coal Ash and Selected Ash Samples for Combustion Test 40.....	54
41	Chemical Composition of Otisca Coal Ash and Selected Ash Samples for Combustion Test 44.....	57
42	Chemical Composition of Kemmerer Coal Ash and Selected Ash Samples for Combustion Test 45.....	58
43	Chemical Composition of Kemmerer Coal Ash and Selected Ash Samples for Combustion Test 46.....	58
44	Chemical Composition of Beulah-Zap Coal Ash and Selected Ash Samples for Combustion Test 47.....	59
45	Ash Material Balance Calculations for the Turbine Simulator Tests 43 through 47.....	61

LIST OF FIGURES

<u>Figure</u>	<u>Page</u>
1 Photograph of UNDEERC 1MM Btu/hr Gas Turbine Simulator.....	5
2 Schematic of the UNDEERC 1MM Btu/hr Gas Turbine Simulator.....	5
3 Photograph of Gas Turbine Simulator Deposition Probes.....	7
4 Photograph of Natural Gas Fired Fluidized-Bed Air Preheater.....	8
5 Exploded View of Natural Gas Fired Fluidized-Bed Air Preheater....	9
6 Schematic of Low-Rank Coal Fuel Preparation Process.....	14
7 Isometric View of the UNDEERC Hydrothermal Treatment Process Development Unit (PDU).....	15
8 Comparison of Gas Turbine Simulator Shakedown Fuels as a Function of Shear Rate.....	17
9 Fuel Viscosity as a Function of Solids Loading for Fuels Tested in Parametric Test Matrix.....	18
10 Fuel Viscosity as a Function of Shear Rate for Fuels Tested in Parametric Test Matrix.....	19
11 Effect of Atomizing Air-to-Fuel Ratio on Measured Combustion Efficiency for Various Fuels in the Gas Turbine Simulator.....	29
12 Effects of Air Staging on NO _x Emissions for Various Fuels Tested in the Gas Turbine Simulator.....	30
13 Typical Operating Conditions from a Short Residence Time Combustion Test (46-47) Using 20-Micron Kemmerer Subbituminous Coal/Water Fuel.....	43
14 Plot of Carbon Burnout Against Atomizing Air-to-Fuel Ratio for Parametric Combustion Tests 43-47.....	44
15 Graph of Carbon Burnout as a Function of Combustion Air Temperature for Parametric Combustion Tests 43-47.....	44
16 Plot of Cyclone Ash Carbon Burnout Against Atomizing Air-to-Fuel Ratio for Parametric Tests 43-47.....	45
17 Graph of Cyclone Ash Carbon Burnout as a Function of Combustion Air Temperature for Parametric Tests 43-47.....	45
18 Photograph of Rich Zone Deposits for Combustion Test 34 Using Otisca Bituminous CWF.....	54

19	Photograph of Quench Zone Deposits for Combustion Test 34 Using Otisca Bituminous CWF.....	54
20	Photograph of Rich Zone Deposits for Combustion Test 35 Using Beulah-Zap Lignite CWF.....	55
21	Photograph of Quench Zone Deposits for Combustion Test 35 Using Beulah-Zap Lignite CWF.....	55
22	Photograph of Rich Zone Deposits for Combustion Test 37 Using Otisca Bituminous CWF.....	55
23	Photograph of Quench Zone Deposits for Combustion Test 37 Using Otisca Bituminous CWF.....	55
24	Photograph of Rich Zone Deposits for Combustion Test 38 Using Kemmerer Subbituminous CWF.....	56
25	Photograph of Quench Zone Deposits for Combustion Test 38 Using Kemmerer Subbituminous CWF.....	56
26	Photograph of Rich Zone Deposits for Combustion Test 40 Using Kemmerer Subbituminous CWF.....	56
27	Photograph of Quench Zone Deposits for Combustion Test 40 Using Kemmerer Subbituminous CWF.....	56
28	Photograph of Rich and Quench Zone Deposits for Combustion Test 44 Using 4.3-Micron Otisca Bituminous CWF.....	59
29	Photograph of Deposition Probe #1 Deposits for Combustion Test 44 Using 4.3-Micron Otisca Bituminous CWF.....	59
30	Photograph of Rich and Quench Zone Deposits for Combustion Test 45 Using 10-Micron Kemmerer Subbituminous CWF.....	60
31	Photograph of Deposition Probe #1 Deposits for Combustion Test 45 Using 10-Micron Kemmerer Subbituminous CWF.....	60
32	Photograph of Rich and Quench Zone Deposits for Combustion Test 46 Using 20-Micron Kemmerer Subbituminous CWF.....	60
33	Photograph of Deposition Probe #1 Deposits for Combustion Test 46 Using 20-Micron Kemmerer Subbituminous CWF.....	60
34	Photograph of Rich and Quench Zone Deposits for Combustion Test 47 Using 15-Micron Beulah-Zap Lignite CWF.....	61
35	Photograph of Deposition Probe #1 Deposits for Combustion Test 47 Using 15-Micron Beulah-Zap Lignite CWF.....	61
36	Schematic of the Pressurized Drop-Tube Furnace and Facilities.....	64

TURBINE COMBUSTION PHENOMENA

1.0 INTRODUCTION

A coal/water slurry fuel has the potential of being injected and burned directly in a gas turbine engine utilizing injection and fuel handling methods similar to those employed with heavy petroleum fuels. Traditionally, gas turbine fuels have been limited to clean fuels, such as natural gas or distillate fuels, which minimize the interrelated degradation processes of deposition, erosion and corrosion. Even with these fuels, traces of mineral components present problems of erosion and alkali deposition on turbine blades and slag accumulations in burners and nozzles. To take advantage of low-cost fuels, the major challenge is to reduce the ash content substantially, preferably to less than 0.1% or modify the form of the ash or the turbine system itself to allow for higher ash levels.

Burning coal in a gas turbine combustor is not a new idea, but commercial success has not been achieved. The major technical problems inhibiting commercialization are: 1) deposits on the pressure and suction sides of the turbine blades reducing the gas flow area and turbine efficiency, 2) acceptable coal burnout given the short residence times inherent with gas turbine combustors, 3) corrosion of turbine blades by condensed alkali sulfates, 4) erosion of turbine blades and other components by ash particles entrained in the products of combustion, and 5) emissions control of NO_x , SO_2 and particulates. It is known that during combustion, release of certain mineral matter species found in both raw and beneficiated coals can lead to deposition of mineral matter on surfaces, regardless of the ash content of the fuel. This deposition can then lead to corrosion, metal loss, and ultimately to derating or unavailability of the power generation system. Alkali metals and sulfur, which exist as impurities in coal, have been identified as key components in the initiation of deposition and the onset of corrosion.

Until recently, low-rank coals were not considered for coal/water slurries because of their high intrinsic moisture level. It is extremely difficult to prepare a pumpable slurry of as-mined lignite with a dry solids loading over 35 percent. However, with the advent of the University of North Dakota's Energy and Environmental Research Center's (UNDEERC's) hydrothermal treatment process, micronized lignite slurries have been produced with solids loadings up to 50 wt% and heating values of 6000 Btu per pound of slurry. Subbituminous coals also respond very well to hydrothermal treatment and produce high-quality slurries. Availability of a slurry with a high enough fuel value to sustain combustion makes it possible to take advantage of desirable characteristics of low-rank coals, namely the higher reactivity of its nonvolatile carbonaceous components. Thus, a low-rank coal slurry should require less residence time in the gas turbine combustor for complete combustion, or inversely, the coal would not have to be micronized as fine to achieve the same level of burnout, thereby reducing fuel preparation costs. Another potential advantage of low-rank coal slurries is their non-agglomerating tendencies relative to bituminous slurries, reducing the importance of atomization to very fine droplet sizes.

2.0 GOALS AND OBJECTIVES

The overall objective of the Turbine Combustion Phenomena Program is to expand the scientific and engineering data base for the combustion of low-rank coal (LRC) fuels in advanced pressurized combustion systems such as those found in gas turbine engine applications. Fundamental research on the use of low-rank coal slurries for gas turbine engine applications will develop data that will; 1) quantify the potential advantages of low-rank coal's higher reactivity and non-agglomerating tendencies, 2) help in determining fuel specifications, and 3) indicate needed design modifications in the gas turbine engines themselves. Research will be directed toward understanding the effects of low-rank coal (LRC) and slurry properties (including ash level and composition, moisture levels, and slurry rheology) on combustion efficiency, vaporization and deposition of inorganics, and erosion of materials in pressurized combustion systems. The intent of this research is to establish the relationships between LRC properties and gas turbine engine operational parameters and the comparison of these relationships with those established for diesel fuel and bituminous coal slurries.

The investigation of turbine combustion phenomena at UNDEERC is a multi-year program. Three-year goals have been established and are discussed in the following text:

2.1 Three-Year Objectives

1. Technology and Market Assessment. To ensure that all sources of information to the project are thoroughly researched, UNDEERC has performed an extensive survey of all published information concerning the use of coal and coal slurries in gas turbine applications. This information provided an understanding of the concerns and needs for the use of coal-derived fuels in these applications. The state-of-the-art for these technologies has been determined and used to provide the proper direction for this program and limit duplication of effort. This effort has built upon a similar assessment of the market and technologies that was performed as a part of the Low-Rank Coal Slurry Combustion program. This objective was accomplished during the first year.
2. Reactivity of Fuel in Pressurized Systems. The reactivities of dry and slurried low-rank coals are higher than those of bituminous coals, but the magnitude of these differences is not well documented. The reactivity of the fuel can also be improved with the use of additives to the slurry, such as methanol. Fast, simple, inexpensive experiments in a modified combustion bomb will provide very basic information about the pressurized combustion behavior of LRC and slurries. This information will be critical in determining the fuel specifications of slurries for use in heat engine applications. Data collected during these tests will include the heat of combustion (calorimetry) of the sample, the sample burning time/reactivity (from pressure sensors), and the analysis of the products of combustion after combusting the test fuel under various conditions. Parameters to be varied include coal type, particle size distribution, gas composition (percent oxygen), combustion bomb conditions at fuel injection, and system pressure. This testing will provide semi-quantitative information in a fast and inexpensive manner.

3. Investigate the Fundamental Characteristics of Burning Low-Rank Coal Slurries in a Turbine System. A bench-scale gas turbine simulator will be designed to measure the pressure, temperature, conversion, gas composition, vaporization of inorganics, deposition on simulated turbine blades and other system components, fuel reactivity, and ash particulate size distributions resulting from the combustion of LRC slurries. These fundamental studies will demonstrate the impact of various fuel properties on the combustor and turbine blades, and lead to the development of fuel specifications for the successful operation of low-rank slurries in a turbine application. This task will continue throughout the first three years of the program.
4. Hot-Gas Cleanup. This effort has assessed available technology to determine specific needs with respect to the removal of undesirable constituents from gas streams derived from high temperature/pressure combustion of LRC slurries, with emphasis on coal-specific problem areas. Initial work has been devoted to a review of the literature on the removal of contaminants from the coal-derived gas streams. Processes that are capable of removing >90% of sulfur and/or nitrogen oxides, >99% of particulates, and which reduce alkali vapors in the gas stream to <25 ppm are desired. The reported work has been evaluated to establish applicability to LRC slurry utilization. A summary of reviewed papers and reports has been prepared to identify processes according to overall performance, thermodynamics, economics, and environmental considerations. Special consideration has been given to gas cleaning methods that produce a salable product or zero discharge of waste, and are cost-effective. Work toward this objective will continue the first three years of the program.

2.2 Third-Year Objectives

Specific objectives for the Turbine Combustion Phenomena project during the third year of this program include:

1. Perform reactivity tests using bituminous and low-rank coal slurries and correlate data to document differences (where available) in heat engine performance. Use data to select coals for testing in turbine simulator and correlate the results with those collected in Task 3.
2. Perform tests with a suite of coal-based slurries on the gas turbine simulator. Parameters to be varied include pressure, temperature, residence time, and equivalence ratios. Correlate the results of the tests with the coal slurry properties to determine the fundamental reactivity and extent of reaction. Areas to be investigated include coal particle agglomeration, ash formation, transportation and deposition, alkali deposition, and gaseous and particulate emissions.
3. Test performance of hot-gas cleanup devices for SO₂ control. Investigate the use of air staging for NO_x control. Evaluate the effect of fuel properties, SO₂ cleanup methods and staging on the particulate control requirements.

3.0 REACTIVITY OF FUEL IN PRESSURIZED SYSTEMS - COMBUSTION BOMB STUDIES

Preliminary calibration and baseline testing work was performed under the two projects, Diesel Utilization of Low-Rank Coal and Turbine Combustion Phenomena. After system development and baseline testing was completed, both projects used the same test plan. The initial $H_2/O_2/N_2$ concentration and pressure was adjusted from the diesel experiments to provide, as closely as possible, the higher temperatures and lower pressures seen in a gas turbine combustor. With the understanding that the pulsed high pressure atomization process seen with a diesel injector is different from the continuous atomization at lower pressures obtained from a conventional turbine nozzle (usually in the presence of atomizing air or steam), it is expected that injection of fuels in the combustion bomb will still give a valid measure of the reactivity of a fuel under turbine combustion conditions. Results from the combustion bomb studies are reported in the Diesel Utilization of Low-Rank Coals Annual Report (1) and are not repeated here.

4.0 CHARACTERISTICS OF BURNING COAL SLURRIES IN A TURBINE SYSTEM

To meet the objectives of the program, a pressurized combustion vessel was built to simulate the operating parameters of a direct-fired gas turbine combustor. One goal in building this equipment was to design the gas turbine simulator as small as possible to reduce both the quantity of test fuel needed and the test fuel preparation costs while not undersizing the combustor such that wall effects have a significant impact on the measured combustion performance. Based on computer modeling, a rich-lean, two-stage non-slagging combustor has been constructed to simulate a direct-fired gas turbine. This design was selected to maximize the information that could be obtained on the impact of the unique properties of low-rank fuels and various hot gas cleanup techniques (such as Ca-based sorbent injection for SO_2 control) on the gas turbine combustor and its turbomachinery.

4.1 Gas Turbine Simulator Description

A description of the gas turbine simulator has been presented in other reports (2,3), but will be given here for clarification of test results. Figure 1 is a photograph of the UNDEERC gas turbine simulator. Figure 2 shows some of the internal details of the gas turbine simulator combustion vessel and deposition sections. The head section of the turbine consists of an 8-inch, 300-lb blind flange that has a horizontal flat-bladed 45° air swirler and a Delavan Swirl-Air nozzle with a 50° spray angle. The combustion vessel itself is made from sections of 304 SS 8-inch schedule 40 pipe while the deposition section is fabricated from sections of 304 SS 4-inch schedule 40 pipe. These sections are jacketed to provide water-cooling of the external pressure vessel wall. The rich zone in this combustor is fabricated from four 8-inch long sections originally lined with 1.25 inches of castable refractory rated to $3400^\circ F$. Later in the program these modules were recast with 1.5 inches of refractory for heat loss and residence time reasons. It was felt a rich zone diameter smaller than the current five inches would probably introduce significant wall effects on the combustion performance. These modules allow the length of the rich zone to be varied from 8 to 32 inches. The lean zone is fabricated from two 10-inch long modules lined with 1 inch of a castable refractory (rated to $3000^\circ F$). The lean zone has since been

Figure 1. Photograph of UNDEERC 1MM Btu/hr Gas Turbine Simulator.

Figure 2. Schematic of the UNDEERC 1MM Btu/hr Gas Turbine Simulator.

relined with 2 inches of refractory. The removal of some of these modules allows the effect of residence time to be investigated under similar flow conditions. The variable geometry of this combustor also is beneficial in extending the range of slurry flow rates that can be feasibly run in the combustor by reducing the external surface through which excessive heat losses can occur. The gas turbine simulator is nominally designed to combust 100 to 150 lbs/hr of slurry, but flow rates from approximately 200 down to 50 lbs/hr (1.5MM to 300,000 Btu/hr) can be burned in this combustor. A Moyno progressive cavity pump is used to pump the coal/water slurry fuels into the turbine while a high pressure gear pump is used to pump the start-up diesel fuel and other distillate fuels into the turbine simulator. A Micromotion mass flow-meter is used to measure the flow rate of the slurry fuels into the combustor.

The quench zone of the simulator originally was a 3-inch ID metal walled section with concentric air passages encircling the inner wall with sixteen 0.4" x 0.15" slots machined through the inner wall. This allowed the rapid mixing of the secondary air to minimize the occurrence of localized "hot spots" and the formation of thermal NO_x . The quench zone has since been cast with the sixteen slots passing through a half inch of refractory. This refractory was installed to decrease the amount of ash deposited around the quench by increasing the velocity of the gas passing through the throat of the quench zone and eliminating a relatively cold metal surface for the ash and slag to deposit on. A rotary control valve and a high temperature guided seat control valve are used to control the flow of combustion air entering the air preheater and the distribution of air between the rich and lean zones, respectively. The combustor is designed to operate at pressures up to 250 psig and lean zone exit temperatures of 2000°F with temperatures in the rich zone up to 2700°F.

A reduced flow area in the deposition section is used to increase the gas velocities up to those typically seen in the expander section of a gas turbine (400 to 800 ft/sec). This reduced area was obtained by lining the 4-inch schedule 40 pipe with refractory to form a 1.25-inch square duct. Four air-cooled probes with various contact angles were machined from thick-walled tubing and installed to simulate the leading edge of turbine blades. Figure 3 is a photograph of a set of deposition probes with a 45° contact angle machined in the exposed portion of the probes. Additional cooling air is added after the first two probes to cool the exit gas stream up to 200°F so that gas temperature as well as metal temperatures can be investigated for their effects on deposition/erosion/corrosion (DEC). These probes are made of different high temperature alloys such as Hastelloy X and Haynes 556 to evaluate their potential to resist DEC. A spray water quench zone is located after the deposition section to spray high pressure water into the combustion gases to cool the gases to less than 750°F before passing through the rotary control valve used to back pressure the turbine simulator.

A natural gas-fired fluidized-bed preheater is used to preheat the high pressure combustion air to temperatures as high as 1000°F. Figure 4 is a photograph of the fluidized-bed air preheater and Figure 5 is an exploded view detailing its construction. This vessel has a 34-inch OD with a 13-inch square combustion zone cast in the refractory lining. A fluidized-bed preheater was selected for its flexibility in providing preheated air over a wide range of temperatures, pressures and flow rates. Heat input to the air can be controlled by a combination of variables, including the bed depth,

superficial gas velocity, and bed temperature. The use of a fluidized-bed reduces the amount of heat exchange surface required due to the higher heat transfer coefficients resulting from the intimate contact of the heat transfer surface with the dense bed of hot particles that are continuously circulating within the combustion zone. The use of 20 vertically suspended heat exchange tubes is unique and offers a number of advantages including relative ease of construction, a more compact in-bed tube bundle configuration, and reduced erosion potential of the tube surfaces. The tubes are in a bayonet configuration in which air is first preheated as it enters an inner tube and travels downward. The final heat transfer occurs as the air moves back up the outer tube. Manifolds are used on both the cold and hot air sides of the preheater to provide an even air flow distribution through all the tubes. The natural gas and low pressure combustion air distribution system into the preheater are integrated together in a sparger system (a series of horizontal pipes with vertical nozzles attached). The natural gas is mixed with the combustion air inside the nozzle before entering the fluidized-bed where it is ignited. A small pilot burner is first ignited with a spark plug and the flame detected by a flame safety system before flow of the primary natural gas is permitted to the main burners.

Combustion efficiencies of the test fuels fired in the turbine simulator are calculated from gas and isokinetic particulate samples taken from both the rich and lean zones of the combustor. Gas and particulate sampling probes have been made from progressively smaller concentric tubes so the probes can

PRE-RUN TUR-B-28
front view

Figure 3. Photograph of Gas Turbine Simulator Deposition Probes.

Figure 4. Photograph of Natural Gas Fired Fluidized-Bed Air Preheater.

Figure 5. Exploded View of Natural Gas Fired Fluidized-Bed Air Preheater.

be water-cooled. In the particulate sampling probes an extra tube is used in addition to the cooling jacket to inject an inert gas through small holes in the inner wall of the sampling probe. This quenches the particulate samples and prevents further oxidation of unconverted char particles. These particulate samples originally were transported a few feet through heat-traced lines to high pressure filter holders with 0.3- μ m borosilicate glass or ashless cellulose filters. Subsequent testing indicated that some of the particulate being sampled was retained in the heat-traced lines. Therefore, the high pressure filter holders were located right after the particulate sampling probes. Gas samples are also transported through heat-traced lines to a sample conditioner where the combustion gas moisture is removed before being analyzed by on-line gas analyzers. These analyzers include NO_x and SO_2 analyzers (0-10,000 ppm), CO_2 and CO infrared analyzers (0-20 mol% and 0-5 mol%, respectively, and O_2 analyzers (0-25 mol%). Rich zone gas samples can also be analyzed for unconverted light hydrocarbons by on-line gas chromatography.

Temperatures in the rich zone have been measured with alumina sheathed type B thermocouples inserted in molybdenum disilicide thermowells while the lean zone and deposition section temperatures are measured with Inconel sheathed type K thermocouples. The combustion air and water jacket exit temperatures are measured with standard SS sheathed type K thermocouples. Combustion zone, preheated air, fuel and atomizing air pressures are all monitored with pressure transducers. Flow and pressure control are accomplished using pneumatic and electronic controllers. A 32-channel programmable recorder and an 84-channel ADAC Microbasys data acquisition system are used to monitor process conditions. The data acquisition system and the recorder both communicate with an IBM XT for data averaging, storage, logging and display. The recorder also supplies eight alarm relay contacts that are used to establish safety interlocks for shutting the turbine down in the event of an alarm condition.

4.2 Gas Turbine Test Matrix

A screening test matrix was designed for investigating the effects of certain variables on the combustion efficiencies obtained from a coal-water fuel in the turbine simulator. Table 1 shows the high and low levels of the process variables to be investigated. These variables include atomizing air flow rate, fuel flow rate, and combustion air temperature and pressure, all of which are varied during a single combustion test. The particle size and residence time variables were investigated between separate combustion tests. At any given set of test conditions, an approximate rich zone equivalence ratio of 1.4 is run since previous work indicated NO_x emissions are minimized at this ratio. Variables not being investigated include the primary air swirl number, recessing of the atomization nozzle, solids loading of the slurry, and atomizing air and fuel temperatures, although any of these parameters could be studied in a subsequent test matrix. Currently, these variables are being held constant with a primary air swirl number of 1.7, the atomizer recessed one-half inch, solids loadings of 50 wt%, and atomizing air and fuel temperatures held at approximately room temperature.

Other test matrices will include tests using a Beulah-Zap North Dakota lignite and Kemmerer subbituminous coals and an Otisca Industries-cleaned Taggart seam bituminous coal to investigate the effects of fuel dependent

properties on the combustion efficiency and DEC experienced in the turbine simulator. These test matrices will also look at the effects of the combustion air temperature, pressure, fuel flow rates, and atomizing air flow rates on combustion efficiency and DEC for each fuel. Tables 2 through 6 detail the test conditions utilized in the final parametric test matrix. These test matrices correspond to the variables listed in Table 1.

4.3 Gas Turbine Simulator Results

4.3.1 Slurry Fuel Preparation

During the year, several production runs of LRC coal/water fuel were undertaken in conjunction with the DOE LRC beneficiation program at the UND Energy and Environmental Research Center. Beulah lignite from North Dakota, and Kemmerer subbituminous coal from Wyoming, were selected for pilot-scale processing because of their ability to be physically and chemically cleaned to

TABLE 1

TEST MATRIX FOR COMBUSTION TESTS ON THE GAS TURBINE SIMULATOR

<u>Variable</u>	<u>(+)</u>	<u>(-)</u>
Fuel Firing Rate (MM Btu/hr)	1.0	0.7
Atomizing Air-to-Fuel Ratio	1.25	0.75
Combustion Air Temperature (°F)	800	400
Combustor Pressure (atm)	12	6
Fuel Particle Size (μm)	10	20
Residence Time (ms)	100	50

All test conditions run at a rich zone equivalence ratio of approximately 1.4

TABLE 2

TEST MATRIX FOR LONG RESIDENCE TIME COMBUSTION TESTS
USING 4.6-MICRON OTISCA TAGGART SEAM BITUMINOUS COAL/WATER FUEL

<u>Test No.</u>	<u>Fuel Flow Rate (lb/hr)</u>	<u>Atom. Air Flow Rate (lb/hr)</u>	<u>Combustor Press. (psig)</u>	<u>Comb. Air Temp. (°F)</u>
43-1	130	98	74	800
43-2	130	163	74	800
43-3	80	98	74	800
43-4	80	60	74	800
43-5	80	60	74	400
43-6	80	98	74	400
43-7	130	163	74	400
43-8	130	98	74	400

TABLE 3

TEST MATRIX FOR SHORT RESIDENCE TIME COMBUSTION TESTS USING
4.6-MICRON OTISCA TAGGART SEAM BITUMINOUS COAL/WATER FUEL

<u>Test No.</u>	<u>Fuel Flow Rate (lb/hr)</u>	<u>Atom. Air Flow Rate (lb/hr)</u>	<u>Combustor Press. (psig)</u>	<u>Comb. Air Temp. (°F)</u>
44-1	130	163	74	800
44-2	130	98	74	800
44-3	90	113	74	800
44-3	90	68	74	800
44-5	90	113	162	800
44-6	90	68	162	800
44-7	130	98	162	800
44-8	130	163	162	800
44-9	130	163	162	400
44-10	130	98	162	400
44-11	90	113	162	400
44-12	90	68	162	400
44-13	90	113	74	400
44-14	90	68	74	400
44-15	130	98	74	400
44-16	130	163	74	400

TABLE 4

TEST MATRIX FOR SHORT RESIDENCE TIME COMBUSTION TESTS USING
10.1-MICRON KEMMERER SUBBITUMINOUS COAL/WATER FUEL

<u>Test No.</u>	<u>Fuel Flow Rate (lb/hr)</u>	<u>Atom. Air Flow Rate (lb/hr)</u>	<u>Combustor Press. (psig)</u>	<u>Comb. Air Temp. (°F)</u>
45-1	160	200	74	800
45-2	160	120	74	800
45-3	110	138	74	800
45-4	110	83	74	800
45-5	110	83	162	800
45-6	110	138	162	800
45-7	160	120	162	800
45-8	160	200	162	800
45-9	160	200	74	400
45-10	160	120	74	400
45-11	160	120	162	400
45-12	160	200	162	400
45-13	110	138	162	400
45-14	110	83	162	400
45-15	110	83	74	400
45-16	110	138	74	400

TABLE 5

TEST MATRIX FOR SHORT RESIDENCE TIME COMBUSTION TESTS USING
20.1-MICRON KEMMERER SUBBITUMINOUS COAL/WATER FUEL

<u>Test No.</u>	<u>Fuel Flow Rate (lb/hr)</u>	<u>Atom. Air Flow Rate (lb/hr)</u>	<u>Combustor Press. (psig)</u>	<u>Comb. Air Temp. (°F)</u>
46-1	160	200	74	800
46-2	160	120	74	800
46-3	110	138	74	800
46-4	110	83	74	800
46-5	110	83	162	800
46-6	110	138	162	800
46-7	160	120	162	800
46-8	160	200	162	800
46-9	160	200	74	400
46-10	160	120	74	400
46-11	110	138	74	400
46-12	110	83	74	400
46-13	110	83	162	400
46-14	110	138	162	400
46-15	160	120	162	400
46-16	160	200	162	400

TABLE 6

TEST MATRIX FOR SHORT RESIDENCE TIME COMBUSTION TESTS USING
15.9-MICRON BEULAH-ZAP LIGNITE COAL/WATER FUEL

<u>Test No.</u>	<u>Fuel Flow Rate (lb/hr)</u>	<u>Atom. Air Flow Rate (lb/hr)</u>	<u>Combustor Press. (psig)</u>	<u>Comb. Air Temp. (°F)</u>
47-1	166	208	74	800
47-2	166	125	74	800
47-3	117	146	74	800
47-4	117	88	74	800
47-5	117	88	162	800
47-6	117	146	162	800
47-7	166	125	162	800
47-8	166	208	162	800
47-9	166	208	74	400
47-10	166	125	74	400
47-11	117	146	74	400
47-12	117	88	74	400
47-13	117	88	162	400
47-14	117	146	162	400
47-15	166	125	162	400
47-16	166	208	162	400

to less than 1 wt% ash on the bench-scale (4). Figure 6 shows the complete scenario for pilot-scale production of deep cleaned LRCs. This treatment scheme includes physical coal cleaning by dense media separation, wet grinding, chemical cleaning by nitric acid leaching, hydrothermal treatment, and wet micronizing.

The physical cleaning step uses a dense-media separation process that consists mainly of classifying coal, feeding it into an air-actuated cone separator system, followed by a washing and recycling section. The clean coal was then pulverized and fed into a continuous acid-leaching column. This chemical cleaning was conducted using a 30 wt% slurry mixed with a 4 wt% nitric acid solution. The sample was concentrated using a solid-bowl centrifuge, reslurried, and fed into the HWD Process Development Unit (PDU).

Figure 7 is a isometric diagram detailing the hydrothermal treatment step used at the UNDEERC. The hot water-drying treatment forces inherent moisture out of the coal structure using carbon dioxide formed during the carboxylation of the coal, thereby increasing the heating value of the product fuel. Tars are also exuded from the coal structure during treatment, sealing the micro-pore structure, reducing the surface area, and increasing the hydrophobicity of the coal. After hot water-drying coal product slurry was then concentrated to 60 to 70 wt% in a centrifuge, reslurried, and micronized to a coal/water fuel (CWF). An anionic dispersant, d319-2 (Ammonium Ligno Sulfonate), was added to the final CWF.

Figure 6. Schematic of Low-Rank Coal Fuel Preparation Process.

Figure 7. Isometric View of the UNDEERC Hydrothermal Treatment Process Development Unit (PDU).

By adsorbing to the particle surface, the charged additive creates repulsive forces that counteract the Van der Waal forces present in the coal. The strength of the repulsive forces governs the degree of flocculation of the suspended particles. At a given viscosity, an increase of 2 wt% can be expected.

The rheological behavior, especially for Newtonian and non-Newtonian nature of the CWF, is of great importance to the quality of the fuel. The behavior of a CWF at low, intermediate, and high shear rates essentially determines its behavior during transportation, pumping, and atomizing. Rheological properties of the hot water-dried CWFs were investigated using a concentric cylinder Haake RV100 viscometer equipped with an MVII-P profiled rotor and sample cup (5,6). Shear stress versus shear rate rheograms were recorded over the shear rate range of 0 to 440 sec^{-1} .

During this reporting period, 17 successful combustion tests using CWF were completed. These tests included seven tests with a commercially available Otisca Industries produced Taggart seam bituminous fuel and five tests each with physically and chemically cleaned Beulah-Zap lignite and a chemically cleaned Kemmerer subbituminous fuel. Table 7 shows the analysis of the slurry fuels combusted in the gas turbine simulator during the shakedown and variable optimization testing. Figure 8 shows apparent viscosity of these fuels as a function of shear rate up to 450 $1/\text{sec}$.

TABLE 7
ANALYSIS OF COAL-WATER FUELS USED IN GAS TURBINE
SIMULATOR SHAKEDOWN TESTS

Supplier	Otisca	AMAX/UNDEERC	UNDEERC	UNDEERC
Coal Name	Taggart	Beulah-Zap	Beulah-Zap	Kemmerer
Coal Type	Bitum.	Lignite	Lignite	Subbit.
Hydrothermal Test No.	N/A	33	34	36
Proximate Analysis (MF)				
Volatile Matter	36.50	39.55	41.18	39.44
Fixed Carbon (by dif.)	62.42	57.09	56.38	57.71
Ash	1.08	3.36	2.44	2.85
Ultimate Analysis (MF)				
Hydrogen	5.66	3.09	4.16	4.27
Carbon	84.35	70.68	72.15	73.28
Nitrogen	1.48	1.45	1.26	2.24
Sulfur	0.52	0.39	0.52	0.15
Oxygen (by dif.)	6.89	21.01	19.46	17.19
Ash	1.08	3.36	2.44	2.85
Heat. Value (Btu/lb, MF)	15,401	11,687	11,852	12,543
Ash Fusion (Deg F-Reducing Atm)				
Init. Deform. Temp.	2243	2060	2010	2146
Softening Temp.	2300	2074	2059	2287
Hemisph. Temp.	2426	2143	2561	2500
Fluid Temp.	2644	2230	2563	2530
Particle Size				
Mean (micron)	4.6	11.0	10.6	15.4
Top (99%<) (micron)	15.2	45.5	36.3	53.5
Ash Analysis (XRFA)				
(Wt% Ash, SO ₃ free)				
SiO ₂	35.0	21.9	40.0	60.7
Al ₂ O ₃	25.3	7.5	14.9	19.8
Fe ₂ O ₃	18.8	65.7	38.0	9.0
TiO ₂	3.8	2.1	3.2	1.3
P ₂ O ₅	0.4	0.0	0.0	0.4
CaO	11.8	2.1	2.9	5.8
MgO	2.5	0.0	0.5	2.6
Na ₂ O	0.8	0.0	0.0	0.0
K ₂ O	1.6	0.5	0.6	0.5
TOTAL	100.0	99.8	100.0	100.1

Figure 8. Comparison of Gas Turbine Simulator Shakedown Fuels as a Function of Shear Rate.

These analyses indicate that the ash fusion temperature for the bituminous fuel was higher than the lignite fuel primarily due to the high level of iron found in the lignite fuel. These high iron concentrations resulted from process piping contamination and from the heavy media gravity separation used to physically clean the Beulah-Zap lignite fuel. In the case of the Amax-cleaned, UNDEERC-hydrothermally treated fuel, the fuel was 2.6 wt% ash as received from Amax, however, after hydrothermal treatment and micronization the ash level had increased to 3.4 wt% ash due to contamination from carbon steel process piping and carbon steel arms in the micronizer. All carbon steel components were replaced with stainless steel before processing of the next batch of Beulah-Zap fuel. As indicated by the analysis, the iron content was reduced significantly but still is approximately twice that of the bituminous fuel. Other results indicate the high ash levels and high iron concentration is partially due to contamination of the feed coal with the magnetite used in the heavy media separation. Because Kemmerer has a relatively low ash content and to eliminate any chance for magnetite contamination, only chemical cleaning was conducted on the Kemmerer coal. Thus, the iron content of the ash is quite low, however, harder ash materials such as quartz that would be susceptible to the effects of physical cleaning have been concentrated in the coal ash. Modifications were made to the heavy media physical cleaning step to reduce the amount of residual magnetite that remained with the float product, resulting in a fuel with relatively low iron levels.

The best LRC fuels available to date were then selected for parametric testing and statistical analysis (runs 43 through 47) in the gas turbine simulator. A summary of solids concentrations versus apparent viscosity for

four fuels, Beulah, two different particle size Kemmerer samples, and a baseline Otisca Ind. produced bituminous fuel, is shown in Figure 9. Figure 10 shows the relationship of apparent viscosity versus shear rate for the four fuels. Tables 8 and 9 indicate the final quality of the coal/water fuels.

There is some question about the rheological behavior of these fuels under the high shear rates experienced in the Delavan atomizer and what effect that might have on atomization and, consequently, on combustion efficiency.

4.3.2 Slurry Combustion Test Results

4.3.2.1 Shakedown Tests 27 Through 42

Tables 10 through 17 show the average turbine operating conditions for the fuels used in the shakedown testing (7,8,9).

An examination of the results shown in Tables 10 through 17 indicates that the Beulah-Zap lignite and Kemmerer subbituminous fuels burned out better than the Otisca bituminous fuel despite using lower atomizing air-to-fuel ratios. Combustion temperatures were similar for the different fuels and tended to decrease in the rich zone as the rich zone equivalence ratio was increased, while the lean zone combustion temperatures increased with a higher rich zone equivalence ratio due to the increased burnout of the fuel in the lean combustion zone. Lower fuel flow rates were needed with the bituminous fuel to achieve the desired thermal input due to the higher heating value of the bituminous fuel. Successful particulate samples were not collected during

Figure 9. Fuel Viscosity as a Function of Solids Loading for Fuels Tested in Parametric Test Matrix.

Figure 10. Fuel Viscosity as a Function of Shear Rate for Fuels Tested in Parametric Test Matrix.

TABLE 8

ANALYSIS OF COAL/WATER FUELS USED IN PARAMETRIC TESTS
ON THE 1MM BTU/HR GAS TURBINE SIMULATOR

Sample: PDU Test No.	Otisca N/A	Kemmerer 38	Beulah-Zap 40
Prox. Analysis (MF)			
Vol. Matter	36.10	41.10	42.66
Fixed Carbon	63.07	56.62	54.78
Ash	0.83	2.28	2.56
Ult. Analysis (MF)			
Hydrogen	5.39	5.03	4.29
Carbon	82.90	75.72	70.89
Nitrogen	1.59	1.30	1.20
Sulfur	0.78	0.26	0.78
Oxygen (by dif.)	8.49	15.40	20.26
Ash	0.83	2.28	2.56
Heating Value (mf, Btu/lb)	15,060	12,925	12,014
Ash Fusion Temperatures (Deg F-Reducing Atm)			
Init. Deform. Temp.	2119	2000	1942
Softening Temp.	2187	2095	1986
Hemisph. Temp.	2362	2140	2068
Fluid Temp.	2370	2201	2329
Part. Size-Mean (microns)	4.6	10.1 & 20.1	15.9
Top Size (99%<) (microns)	15.2	34.9 & 73.6	59.6

TABLE 9

X-RAY FLUORESCENCE ANALYSIS OF COAL/WATER FUELS USED IN
PARAMETRIC TESTS ON THE 1MM BTU/HR GAS TURBINE SIMULATOR

High Temperature Ash Results (% of ash, SO ₃ -free)	Otisca Fuel	Kemmerer Fuel	Beulah Fuel
SiO ₂	37.0	49.0	25.2
Al ₂ O ₃	28.8	22.0	20.5
Fe ₂ O ₃	20.1	14.5	29.2
TiO ₂	4.4	1.2	1.8
P ₂ O ₅	0.4	0.4	1.5
CaO	5.7	9.1	16.3
MgO	1.6	3.5	4.8
Na ₂ O	0.0	0.0	0.0
K ₂ O	1.8	0.2	0.7
TOTAL	99.8	99.9	100.0

all the test periods shown especially in earlier combustion tests due to problems with particulate sample probes plugging or burning up due to inadequate cooling. Future experiments used longer sampling times and better sampling techniques to improve the scatter in the particulate sampling results.

Particulate and gas samples were collected during these tests to calculate combustion efficiencies. Due to the relatively low ash levels of the potential turbine fuels, high levels of POC carbon can be measured in the particulate samples while still obtaining a high combustion efficiency. The particulate and gas sampling methodology is the same as that used by Rosfjord (10,11). Carbon burnout was also calculated using the equation given below by Wenglarz, et al. (12) with reasonable agreement.

$$\text{burnout fraction} = (1 - W_a/W_x)/(1 - W_a) \quad (1)$$

where W_x = weight fraction of ash in particulate sample

W_a = weight fraction of ash in the coal from which slurry was made

Figure 11 plots the combustion efficiency against the atomizing air-to-fuel ratio for the various fuels and combustor configurations in the shakedown combustion tests. This figure indicates that the LRC fuels are burning out better at lower atomizing air-to-fuel ratios and also do not appear to be as sensitive to the atomizing air-to-fuel ratio as bituminous fuel. This figure also indicates that the new atomizing nozzle tip has improved the combustion efficiency of the bituminous fuel from 95% to 99% at the same atomizing air-to-fuel ratio. This figure shows that combustion efficiencies comparable to the LRC fuels were obtained for the bituminous fuel at the longer residence time configuration.

TABLE 10

VARIOUS OPERATING CONDITIONS ACHIEVED IN GAS TURBINE SIMULATOR COMBUSTION
TESTS 27 AND 28 USING BEULAH-ZAP LIGNITE COAL/WATER FUEL

Run Number	27-1	27-2	27-3	28-1	28-2	28-3	28-4	28-5
Combustor Configuration (rich/lean modules)	4/3	4/3	4/3	4/3	4/3	4/3	4/3	4/3
Atomizer Type								
Fuel Flow Rate (lb/hr)	DEL 2.5 144.7	DEL 2.5 144.7	DEL 2.5 142.7	DEL 2.5 151.2	DEL 2.5 154.6	DEL 2.5 128.9	DEL 2.5 125.2	DEL 2.5 142.3
Atom. Air Flow Rate (lb/hr)	279.1	279.1	279.1	277.8	243.8	243.1	233.2	244.3
Atom. Air/Fuel Ratio	1.93	1.96	1.96	1.84	1.57	1.89	1.86	1.72
Atomizer Pressure Ratio	2.50	2.50	2.50	2.50	2.00	2.00	2.00	2.00
Rich Zone Equivalence Ratio	1.16	1.12	1.12	1.20	1.23	1.03	0.83	1.27
Lean Zone Equivalence Ratio	0.46	0.44	0.44	0.47	0.52	0.44	0.41	0.50
Primary Air Flow (scfm)	45.6	47.2	47.2	46.8	54.0	53.4	78.3	41.2
Secondary Air Flow (scfm)	168.7	174.5	174.5	169.1	148.6	145.7	138.5	154.0
Primary Air Temp. (°F)	699	699	699	697	658	634	479	656
Secondary Air Temp. (°F)	829	828	828	825	763	734	536	760
Rich Zone Pressure (psig)	44.7	43	43	44.6	73.8	75.0	70.6	75.2
Lean Zone Pressure (psig)	43.5	42	42	43.4	73.0	73.7	69.7	76.0
Spray Quench Zone Pressure (psig)	37.9	35.8	35.8	37.0	68.5	71.0	66.0	68.9
Rich Zone Resid. Time (ms)	118	113	113	117	184	194	139	221
Lean Zone Resid. Time (ms)	65	65	65	63	113	122	126	118
Rich Zone Exit Temp. (°F)	2,187	2,220	2,220	2,139	1,994	2,051	2,161	1,854
Lean Zone Exit Temp. (°F)	2,009	1,876	1,876	2,038	1,709	1,847	1,430	2,006
Dep. Probes: 1 Gas Temp. (°F)	1,979	1,853	1,853	2,208	1,887	1,811	1,486	1,965
Dep. Probes: 2 Gas Temp. (°F)	1,965	1,818	1,818	1,944	2,100	1,773	1,500	1,940
Dep. Probes: 1 Met. Temp. (°F)	--	--	--	--	--	--	--	--
Dep. Probes: 2 Met. Temp. (°F)	--	--	--	--	--	--	--	--
SO ₂ -A {Lean} (ppm)	44.8	52.6	52.6	0	24.4	66.6	21.7	0
SO ₂ -B {Rich} (ppm)	*	*	*	*	*	*	*	*
NO _x (ppm) 151	220	248	248	153	78.1	75.7	95.8	120
CO ₂ (mol%) 9.62	9.59	11.3	11.3	11.3	10.2	8.56	11.2	11.4
CO (ppm) 65.4	69.7	63.8	63.8	64.4	53.6	53.5	54.2	56.7
O ₂ -A {Lean} (mol%)	12.9	12.9	12.9	9.26	10.8	11.7	14.8	10.9
O ₂ -B {Rich} (mol%)	*	*	*	*	*	*	*	*
NO _x @ 15% O ₂ (ppm)	112	162	162	126	90.0	50.1	73.1	56.6
Rich Zone Combustion Efficiency (%)	ND	ND	ND	ND	69.7	ND	ND	ND
Lean Zone Combustion Efficiency (%)	ND	ND	ND	ND	99.0	ND	ND	ND
Rich Zone Carbon Burnout (%)	ND	ND	ND	ND	98.7	ND	ND	ND
Lean Zone Carbon Burnout (%)	ND	ND	ND	ND	99.5	ND	ND	ND

* Plugging of the rich zone gas sample probe.

-- No deposition probes installed

ND Not determined due to sample probe plugging

TABLE 11

VARIOUS OPERATING CONDITIONS ACHIEVED IN GAS TURBINE SIMULATOR COMBUSTION
TEST 31 USING OTISCA TAGGART SEAM BITUMINOUS COAL/WATER FUEL

Run Number	31-1	31-2	31-3	31-4	31-5	31-6	31-7	31-8	31-9
Combusitor Configuration		4/3	4/3	4/3	4/3	4/3	4/3	4/3	4/3
Atomizer Type		DEL 2.5	DEL 2.5	DEL 2.5	DEL 2.5	DEL 2.5	DEL 2.5	DEL 2.5	DEL 2.5
Fuel Flow Rate (lb/hr)		97.7	97.9	98.5	98.3	98.7	98.2	97.9	97.8
Atom. Air Flow Rate (lb/hr)		189.2	189.6	189.1	189.1	189.1	150.4	151.3	150.9
Atom. Air/Fuel Ratio		1.94	1.93	1.92	1.92	1.91	1.53	1.55	1.54
Atomizer Pressure Ratio		1.80	1.93	2.01	1.97	1.93	1.76	1.63	1.66
Rich Zone Equivalence Ratio		1.40	1.28	0.98	1.10	1.47	1.09	1.18	1.23
Lean Zone Equivalence Ratio		0.41	0.39	0.41	0.40	0.47	0.40	0.42	0.44
Primary Air Flow (scfm)		31.6	41.6	69.4	56.7	30.0	65.8	56.6	53.0
Secondary Air Flow (scfm)		200.8	208.9	165.8	188.0	169.5	187.8	183.6	172.0
Primary Air Temp. (°F)		715	717	732	728	705	739	725	719
Secondary Air Temp. (°F)		860	845	844	845	843	848	837	831
Rich Zone Pressure (psig)		76.7	72.6	68.8	71.9	71.4	62.8	69.5	72.6
Lean Zone Pressure (psig)		75.0	70.8	66.7	69.7	69.1	60.6	67.4	70.5
Spray Quench Zone Pressure (psig)		63.8	57.5	53.3	56.6	60.5	46.0	56.1	62.5
Rich Zone Resid. Time (ms)		258	223	158	187	250	164	196	228
Lean Zone Resid. Time (ms)		107	100	101	103	115	93	107	124
Rich Zone Exit Temp. (°F)		1,994	2,073	2,284	2,222	1,970	2,258	2,172	1,941
Lean Zone Exit Temp. (°F)		1,927	1,871	1,857	1,823	1,894	1,780	1,758	1,583
Dep. Probes: 1 Gas Temp. (°F)		1,920	1,862	1,845	1,819	1,897	1,780	1,760	1,596
Dep. Probes: 2 Gas Temp. (°F)		1,811	1,763	1,725	1,710	1,780	1,627	1,622	1,480
Dep. Probes: 1 Met. Temp. (°F)		1,807	1,729	1,711	1,680	1,764	1,680	1,667	1,526
Dep. Probes: 2 Met. Temp. (°F)		1,714	1,666	1,624	1,611	1,673	1,539	1,527	1,386
SO ₂ -A {Lean} (ppm)		265	269	261	243	278	294	293	266
SO ₂ -B {Rich} (ppm)		*	*	*	*	*	*	*	*
NO _x (ppm) 164		118	180	104	132	159	126	87.6	244
CO ₂ (mol%) 9.13		8.47	8.51	7.94	8.43	7.75	7.57	6.34	8.54
CO (ppm) 44.1		43.7	65.8	72.1	81.8	111	156	185	62.5
O ₂ -A {Lean} (mol%)		13.3	13.0	12.7	13.2	12.6	13.3	13.6	14.7
O ₂ -B {Rich} (mol%)		*	*	*	*	*	*	*	*
NO _x @ 15% O ₂ (ppm)		127	88.9	130	79.8	94.0	123	102	83.6
Rich Zone Combustion Efficiency (%)		72.7	ND	64.0	ND	73.6	67.4	ND	ND
Lean Zone Combustion Efficiency (%)		99.9	ND	99.9	ND	99.8	99.7	ND	ND
Rich Zone Carbon Burnout (%)		95.5	ND	98.2	ND	95.2	95.9	ND	ND
Lean Zone Carbon Burnout (%)		95.6	ND	96.3	ND	95.0	97.0	ND	ND

* Plugging of the rich zone gas sampling probe.

TABLE 12

VARIOUS OPERATING CONDITIONS ACHIEVED IN GAS TURBINE SIMULATOR COMBUSTION
TEST 32 USING OTISCA TAGGART SEAM BITUMINOUS COAL/WATER FUEL

Run Number	32-1	32-2	32-3	32-4	32-5	32-6	32-7	32-8	32-9
Compressor Configuration		2/2	2/2	2/2	2/2	2/2	2/2	2/2	2/2
Atomizer Type		DEL 2.5	DEL 2.5	DEL 2.5	DEL 2.5	DEL 2.5	DEL 2.5	DEL 2.5	DEL 2.5
Fuel Flow Rate (lb/hr)		85.5	85.0	84.9	85.5	86.3	99.7	100.1	100.1
Atom. Air Flow Rate (lb/hr)		97.9	88.0	91.8	96.2	84.0	95.1	94.1	98.2
Atom. Air/Fuel Ratio		1.14	1.03	1.08	1.12	0.97	0.95	0.94	0.98
Atomizer Pressure Ratio		4.65	4.39	4.28	4.51	5.99	4.8P	4.09	4.06
Rich Zone Equivalence Ratio		1.09	1.23	1.21	1.13	1.25	1.09	1.38	1.43
Lean Zone Equivalence Ratio		0.39	0.39	0.39	0.39	0.45	0.49	0.50	0.49
Primary Air Flow (scfm)		66.2	57.1	57.7	63.3	58.0	55.6	63.7	59.5
Secondary Air Flow (scfm)		165.5	174.6	174.4	169.3	143.7	130.7	146.4	154.3
Primary Air Temp. (°F)		575	580	610	630	664	770	757	754
Secondary Air Temp. (°F)		657	669	705	724	764	853	860	866
Rich Zone Pressure (psig)		63.4	68.1	70.4	65.5	45.9	58.9	73.1	74.1
Lean Zone Pressure (psig)		61.3	66.2	68.5	63.5	43.9	57.1	71.2	72.3
Spray Quench Zone Pressure (psig)		52.3	57.8	61.1	56.0	32.3	48.0	65.0	65.3
Rich Zone Resid. Time (ms)		92	131	121	96	79	72	116	167
Lean Zone Resid. Time (ms)		84	88	93	88	69	85	102	99
Rich Zone Exit Temp. (°F)		2,113	1,630	1,842	2,137	2,087	2,186	1,826	1,196
Lean Zone Exit Temp. (°F)		1,886	1,928	1,851	1,796	2,031	1,864	1,870	1,996
Dep. Probes: 1 Gas Temp. (°F)		1,880	1,928	1,860	1,787	2,015	1,867	1,870	2,005
Dep. Probes: 2 Gas Temp. (°F)		1,614	1,680	1,614	1,545	1,753	1,585	1,594	1,714
Dep. Probes: 1 Met. Temp. (°F)		1,812	1,840	1,795	1,804	1,905	1,711	1,809	1,916
Dep. Probes: 2 Met. Temp. (°F)		1,578	1,628	1,551	1,513	1,698	1,572	1,579	1,678
SO ₂ -A (Lean) (ppm)		263	217	243	255	266	305	321	331
SO ₂ -B (Rich) (ppm)		*	*	*	*	*	*	*	*
NO _x (ppm) 164		195	134	151	211.0	257	189	223	215
CO ₂ (mol%) 5.70		5.03	4.50	4.58	7.21	5.57	5.44	5.69	5.74
CO (ppm) 113		111	178	136	109	144	110	101	89.1
O ₂ -A (Lean) (mol%)		13.1	13.6	13.6	13.5	12.0	13.4	13.4	13.2
O ₂ -B (Rich) (mol%)		*	*	*	*	*	*	*	*
NO _x @ 15% O ₂ (ppm)		124	158	108	120	140	202	149	171
Rich Zone Combustion Efficiency (%)		65.3	70.8	70.4	ND	ND	ND	ND	ND
Lean Zone Combustion Efficiency (%)		99.6	99.8	99.5	ND	ND	ND	ND	ND
Rich Zone Carbon Burnout (%)		89.6	99.0	95.5	ND	ND	ND	ND	ND
Lean Zone Carbon Burnout (%)		88.0	85.3	87.5	ND	ND	ND	ND	ND

* Plugging of the rich-zone gas sampling probe.

TABLE 13

OPERATING CONDITIONS FROM GAS TURBINE SIMULATOR COMBUSTION TEST 34 USING
OTISCA BITUMINOUS COAL/WATER FUEL

Run Number	34-1	34-2	34-3	34-4	34-5
Combusitor Configuration	2/2	2/2	2/2	2/2	2/2
Atomizer	DEL 2.5	DEL 2.5	DEL 2.5	DEL 2.5	DEL 2.5
Fuel Flowrate (lb/hr)	81.2	81.0	80.7	80.6	79.4
Atom. Air Flowrate (lb/hr)	180.9	181.9	130.1	130.7	130.9
Atom. Air/Fuel Ratio	2.23	2.24	1.61	1.62	1.65
Atomizer Pressure Ratio	1.88	1.91	1.50	1.51	1.68
Rich Zone Equivalence Ratio	0.87	0.89	1.35	1.10	1.19
Lean Zone Equivalence Ratio	0.33	0.33	0.38	0.37	0.37
Primary Air Flow (scfm)	37.5	32.1	31.9	30.2	30.7
Secondary Air Flow (scfm)	180.3	180.6	181.8	173.4	172.0
Primary Air Temp (°F)	684	674	680	663	680
Secondary Air Temp (°F)	855	852	851	831	838
Rich Zone Pressure (psig)	70.2	69.8	70.2	71.3	61.8
Lean Zone Pressure (psig)	68.4	68.0	68.3	69.3	60.0
Spray Quench Zone Pres (psig)	60.4	60.5	61.0	63.0	51.5
Rich Zone Resid. Time (ms)	71.7	78.1	121.8	114.5	103.8
Lean Zone Resid. Time (ms)	80.1	80.6	90.9	88.4	86.1
Rich Zone Exit Temp (°F)	2395	2256	2096	1936	2093
Lean Zone Exit Temp (°F)	1899	1890	1901	1928	1820
Dep. Probes 1 Gas Temp (°F)	1887	1879	1887	1917	1812
Dep. Probes 2 Gas Temp (°F)	1769	1773	1707	1731	1635
Dep. Probes 1 Met. Temp (°F)	1757	1735	1738	1741	1635
Dep. Probes 2 Met. Temp (°F)	1644	1634	1591	1603	1513
SO ₂ -A {Lean} Zone (ppm)	47.6	31.9	76.5	39.9	69.1
SO ₂ -B {Rich} Zone (ppm)	446.5	525.6	370.1	305.2	556.6
NO _x (ppm)	135.9	128.4	181.5	188.5	158.8
CO ₂ (mol%)	8.77	8.85	9.00	9.67	7.95
CO (ppm)	250.8	260.7	397.0	360.5	472.3
O ₂ -A {Lean} Zone (mol%)	14.0	13.6	13.3	12.5	14.8
O ₂ -B {Lean} Zone (mol%)	0.00	0.00	0.00	0.00	0.00
NO _x @ 15% O ₂ (ppm)	117.3	104.2	141.8	134.0	155.4
Rich Zone Combustion Efficiency (%)	96.5	55.1	70.3	67.0	61.1
Lean Zone Combustion Efficiency (%)	99.3	99.2	95.1	95.1	98.9
Rich Zone Carbon Burnout (%)	90.4	84.5	68.6	ND	ND
Lean Zone Carbon Burnout (%)	99.3	97.5	88.7	85.7	90.8

ND Not Determined

TABLE 14

OPERATING CONDITIONS FROM GAS TURBINE SIMULATOR COMBUSTION TESTS 35 AND 36
USING A BEULAH-ZAP LIGNITE COAL/WATER FUEL

Run Number	35-1	35-2	35-3	35-4	35-5	35-6	36-1
Combustor Configuration	2/2	2/2	2/2	2/2	2/2	2/2	2/2
Atomizer	DEL 2.5	DEL 2.5	DEL 2.5	DEL 2.5	DEL 2.5	DEL 2.5	DEL 1.0
Fuel Flowrate (lb/hr)	102.7	101.9	101.0	101.0	101.3	101.3	135.5
Atom. Air Flowrate (lb/hr)	140.4	141.1	129.7	101.80	101.3	101.1	116.2
Atom. Air/Fuel Ratio	1.37	1.38	1.28	1.01	1.00	1.00	0.86
Atomizer Pressure Ratio	1.46	1.47	1.39	1.19	1.24	1.22	2.42
Rich Zone Equivalence Ratio	1.03	1.15	1.25	1.00	1.28	1.15	1.15
Lean Zone Equivalence Ratio	0.32	0.32	0.34	0.33	0.34	0.33	0.41
Primary Air Flow (scfm)	45.3	35.5	33.6	55.3	36.0	44.4	53.3
Secondary Air Flow (scfm)	192.7	202.4	191.7	176.7	193.0	191.3	191.6
Primary Air Temp (°F)	689	672	659	686	671	675	705
Secondary Air Temp (°F)	815	809	801	797	799	798	821
Rich Zone Pressure (psig)	71.5	71.5	71.9	73.4	66.4	70.1	55.1
Lean Zone Pressure (psig)	69.9	69.8	70.0	71.4	64.1	67.8	54.2
Spray Quench Zone Pres (psig)	59.8	60.1	61.8	61.6	51.8	54.6	36.3
Rich Zone Resid. Time (ms)	108.9	126.4	137.5	109.9	133.1	124.9	64
Lean Zone Resid. Time (ms)	80.2	80.1	84.1	86.1	79.9	82.1	60
Rich Zone Exit Temp (°F)	2030	1877	1785	2035	1795	1878	2180
Lean Zone Exit Temp (°F)	1969	1973	2009	1997	1985	1978	1993
Dep. Probes 1 Gas Temp (°F)	1951	1956	1994	1984	1980	1968	1975
Dep. Probes 2 Gas Temp (°F)	1747	1754	1773	1781	1791	1777	1752
Dep. Probes 1 Met. Temp (°F)	1733	1733	1756	1737	1729	1719	1812
Dep. Probes 2 Met. Temp (°F)	1602	1611	1632	1635	1636	1620	1617
SO ₂ -A {Lean} Zone (ppm)	55.6	51.5	64.4	67.8	72.5	75.9	172.6
SO ₂ -B {Rich} Zone (ppm)	141.1	13.0	26.4	25.1	160.1	461.3	99.0
NO _x (ppm)	135.2	147.7	163.4	154.9	302.3	166.4	214.7
CO ₂ (mol%)	9.31	9.28	9.65	9.34	14.92	8.95	9.6
CO (ppm)	71.6	76.4	87.1	93.4	1142.0	157.5	771.6
O ₂ -A {Lean} Zone (mol%)	12.7	12.7	12.2	12.3	12.7	12.8	11.6
O ₂ -B {Rich} Zone (mol%)	0.00	0.00	0.00	0.00	0.00	0.00	0.0
NO _x @ 15% O ₂ (ppm)	98.0	107.4	112.3	107.4	219.3	122.8	136.6
Rich Zone Combustion Efficiency (%)	68.10	69.4	70.7	67.0	70.5	95.4	95.2
Lean Zone Combustion Efficiency (%)	96.50	97.6	98.5	98.9	91.7	98.5	98.5

TABLE 15

OPERATING CONDITIONS FROM GAS TURBINE COMBUSTION TEST 37 USING OTISCA
BITUMINOUS COAL/WATER FUEL

RUN NUMBER	37-1	37-2	37-3	37-4	37-5	37-6
Combusitor Config. (rich/lean)	2/2	2/2	2/2	2/2	2/2	2/2
Atomizer	DEL 1.0	DEL 1.0	DEL 1.0	DEL 1.0	DEL 1.0	DEL 1.0
Fuel Flowrate (lb/hr)	91.5	98.1	98.1	97.7	98.4	98.61
Atom. Air Flowrate (lb/hr)	148.5	147.0	146.9	147.7	132.3	101.1
Atom Air/Fuel Ratio	1.62	1.50	1.50	1.51	1.34	1.03
Atomizer Pressure Ratio	2.92	2.78	2.70	2.72	2.59	2.17
Rich Zone Equivalence Ratio	1.54	1.61	1.61	1.57	1.65	1.39
Lean Zone Equivalence Ratio	0.38	0.42	0.43	0.40	0.41	0.37
Primary Air Flow (scfm)	41.8	43.6	44.0	45.4	45.4	65.3
Secondary Air Flow (scfm)	223.1	207.5	206.2	220.2	219.3	234.6
Primary Air Temp (°F)	738	645	691	695	694	707
Secondary Air Temp (°F)	887	778	830	838	836	824
Rich Zone Pressure (psig)	60.8	64.6	67.3	67.2	66.9	64.61
Lean Zone Pressure (psig)	59.2	63.1	65.6	65.7	65.8	64.01
Spray Quench Zone Pres (psig)	47.2	49.7	49.5	46.7	45.3	36.2
Rich Zone Resid. Time (ms)	92	96	100	97	100	81
Lean Zone Resid. Time (ms)	67	72	73	71	71	66
Rich Zone Exit Temp (°F)	2,398	2,296	2,281	2,317	2,291	2495
Lean Zone Exit Temp (°F)	1,989	2,036	2,079	2,038	2,057	1924
Dep. Probes 1 Gas Temp (°F)	1,947	1,946	2,004	1,962	1,978	1858
Dep. Probes 2 Gas Temp (°F)	1,816	1,855	1,883	1,861	1,879	1759.5
Dep. Probes 1 Met. Temp (°F)	1,807	1,781	1,861	1,755	1,763	1678.5
Dep. Probes 2 Met. Temp (°F)	1,677	1,711	1,729	1,690	1,709	1616.5
SO ₂ -A {Lean} (ppm)	55.6	54.7	85.7	80.5	104.8	46.8
SO ₂ -B {Rich} (ppm)	27.9	2.8	15.9	31.7	30.5	236.1
NO _x (ppm)	143.3	149.0	156.5	151.3	169.4	126.2
CO ₂ (mol%)	7.5	7.2	8.1	7.8	7.8	7.08
CO (ppm)	162.0	665.0	79.0	207.0	245.0	2095.0
O ₂ -A {Lean} (mol%)	13.1	12.6	12.4	12.9	12.7	13.7
O ₂ -B {Rich} (mol%)	3.1	8.5	0.0	0.0	0.1	0.33
NO _x @ 15% O ₂ (ppm)	109.3	106.6	108.8	111.5	122.2	103.2
Rich Zone Combustion Efficiency (%)	69.6	71.1	ND	ND	ND	90.5
Lean Zone Combustion Efficiency (%)	99.3	98.2	ND	ND	ND	93.3
Lean Zone Carbon Burnout	74.9	55.2	ND	ND	ND	44.5
Lean Zone Carbon Burnout	99.5	99.5	ND	ND	ND	92.4

ND Not Determined

TABLE 16

OPERATING CONDITIONS FROM GAS TURBINE COMBUSTION TEST 38 AND 39
USING KEMMERER SUBBITUMINOUS COAL/WATER FUEL

Run Number	38-1	38-2	38-3	38-4	39-1
Combusitor Config. (rich/lean)	2/2	2/2	2/2	2/2	2/2
Atomizer	DEL 1.0	DEL 1.0	DEL 1.0	DEL 1.0	DEL 1.0
Fuel Flowrate (lb/hr)	121.8	129.5	99.4	99.7	125.3
Atom. Air Flowrate (lb/hr)	173.7	126.2	152.5	101.6	183.9
Atom Air/Fuel Ratio	1.43	0.97	1.53	1.02	1.47
Atomizer Pressure Ratio	3.21	2.30	2.84	1.77	3.61
Rich Zone Equivalence Ratio	1.53	1.90	1.43	1.39	1.57
Lean Zone Equivalence Ratio	0.51	0.45	0.43	0.40	0.53
Primary Air Flow (scfm)	42.0	40.3	36.4	49.4	40.0
Secondary Air Flow (scfm)	157.0	213.6	156.5	171.1	153.3
Primary Air Temp (°F)	676	665	671	716	386.2
Secondary Air Temp (°F)	801	777	802	835	447.9
Rich Zone Pressure (psig)	68.5	69.5	61.9	71.9	60.91
Lean Zone Pressure (psig)	66.8	64.8	59.6	69.2	59.21
Spray Quen Zone Pres (psig)	57.2	49.9	45.2	50.6	39.71
Rich Zone Resid. Time (ms)	96	108	103	113	88.41
Lean Zone Resid. Time (ms)	88	75	86	92	81.0
Rich Zone Exit Temp (°F)	2,232	2,139	2,252	2,252	2160
Lean Zone Exit Temp (°F)	2,003	1,922	1,983	1,934	1956
Dep. Probes 1 Gas Temp (°F)	1,903	1,848	1,917	1,853	1973
Dep. Probes 2 Gas Temp (°F)	1,898	1,861	1,813	1,774	1910
Dep. Probes 1 Met. Temp (°F)	1,640	1,5220	1,588	1,476	1764
Dep. Probes 2 Met. Temp (°F)	1,539	1,546	1,399	1,556	1370
SO ₂ -A {Lean} (ppm)	109.5	110.2	105.2	70.3	141.2
SO ₂ -B {Rich} (ppm)	1.6	1.5	0.0	0.7	20.4
NO _x (ppm)	250.3	261.3	269.9	206.8	362.7
CO ₂ (mol%)	8.7	8.1	8.4	7.9	11.3
CO (ppm)	43.6	69.1	69.9	61.3	49.8
O ₂ -A {Lean} (mol%)	11.1	12.5	12.6	12.6	8.8
O ₂ -B {Rich} (mol%)	0.0	13.3	0.0	0.0	0.0
NO _x @ 15% O ₂ (ppm)	152.0	185.3	193.2	147.0	178.6
Rich Zone Combustion Efficiency (%)	84.0	77.1	80.8	76.5	80.6
Lean Zone Combustion Efficiency (%)	99.9	99.8	99.8	99.8	99.9

TABLE 17

OPERATING CONDITIONS FROM GAS TURBINE COMBUSTION TESTS 40 AND 42
USING KEMMERER SUBBITUMINOUS AND OTISCA BITUMINOUS COAL/WATER FUEL

Run Number	40-1	40-2	40-3	40-4	42
Coal	Kemmerer	Kemmerer	Kemmerer	Kemmerer	Otisca
Atomizer	DEL 1.0	DEL 1.0	DEL 1.0	DEL 1.0	DEL 1.0
Combustor Configuration					
(Sections in rich/lean zones)	2/2	2/2	2/2	2/2	4/3
Fuel Flowrate (lb/hr)	119,3119.2	117.6	116.2	126.4	
Atom. Air Flowrate (lb/hr)	112,590.7	88.4	87.7	140.9	
Atom. Air/Fuel Ratio	0.940.76	0.75	0.75	1.11	
Atomizer Pressure Ratio	3.423.20	3.17	3.37	3.95	
Rich Zone Equivalence Ratio	1.081.34	1.51	1.60	2.73	
Lean Zone Equivalence Ratio	0.370.42	0.43	0.42	0.52	
Primary Air Flow (scfm)	63,366.6	56.7	51.8	27.5	
Secondary Air Flow (scfm)	203,4187.0	186.0	193.6	239.2	
Primary Air Temp (°F)	710 723	729	386	686	
Secondary Air Temp (°F)	803 811	829	424	749	
Rich Zone Pressure (psig)	73,574.1	75.2	75.6	71.0	
Lean Zone Pressure (psig)	71,771.3	65.5	61.9	68.8	
Spray Quench Zone Pres (psig)	62,563.5	53.8	46.6	55.7	
Rich Zone Resid. Time (ms)	78 94	110	144	218	
Lean Zone Resid. Time (ms)	75 82	79	81	88	
Rich Zone Exit Temp (°F)	23932325	2160	1655	2639	
Lean Zone Exit Temp (°F)	19011963	1953	1781	1991	
Sct1 Dep. Probe Gas Temp (°F)	18511899	1905	1734	1901	
Sct2 Dep. Probe Gas Temp (°F)	17271796	1821	1626	1829	
Sct1 Dep. Probe Metal Temp (°F)	17161658	1768	1568	1801	
Sct2 Dep. Probe Metal Temp (°F)	15801657	1719	1515	1683	
SC ₂ -A {Lean} (ppm)	109 124	122	91	220	
SC ₂ -B {Rich} (ppm)	28,919.4	16.3	3.0	462.9	
N ₂ x (ppm)	137 178	305	315	173	
CO ₂ (mol%)	7.8 8.2	8.0	7.6	8.5	
CO (ppm)	55,144.0	45.2	786	61.1	
O ₂ -A {Lean} Zone (mol%)	14.0	13.6	13.3	12.5	14.8
O ₂ -B {Lean} Zone (mol%)	0.00	0.00	0.00	0.00	0.00
NO _x @ 15% O ₂ (ppm)	117.3	104.2	141.8	134.0	155.4
Rich Zone Combustion Efficiency (%)	96.5	55.1	70.3	67.0	61.1
Lean Zone Combustion Efficiency (%)	99.3	99.2	95.1	95.1	98.9
Rich Zone Carbon Burnout (%)	90.4	84.5	68.6	ND	ND
Lean Zone Carbon Burnout (%)	99.3	97.5	88.7	85.7	90.8

ND Not Determined

Figure 11. Effect of Atomizing Air-to-Fuel Ratio on Measured Combustion Efficiency for Various Fuels in the Gas Turbine Simulator.

Figure 12 shows the effects of combustion air staging on NO_x emissions from both the LRC fuels and the Otisca bituminous fuel combustion tests. The NO_x emissions decreased from 130 ppm to 90 ppm at 15% O_2 for the long residence time bituminous tests while the short residence time bituminous tests showed a decrease from approximately 200 ppm to 130 ppm (at 15% O_2). The higher NO_x emissions from the shorter residence time combustion tests is consistent with results reported by Rosfjord (9) and has been attributed to the reduced time available for the nitrogen compounds (i.e., NO_x , NH_3 , HCN , etc.) to form N_2 . The better atomization achieved from the new atomizing tip for the Otisca run also reduced the NO_x emissions probably by reducing the quantity of unburned carbon particles (which would still contain organically bound nitrogen) leaving the rich combustion zone. With more of the fuel bound nitrogen liberated into the gas phase more of the nitrogen compounds can be converted to nitrogen. The Kemmerer and Beulah-Zap fuels gave NO_x emissions slightly less than the short residence time Otisca fuel despite possessing higher nitrogen contents.

Tables 18, 19, and 20 compare fly ash samples collected from the cyclone pot located after the control valve used to backpressure the turbine simulator. These analyses also highlight the superior burnout experienced by the LRC fuels compared to bituminous fuel even under a longer residence time profile for the bituminous fuel. While the LRC fuels are experiencing better burnout than the bituminous fuels, it is possible that differences in slurry

Figure 12. Effects of Air Staging on NO_x Emissions for Various Fuels Tested in the Gas Turbine Simulator.

TABLE 18

COMPARISON OF BEULAH-ZAP AND OTISCA COMBUSTION TEST FLY ASHES

Fuel Type	Beulah-Zap Lignite	Beulah-Zap Bituminous	Otisca Bituminous	Otisca
Turbine Test No.	27	28	31	32
Avg. Residence Time (ms)	180	311	312	205
Proximate Analysis (MF)				
Moisture	N/A	N/A	N/A	N/A
Volatile Matter	11.17	11.39	5.32	3.60
Fixed Carbon (Ind)	8.90	0.00	84.58	88.45
Ash	79.93	88.61	10.10	7.95
Ultimate Analysis (MF)				
Hydrogen	0.00	0.34	0.30	0.18
Carbon	14.01	6.92	85.93	89.42
Nitrogen	0.25	0.28	1.04	0.99
Sulfur	0.30	0.08	0.53	0.58
Oxygen (Ind)	5.50	3.77	2.08	0.86
Ash	79.93	88.61	10.10	7.95
Carbon Burnout (%)	99.1	99.6	90.3	87.4
Fly Ash Particle Size				
Mean (micron)	9.4	5.1	13.2	22.3
Top (99%<) (micron)	49.6	23.0	184.2	233.0

TABLE 19
COMPARISON OF BEULAH-ZAP AND OTISCA COMBUSTION TEST FLY ASHES

Fuel Type	Otisca Bitum.	Beulah-Zap Lignite	Beulah-Zap Lignite	Otisca Bitum.
Turbine Test No.	34	35	36	37
Avg. Residence Time (ms)	183	205	124	162
Proximate Analysis (MF)				
Moisture	N/A	N/A	N/A	N/A
Volatile Matter	4.56	8.16	8.66	7.13
Fixed Carbon (Ind)	86.80	0.00	0.56	56.84
Ash	8.64	91.84	90.78	36.03
Ultimate Analysis (MF)				
Hydrogen	0.22	0.08	0.21	0.45
Carbon	88.04	7.84	7.97	58.95
Nitrogen	1.16	0.18	0.13	0.81
Sulfur	0.75	0.35	0.25	1.19
Oxygen (Ind)	1.17	-0.29	0.64	2.55
Ash	8.64	91.84	90.78	36.03
Carbon Burnout (%)	88.5	99.7	99.7	98.1
Fly Ash Particle Size				
Mean (micron)	9.5	5.8	4.7	7.6
Top (99%<) (micron)	45.2	28.5	15.9	32.6

TABLE 20
COMPARISON OF OTISCA AND KEMMERER COMBUSTION TEST FLY ASHES

Fuel Type	Kemmerer Subbit.	Kemmerer Subbit.	Kemmerer Subbit.	Otisca Bitum.
Turbine Test No.	38	39	40	42
Avg. Residence Time (ms)	190	169	186	306
Proximate Analysis (MF)				
Moisture	N/A	N/A	N/A	N/A
Volatile Matter	1.74	2.08	3.14	5.06
Fixed Carbon (Ind)	0.14	0.81	1.13	70.35
Ash	98.12	97.11	95.73	24.59
Ultimate Analysis (MF)				
Hydrogen	0.01	0.03	0.02	0.18
Carbon	1.50	2.48	3.20	72.36
Nitrogen	0.03	0.08	0.12	0.94
Sulfur	0.34	0.30	0.25	0.72
Oxygen (Ind)	0.00	0.00	0.66	1.19
Ash	98.12	97.11	95.73	24.59
Carbon Burnout (%)	99.9	99.9	99.9	96.7
Fly Ash Particle Size				
Mean (micron)	9.3	6.2	4.5	8.7
Top (99%<) (micron)	27.6	46.9	21.6	40.8

rheology (and therefore in atomization) might account for some of the difference in the observed burnout rather than differences in fuel reactivity. Future work will attempt to clarify these differences. The LRC fly ash shows a decrease in particle size as compared to the starting fuel while the bituminous fuel showed an increase in particle size compared to the starting fuel. This particle size analysis provides some evidence of the non-agglomerating properties of low-rank coal compared to bituminous fuels.

Test 36 was the first shakedown test to use a new, higher shear Delavan Swirl Air nozzle that should atomize the CWF better. This atomizer supplied better atomization and carbon burnout (see combustion tests 37 and 42) at the expense of needing a higher pressure ratio across the atomizer. The new atomizer did not appreciably affect the carbon burnout of the LRC fuels, possibly due to their higher reactivities and non-agglomerating properties.

4.3.2.2 Parametric Testing Runs 43 Through 47

After the shakedown testing phase was completed, the turbine simulator combustion system was modified by adding a knife-gate valve to the bottom of the cyclone located after the back-pressure control valve. This change enabled the fly ash to be collected after each test period instead of at the end of a run that consisted of several test periods. Tables 27 through 31 show the particle size, percent ash, and carbon burnout for the cyclone ash at the individual test conditions used for the parametric testing.

Tables 26 through 30 show the average operating conditions obtained at each test condition during the parametric combustion tests on the gas turbine simulator. Tables 26 through 30 again indicate that the LRC fuels are experiencing much higher burnout than the bituminous fuel. Figure 13 shows some typical operating conditions from a short residence time combustion test (test 46-47) using 20-micron Kemmerer subbituminous fuel. Not all of the desired test conditions in these tests were achievable. In test 45, a stable flame could not be maintained at the low atomizing air-to-fuel ratio and low combustion air temperature set points (tests 45-10, 45-11, 45-14, 45-15). Test condition 47-13 also was not obtained due to an unstable flame resulting

TABLE 21

COMPARISON OF CYCLONE FLY ASHES FOR COMBUSTION TEST 43 USING OTISCA BITUMINOUS COAL/WATER FUEL

Test No.	Particle Size (μm)		Percent Ash	Carbon Burnout (%)
	Mean	Top (99%<)		
43-1	7.3	27.5	8.88	91.4
43-2	7.9	26.6	31.89	98.2
43-3	8.8	45.5	18.84	96.4
43-4	11.1	55.3	11.82	93.8
43-5	10.0	73.7	6.43	87.8
43-6	11.3	140.0	6.42	87.8
43-7	7.1	22.1	13.05	94.4
43-8	8.8	64.4	8.08	90.5

TABLE 22

COMPARISON OF CYCLONE FLY ASHES FOR COMBUSTION TEST 44 USING OTISCA
BITUMINOUS COAL/WATER FUEL

Test No	Particle Size (μm)		Percent Ash	Carbon Burnout (%)
	Mean	Top (99%<)		
44-1	8.8	46.6	23.27	97.2
44-2	10.0	43.2	9.55	91.9
44-3	11.7	73.9	13.08	94.1
44-4	14.4	65.1	7.58	89.8
44-5	11.5	31.7	9.34	91.9
44-6	22.5	148.8	9.69	92.0
44-7	10.2	108.3	8.57	91.1
44-8	16.7	102.9	16.71	95.8
44-9	7.0	26.3	10.95	93.2
44-10	9.1	74.5	4.19	80.9
44-11	11.0	72.2	3.36	75.9
44-12	12.8	123.7	3.65	77.9
44-13	15.1	110.8	5.07	84.3
44-14	22.3	154.7	9.21	91.7
44-15	12.7	101.2	7.94	90.3
44-16	18.5	104.0	10.12	92.5

TABLE 23

COMPARISON OF CYCLONE FLY ASHES FOR COMBUSTION TEST 45 USING 10-MICRON
PARTICLE SIZE KEMMERER SUBBITUMINOUS COAL/WATER FUEL

Test No.	Particle Size (μm)		Percent Ash	Carbon Burnout (%)
	Mean	Top (99%<)		
45-1	6.9	48.7	ND	ND
45-2	5.6	54.5	90.57	99.76
45-3	5.6	33.5	91.86	99.79
45-4	7.8	75.7	83.36	99.54
45-5	9.0	131.9	18.85	89.95
45-6	8.4	89.9	30.36	94.65
45-7	14.6	84.4	96.71	99.92
45-8	6.9	65.8	95.78	99.90
45-9	8.3	49.8	20.51	90.95
45-12	7.1	65.9	74.31	99.20
45-13	11.5	104.0	80.21	99.43
45-16	9.8	114.2	22.48	91.53

ND Not Determined

TABLE 24

COMPARISON OF CYCLONE FLY ASHES FOR COMBUSTION TEST 46 USING 20-MICRON
PARTICLE SIZE KEMMERER SUBBITUMINOUS COAL/WATER FUEL

Test No.	Particle Size (μm)		Percent Ash	Carbon Burnout (%)
	Mean	Top (99%<)		
46-1	7.9	86.8	91.43	99.78
46-2	6.7	60.0	69.48	98.97
46-3a	8.8	110.8	80.85	99.45
46-3b	9.9	89.9	86.29	99.62
46-4	6.1	65.1	92.03	99.80
46-5	8.6	115.3	83.57	99.55
46-6	10.7	116.8	72.99	99.13
46-7	24.5	148.8	94.40	99.86
46-8	15.9	118.9	96.81	99.93
46-9a	5.3	55.7	96.24	99.91
46-9b	4.9	24.9	78.87	99.37
46-10a	6.1	45.2	60.40	98.47
46-10b	4.3	19.6	70.99	99.05
46-11	5.6	38.3	78.16	99.35
46-12	6.3	56.1	86.13	99.63
46-13	7.5	104.0	86.38	99.63
46-14	5.3	60.0	94.03	99.85
46-15	6.3	61.4	97.46	99.94
46-16	6.4	72.2	99.33	99.98

TABLE 25

COMPARISON OF CYCLONE FLY ASHES FOR COMBUSTION TEST 47 USING BEULAH-ZAP
LIGNITE COAL/WATER FUEL

Test No.	Particle Size (μm)		Percent Ash	Carbon Burnout (%)
	Mean	Top (99%<)		
47-1	8.8	66.9	99.90	99.99
47-2	6.0	37.1	80.06	99.35
47-3	7.5	55.7	98.84	99.97
47-4	9.1	75.7	85.16	99.55
47-5	8.4	57.7	64.49	98.56
47-6	6.1	59.5	89.67	99.70
47-7	6.8	49.8	53.54	97.72
47-8	7.9	49.8	99.26	99.98
47-9	7.3	49.8	87.66	99.63
47-10	7.8	45.2	64.33	98.55
47-11a	4.9	30.9	96.45	99.90
47-11b	8.0	51.1	60.24	98.27
47-12	7.2	37.1	47.39	97.08
47-14	8.1	45.2	47.83	97.14
47-16	10.3	69.0	91.27	99.75

TABLE 26

AVERAGE OPERATING CONDITIONS FROM LONG RESIDENCE TIME COMBUSTION TEST 43
USING OTISCA TAGGART SEAM BITUMINOUS COAL/WATER FUEL

Parameter	Test 1	Test 2	Test 3	Test 4	Test 5	Test 6	Test 7	Test 8
Fuel Flow Rate (lb/hr)	121.7	122.1	80.5	86.2	82.6	82.5	126.1	128.1
Atomizing Air Flow Rate (lb/hr)	99.6	163.8	95.0	69.3	65.4	102.1	157.6	91.1
Atom Air/Fuel Ratio	0.82	1.34	1.18	0.80	0.79	1.23	1.24	0.71
Atomizer Pressure Ratio	3.95	5.77	4.18	2.93	4.12	3.65	5.65	4.74
Rich Zone Equivalence Ratio	1.53	1.39	1.46	1.26	0.99	1.46	1.36	2.01
Lean Zone Equivalence Ratio	0.53	0.40	0.36	0.39	0.43	0.47	0.47	0.58
Primary Air Flow Rate (scfm)	91.6	69.2	44.5	65.4	83.5	45.0	75.5	55.7
Secondary Air Flow Rate (scfm)	261.9	252.9	193.7	174.8	127.6	136.3	202.4	181.7
Primary Air Temperature (°F)	699	657	698	758	566	379	376	275
Secondary Air Temperature (°F)	788	750	816	856	643	433	417	416
Rich Zone Pressure (psig)	70.8	72.0	70.2	71.9	61.4	71.2	66.6	66.1
Lean Zone Pressure (psig)	69.2	70.0	68.3	69.5	59.3	70	64	64.3
Spray Zone Pressure (psig)	57.0	59.1	61.9	62.7	53.5	65.3	53.2	58.5
Rich Zone Residence Time (ms)	110	169	273	216	190	274	123	189
Lean Zone Residence Time (ms)	31	33	49	47	57	71	36	59
Rich Zone Exit Temperature (°F)	2190	1859	1758	1958	1650	1717	2168	1870
Lean Zone Exit Temperature (°F)	1786	1977	1774	1814	1498	1517	1893	1234
Dep. Probes 1 Gas Temp (°F)	1786	1958	1752	1797	1498	1511	1884	1221
Dep. Probes 2 Gas Temp (°F)	1660	1860	1598	1578	1297	1289	1727	1047
Dep. Probes 1 Metal Temp (°F)	1668	1722	1510	1581	1313	1346	1757	1118
Dep. Probes 2 Metal Temp (°F)	1537	1708	1394	1471	1195	1196	1635	979
SO ₂ -A {lean} (ppm)	164.8	206.7	169.3	188.5	153.3	166.5	252.1	135.2
SO ₂ -B {rich} (ppm)	513	49.9	0.81	58.28	0	0	18.12	189.1
NO _x (ppm)	141.2	154.9	113.6	162.8	103.2	95.53	148	85.91
CO ₂ (mol%)	7.00	8.38	7.39	7.50	5.69	7.18	9.13	5.00
CO (ppm)	487	108.7	327.8	200.7	2035	1227	152	1578
O ₂ -A {lean} (mol%)	13.77	12.38	13.93	13.4	14.45	13.15	11.16	15.8
O ₂ -B {rich} (mol%)	5.68	2.12	0	0	1.54	1.06	1.07	3.02
NO _x @ 15% O ₂	117	107	96	128	94	73	90	99
Rich Zone Comb Efficiency (%)	79.9	55.6	71.2	91.9	89.8	87.1	80.1	77.0
Lean Zone Comb Efficiency (%)	98.8	99.3	97.0	99.5	97.3	96.5	98.0	98.2
Rich Zone Carbon Burnout (%)	76.6	86.1	78.4	82.44	82.4	89.9	91.3	91.0
Lean Zone Carbon Burnout (%)	91.4	98.2	96.4	93.8	87.8	87.8	94.4	90.5
Cyclone Ash Carbon Burnout	91.4	98.2	96.4	93.8	87.8	87.8	94.4	90.5

TABLE 27

AVERAGE OPERATING CONDITIONS FROM SHORT RESIDENCE TIME COMBUSTION TEST 44 USING OTISCA TAGGART SEAM BITUMINOUS COAL/WATER FUEL

RUN TURB44 TEST SUMMARY

Parameter	Test 1	Test 2	Test 3	Test 4	Test 5	Test 6	Test 7	Test 8	Test 9
Fuel Flow Rate (lb/hr)	128.4	132.7	91.0	94.6	88.0	91.2	129.5	124.2	128.4
Atomizing Air Flow Rate (lb/hr)	154.5	101.1	115.3	75.0	111.6	73.2	101.1	159.4	167.2
Atom Air/Fuel Ratio	1.20	0.76	1.27	0.79	1.27	0.80	0.78	1.28	1.30
Atomizer Pressure Ratio	5.65	4.33	3.27	1.72	1.80	1.38	2.05	2.66	2.73
Rich Zone Equivalence Ratio	2.45	3.65	1.36	1.38	3.30	1.22	1.20	1.41	1.43
Lean Zone Equivalence Ratio	0.44	0.47	0.36	0.39	0.39	0.38	0.30	0.34	0.34
Primary Air Flow Rate (scfm)	27.7	20.4	52.0	62.4	7.2	70.0	101.8	66.8	67.1
Secondary Air Flow Rate (scfm)	274.6	278.2	207.9	195.0	222.6	184.8	358.5	313.2	321.5
Primary Air Temperature (°F)	678	666	715	739	720	731	668	615	368
Secondary Air Temperature (°F)	738	734	816	823	806	811	735	709	406
Rich Zone Pressure (psig)	68.9	70.0	69.2	77.2	168	162.4	164.8	155.8	164
Lean Zone Pressure (psig)	65.9	66.2	67.2	75.1	170.5	159.9	159.2	150.2	161.7
Spray Zone Pressure (psig)	48.9	52.9	59.6	68.11	167.2	156.4	140.2	110.5	155.5
Rich Zone Residence Time (ms)	89	117	94	100	322	203	133	157	164
Lean Zone Residence Time (ms)	55	56	48	54	124	109	65	67	74
Rich Zone Exit Temperature (°F)	2757	2467	2566	2579	2838	2284	2487	2323	2267
Lean Zone Exit Temperature (°F)	1904	1961	1983	1972	1869	1918	1692	1957	1722
Dep. Probes 1 Gas Temp (°F)	1887	1939	1976	1967	1861	1924	1700	1951	1725
Dep. Probes 2 Gas Temp (°F)	1788	1795	1770	1687	1674	1667	1613	1860	1679
Dep. Probes 1 Metal Temp (°F)	1797	1815	1771	1770	1610	1729	1598	1728	1567
Dep. Probes 2 Metal Temp (°F)	1697	1707	1641	1604	1546	1573	1507	1711	1541
SO ₂ -A {lean} (ppm)	109	142	195.4	126.3	209.5	180.3	121.5	174.5	109.8
SO ₂ -B {rich} (ppm)1	449.6	471.2	184.2	11.76	102.4	21.1	23.48	22.74	30.72
NO _x (ppm)	136.3	130.5	98.0	110	130.3	64.1	64.12	154.1	91.59
CO ₂ (mol%)	7.323	7.349	7.831	7.345	6.945	7.312	5.909	7.836	7.233
CO (ppm)	122	536.3	72.59	307.9	52.36	80.3	910.4	81.54	2368
O ₂ -A {lean} (mol%)	13.27	13.15	12.75	11.96	12.2	12.64	14.95	11.37	13.12
O ₂ -B {rich} (mol%)	0.952	0.273	0	1.359	9.257	20.93	20.97	21.01	0
NO _x @ 15% O ₂	105	99	71	84	75	93	63	96	69
Rich Zone Comb Efficiency (%)	88.4	85.7	71.7	96.3	97.9	77.9	70.0	ND	51.0
Lean Zone Comb Efficiency (%)	95.8	97.8	99.1	98.8	99.9	99.7	97.6	99.8	80.3
Rich Zone Carbon Burnout (%)	80.6	75.2	90.5	86.0	89.3	54.1	72.0	59.0	72.0
Lean Zone Carbon Burnout (%)	96.3	95.4	98.8	96.6	97.8	92.2	90.7	99.7	84.5
Cyclone Ash Carbon Burnout (%)	97.2	91.9	94.1	89.8	91.9	92.0	91.1	95.8	93.2

ND Not Determined

TABLE 27 (continued)

AVERAGE OPERATING CONDITIONS FROM SHORT RESIDENCE TIME COMBUSTION TEST 44
USING OTISCA TAGGART SEAM BITUMINOUS COAL/WATER FUEL

Parameter	Test 10	Test 11	Test 12	Test 13	Test 14	Test 15	Test 16
Fuel Flow Rate (lb/hr)	127.3	84.5	94.0	85.3	94.6	132	135.8
Atomizing Air Flow Rate (lb/hr)	86.9	101.2	79.5	114.3	79.2	102.8	164.2
Atom Air/Fuel Ratio	0.68	1.20	0.84	1.34	0.84	0.78	1.21
Atomizer Pressure Ratio	2.42	4.12	1.95	5.62	2.94	4.25	6.40
Rich Zone Equivalence Ratio	1.42	1.30	1.32	1.26	1.53	1.45	1.49
Lean Zone Equivalence Ratio	0.46	0.49	0.54	0.41	0.49	0.38	0.40
Primary Air Flow Rate (scfm)	83.5	52.6	64.7	53.5	53.8	81.8	69.8
Secondary Air Flow Rate (scfm)	215.5	121	115.3	160.4	149.5	287.6	281.7
Primary Air Temperature (°F)	397	417	455	444	458	410	375
Secondary Air Temperature (°F)	433	456	489	495	501	450	414
Rich Zone Pressure (psig)	150.3	108.7	116.6	69.0	68	77	71.8
Lean Zone Pressure (psig)	149	107.2	115.2	66.8	66.1	74.0	67.6
Spray Zone Pressure (psig)	144.2	104.6	112.8	61.2	60.2	61.1	55.1
Rich Zone Residence Time (ms)	147	154	169	149	114	96	220
Lean Zone Residence Time (ms)	92	108	116	60	60	40	38
Rich Zone Exit Temperature (°F)	2362	2393	2038	1472	2108	2898	490
Lean Zone Exit Temperature (°F)	1600	1726	1610	1741	1950	1710	1623
Dep. Probes 1 Gas Temp (°F)	1639	1777	1650	1745	1988	1717	1632
Dep. Probes 2 Gas Temp (°F)	1569	1636	1396	1519	1696	1593	1630
Dep. Probes 1 Metal Temp (°F)	1643	1690	1507	1599	1857	1603	1550
Dep. Probes 2 Metal Temp (°F)	1478	1501	1269	1402	1599	1473	1510
SO ₂ -A {lean} (ppm)	22.61	62.79	61.5	166.9	143.8	105.4	120.3
SO ₂ -B {rich} (ppm)	1.36	1.744	2.713	1.163	0	0.428	1.809
NO _x (ppm)	121	167.3	158.3	239.7	353.8	225.6	210.6
CO ₂ (mol%)	6.92	7.52	6.96	7.47	9.01	6.91	6.47
CO (ppm)	1899	1326	471.3	540.7	330.3	1766	3659
O ₂ -A {lean} (mol%)	13.49	13.14	14.69	12.83	12.55	12.68	12.59
O ₂ -B {rich} (mol%)	5.36	5.42	20.77	12.9	10.4	20.82	20.81
NO _x @ 15% O ₂	96	127	150	176	251	162	150
Rich Zone Comb Efficiency (%)	72.7	96.4	97.2	78.4	49.9	70.3	70.7
Lean Zone Comb Efficiency (%)	94.7	93.9	98.7	98.5	99.5	97.0	92.5
Rich Zone Carbon Burnout (%)	82.9	79.7	90.1	91.0	80.8	59.0	56.3
Lean Zone Carbon Burnout (%)	93.1	75.9	84.8	87.5	96.9	87.6	81.0
Cyclone Ash Carbon Burnout (%)	80.9	75.9	77.9	84.3	91.7	90.3	92.5

TABLE 28

AVERAGE OPERATING CONDITIONS FROM SHORT RESIDENCE TIME COMBUSTION TEST 45
USING 10-MICRON KEMMERER SUBBITUMINOUS COAL/WATER FUEL

RUN TURB45 TEST SUMMARY

Parameter	Test 1	Test 2	Test 3	Test 4	Test 5	Test 6
Fuel Flow Rate (lb/hr)	149.7	163.5	110.3	114.5	112.1	101.3
Atomizing Air Flow Rate (lb/hr)	205.1	142.9	142.8	88.6	93.7	133.7
Atom Air/Fuel Ratio	1.37	0.87	1.29	0.77	0.84	1.32
Atomizer Pressure Ratio	5.14	3.83	3.37	2.81	1.81	2.30
Rich Zone Equivalence Ratio	1.32	1.42	1.35	1.51	1.71	1.24
Lean Zone Equivalence Ratio	0.31	0.35	0.32	0.34	0.34	0.24
Primary Air Flow Rate (scfm)	76	90.8	55.8	60.7	49.1	57.9
Secondary Air Flow Rate (scfm)	392	369	274	270	271	361
Primary Air Temperature (°F)	653	608	601	649	658	643
Secondary Air Temperature (°F)	732	670	685	736	759	734
Rich Zone Pressure (psig)	87.9	100.6	87.3	77.8	137.4	158.9
Lean Zone Pressure (psig)	75.5	76.8	51.8	55.2	125.4	141.7
Spray Zone Pressure (psig)	59.7	59.8	39.2	40.7	118.3	131.8
Rich Zone Residence Time (ms)	84	95	120	126	275	210
Lean Zone Residence Time (ms)	30	31	31	33	69	63
Rich Zone Exit Temperature (°F)	2168	2061	2081	1813	1420	2071
Lean Zone Exit Temperature (°F)	1886	1987	1904	1961	1883	1701
Dep. Probes 1 Gas Temp (°F)	1891	1977	1910	1986	1924	1728
Dep. Probes 2 Gas Temp (°F)	1850	1905	1831	1869	1844	1700
Dep. Probes 1 Metal Temp (°F)	138	132	130	124	119	123
Dep. Probes 2 Metal Temp (°F)	1720	1756	1663	1719	1685	1545
SO ₂ -A {lean} (ppm)	97.31	114.5	109	108.7	23.94	60.38
SO ₂ -B {rich} (ppm)	1.48	0.543	0	1.163	0	0
NO _x (ppm)	274.4	253.8	302.9	298.6	216.9	198.3
CO ₂ (mol%)	7.297	7.335	7.468	7.757	7.527	6.049
CO (ppm)	67.32	64.13	80.06	311.5	1387	379.6
O ₂ -A {lean} (mol%)	13.24	13.75	12.59	11.96	12.29	14.39
O ₂ -B {rich} (mol%)	0	0.664	0	0	2.538	3.766
NO _x @ 15% O ₂	212	210	216	198	149	180
Rich Zone Comb Efficiency (%)	69.3	83.7	75.1	77.4	78.2	81.1
Lean Zone Comb Efficiency (%)	99.4	99.2	98.8	97.6	97.7	82.2
Rich Zone Carbon Burnout (%)	87.1	93.7	88.3	77.2	62.0	77.3
Lean Zone Carbon Burnout (%)	98.1	98.4	98.3	95.6	96.4	95.2
Cyclone Ash Carbon Burnout (%)	ND	99.76	99.79	99.54	89.95	94.65

ND Not Determined

TABLE 28 (continued)

AVERAGE OPERATING CONDITIONS FROM SHORT RESIDENCE TIME COMBUSTION TEST 45
USING 10-MICRON KEMMERER SUBBITUMINOUS COAL/WATER FUEL

Parameter	Test 7	Test 8	Test 9	Test 12	Test 13	Test 14
Fuel Flow Rate (lb/hr)	158.9	143.2	160.4	147.5	118.3	112.2
Atomizing Air Flow Rate (lb/hr)	125.3	191.6	204.2	197.3	140.2	141
Atom Air/Fuel Ratio	0.79	1.34	1.27	1.34	1.18	1.26
Atomizer Pressure Ratio	2.08	3.04	5.40	2.95	2.32	4.23
Rich Zone Equivalence Ratio	1.83	1.13	1.25	1.44	0.89	1.31
Lean Zone Equivalence Ratio	0.36	0.29	0.48	0.39	0.35	0.39
Primary Air Flow Rate (scfm)	64.7	92.2	71.1	65	108	59.4
Secondary Air Flow Rate (scfm)	371	379	180	287	206	211
Primary Air Temperature (°F)	615	604	423	388	443	441
Secondary Air Temperature (°F)	693	672	458	430	483	491
Rich Zone Pressure (psig)	169.8	159.8	72.4	147	128.6	64.3
Lean Zone Pressure (psig)	150.5	146.3	64.0	137.9	121.3	51.2
Spray Zone Pressure (psig)	119.9	102.3	36.3	127.5	116.4	38.2
Rich Zone Residence Time (ms)	198	130	74	164	121	94
Lean Zone Residence Time (ms)	59	56	19	65	79	37
Rich Zone Exit Temperature (°F)	1873	2269	1567	1850	1841	1970
Lean Zone Exit Temperature (°F)	1899	1698	1638	1763	1234	1761
Dep. Probes 1 Gas Temp (°F)	1971	1764	1645	1998	1207	1632
Dep. Probes 2 Gas Temp (°F)	1961	1775	1941	1959	1223	1885
Dep. Probes 1 Metal Temp (°F)	119	126	5795	101	99	95
Dep. Probes 2 Metal Temp (°F)	1798	1635	5718	1800	1127	1690
SO ₂ -A {lean} (ppm)	67.83	69.46	304.7	87.91	63.96	109.1
SO ₂ -B {rich} (ppm)	0	0	20.17	1.628	0	0
NO _x (ppm)	286.9	154.8	348.6	243	136.8	377
CO ₂ (mol%)	7.06	6.22	10.2	8.89	6.12	10.2
CO (ppm)	910.5	258.5	53.95	2759	4370	2543
O ₂ -A {lean} (mol%)	11.94	13.79	10.8	10.72	14.85	10.15
O ₂ -B {rich} (mol%)	8.57	0.03	1.04	0	7.17	0.81
NO _x @ 15% O ₂	190	128	205	141	133	208
Rich Zone Comb Efficiency (%)	79.4	73.4	75.7	62.5	ND	59.0
Lean Zone Comb Efficiency (%)	96.3	98.9	97.4	90.7	ND	94.8
Rich Zone Carbon Burnout (%)	77.2	97.1	89.7	80.0	ND	83.6
Lean Zone Carbon Burnout (%)	98.2	98.5	92.9	95.8	ND	97.6
Cyclone Ash Carbon Burnout (%)	99.92	99.9	90.5	99.2	99.43	91.53

ND - Not determined plugged sampling line

Test 10, 11, 14, 15 could not sustain a stable flame

TABLE 29

AVERAGE OPERATING CONDITIONS FROM SHORT RESIDENCE TIME COMBUSTION TEST 46
USING 20-MICRON KEMMERER SUBBITUMINOUS COAL/WATER FUEL

Parameter	Test 9b	Test 10	Test 11	Test 12	Test 13	Test 14	Test 15	Test 16
Fuel Flow Rate (lb/hr)	144.0	161.8	113.9	119.9	111.5	107.7	154	142.5
Atomizing Air Flow Rate (lb/hr)	204.0	130.5	137	105.9	105.3	138.1	128.1	202.3
Atom Air/Fuel Ratio	1.41	0.81	1.20	0.88	0.94	1.28	0.83	1.42
Atomizer Pressure Ratio	6.46	4.07	5.54	3.78	2.67	3.00	2.50	3.36
Rich Zone Equivalence Ratio	1.40	1.51	1.41	1.60	1.58	1.38	1.46	1.45
Lean Zone Equivalence Ratio	0.37	0.40	0.40	0.43	0.40	0.34	0.43	0.41
Primary Air Flow Rate (scfm)	62.0	82.1	54.2	54.5	50.1	51.3	81	58.2
Secondary Air Flow Rate (scfm)	293	300.4	208.3	206.8	210	237.7	259.8	257.8
Primary Air Temperature (°F)	402	410	400	2345	428	447	432	415
Secondary Air Temperature (°F)	451	454	450	473	483	511	478	470
Rich Zone Pressure (psig)	72.7	7.9	74.4	79.8	147	139.7	127.8	147.9
Lean Zone Pressure (psig)	58	63.9	68.9	68.7	141.1	134.2	120.9	139.4
Spray Zone Pressure (psig)		54.9	64.3	64	138.9	131.3	116.2	136.4
Rich Zone Residence Time (ms)	61	61	85	94	175	151	97	118
Lean Zone Residence Time (ms)	14	14	21	21	39	35	26	31
Rich Zone Exit Temperature (°F)	219	2180	2007	1964	1917	2041	2143	2080
Lean Zone Exit Temperature (°F)	173	1819	1874	1908	1913	1753	1977	1919
Dep. Probes 1 Gas Temp (°F)	272	1798	2123	1903	1793	1851	1939	1852
Dep. Probes 2 Gas Temp (°F)	1224	1260	1223	1263	1238	1202	1289	1285
Dep. Probes 1 Metal Temp (°F)	630	679	761	752	697	604	754	718
Dep. Probes 2 Metal Temp (°F)	1323	1377	1441	1498	1446	1400	1580	1557
SO ₂ -A {lean} (ppm)	99.3	104.3	158.7	175.3	162.8	17.98	43.03	2.03
SO ₂ -B {rich} (ppm)	11.0	7.631	17.76	23.17	23.94	18.65	15.7	16.28
NO _x (ppm)	302	262.3	339.1	299.1	306.1	157.5	245.4	169.7
CO ₂ (mol%)	8.44	9.12	8.86	9.18	8.98	7.55	9.74	0.06
CO (ppm)	956.0	445.3	83.85	35.15	410.7	769.8	10.18	586.2
O ₂ -A {lean} (mol%)	12.5	11.57	11.68	10.42	10.67	11.1	11.35	11.19
O ₂ -B {rich} (mol%)	0.83	0.62	0.05	0	0	0	1.027	0
NO _x @ 15% O ₂	214	166	218	169	177	95	152	103
Rich Zone Comb Efficiency (%)	77.6	69.3	73.1	75.5	66.8	65.1	78.8	74.1
Lean Zone Comb Efficiency (%)	96.1	93.8	98.8	97.5	99.4	98.8	99.7	98.5
Rich Zone Carbon Burnout (%)	79.7	71.1	79.8	82.6	83.2	81.0	78.5	81.4
Lean Zone Carbon Burnout (%)	95.3	93.9	97.6	98.2	99.9	99.5	99.3	99.3
Cyclone Ash Carbon Burnout (%)	99.37	98.47	99.05	99.35	99.63	99.85	99.94	99.98

TABLE 30

AVERAGE OPERATING CONDITIONS FROM SHORT RESIDENCE TIME COMBUSTION TEST 47 USING 15-MICRON BEULAH-ZAP LIGNITE COAL/WATER FUEL

RUN TURB47 TEST SUMMARY

Parameter	Test 1	Test 2	Test 3	Test 4	Test 5	Test 6	Test 7	Test 8	Test 9
Fuel Flow Rate (lb/hr)	156.2	160.5	117.8	120.8	119.1	117.6	158.6	161	160.4
Atomizing Air Flow Rate (lb/hr)	199.5	126.9	148.3	102	101.1	146.7	1255	203.7	204.2
Atom Air/Fuel Ratio	1.28	0.79	1.26	0.84	0.85	1.25	0.79	1.26	1.27
Atomizer Pressure Ratio	7.59	5.56	6.62	3.13	1.89	3.59	3.81	3.87	5.40
Rich Zone Equivalence Ratio	1.10	1.42	1.33	1.44	1.39	1.36	1.29	1.36	1.25
Lean Zone Equivalence Ratio	0.39	0.42	0.40	0.44	0.39	0.34	0.43	0.43	0.48
Primary Air Flow Rate (scfm)	83.5	73.3	47.3	52.8	54.8	45.8	82.3	62.7	71.1
Secondary Air Flow Rate (scfm)	224.8	233.9	179.1	167.9	195.8	231.8	218.5	221.7	180.7
Primary Air Temperature (°F)	715	696	690	731	745	713	713	717	423
Secondary Air Temperature (°F)	773	758	765	798	816	803	780	800	458
Rich Zone Pressure (psig)	66.2	76.7	66.5	75.7	138.3	136.2	152.3	144.1	72.4
Lean Zone Pressure (psig)	55.41	64.11	56.1	67.1	131.3	128	144.8	136	64.0
Spray Zone Pressure (psig)	45.2	52.3	46.8	51.7	125	124.1	137.9	125.5	36.3
Rich Zone Residence Time (ms)	63	90	96	150	251	231	174	150	74
Lean Zone Residence Time (ms)	14	16	19	23	38	34	33	31	19
Rich Zone Exit Temperature (°F)	1633	1444	1611	1058	1058	1165	1257	1454	1567
Lean Zone Exit Temperature (°F)	1831	1891	1808	1905	1857	1729	2005	1889	1638
Dep. Probes 1 Gas Temp (°F)	1764	1806	1710	1814	1708	1597	1813	1715	1645
Dep. Probes 2 Gas Temp (°F)	1958	2016	1891	1956	1876	1820	2087	2095	1941
Dep. Probes 1 Metal Temp (°F)	5881	5880	5792	5887	5838	5727	5849	5714	5795
Dep. Probes 2 Metal Temp (°F)	5787	5804	5739	5741	5713	5685	5788	5804	5718
SO ₂ -A {lean} (ppm)	216.2	209.4	205.6	252.3	342.4	439.9	227.3	192.8	304.7
SO ₂ -B {rich} (ppm)	24.42	24.42	24.85	93.8	36.9	22.23	20.8	1.28	20.17
NO _x (ppm)	324.3	428	369.3	372.3	311.7	250.6	297.4	280.9	348.6
CO ₂ (mol%)	13.27	14.34	13.42	14.31	13.42	10.07	12.21	9.857	10.22
CO (ppm)	109	90.74	104.5	597.7	680.3	444.5	169.9	48.57	53.95
O ₂ -A {lean} (mol%)	11.05	8.38	9.08	7.90	8.31	11.7	6.34	10.33	10.8
O ₂ -B {rich} (mol%)	0.97	0	0	0	0	0.12	0	0.22	1.04
NO _x @ 15% O ₂	195	203	18985	170	147	161	121	157	205
Rich Zone Comb Efficiency (%)	71.9	74.6	75.6	87.4	79.5	80.9	75.2	67.6	75.7
Lean Zone Comb Efficiency (%)	99.9	99.9	99.5	97.4	95.2	99.2	99.1	99.7	97.4
Rich Zone Carbon Burnout (%)	97.3	90.5	96.1	94.4	86.9	95.8	88.8	91.9	89.7
Lean Zone Carbon Burnout (%)	100	99.8	99.4	96.4	92.8	98.4	94.4	98.9	92.9
Cyclone Ash Carbon Burnout (%)	99.997	99.35	99.97	99.55	98.56	99.7	97.72	99.98	99.63

TABLE 30 (continued)

AVERAGE OPERATING CONDITIONS FROM SHORT RESIDENCE TIME COMBUSTION TEST 47 USING 15-MICRON BEULAH-ZAP LIGNITE COAL/WATER FUEL

FUN TURB47 TEST SUMMARY (continued)

Parameter	Test 10a	Test 10b	Test 11a	Test 11b	Test 12	Test 14a	Test 14b	Test 16
Fuel Flow Rate (lb/hr)	145.4	157.4	122.1	120.9	124.7	116.3	118.7	162.1
Atomizing Air Flow Rate (lb/hr)	114.4	120.6	148.3	145.6	104	148.8	147	203.1
Atom Air/Fuel Ratio	0.79	0.77	1.21	1.20	0.83	1.28	1.24	1.25
Atomizer Pressure Ratio	8.64	8.54	6.24	4.10	2.64	3.48	2.30	2.85
Rich Zone Equivalence Ratio	1.16	1.22	1.36	1.27	1.46	1.28	1.48	1.44
Lean Zone Equivalence Ratio	0.38	0.42	0.41	0.45	0.44	0.46	0.42	0.45
Primary Air Flow Rate (scfm)	87.4	88.6	48.3	53.9	53.7	49.5	40.3	57.1
Secondary Air Flow Rate (scfm)	226.9	213.5	185.7	154.3	172.5	141	179.3	218.4
Primary Air Temperature (°F)	434	398	412	428	435	445	409	403
Secondary Air Temperature (°F)	474	419	464	464	473	500	454	441
Rich Zone Pressure (psig)	72.4	66.7	71.6	69.0	77.4	146.2	156	146.2
Lean Zone Pressure (psig)	58.8	58.3	6.8	60.1	65.5	137.5	142.2	137.6
Spray Zone Pressure (psig)	51.6	36.1	52.2	20.9	21.9	135.3	131.4	122
Rich Zone Residence Time (ms)	64	79	89	106	142	165	277	157
Lean Zone Residence Time (ms)	16	16	19	23	23	46	46	34
Rich Zone Exit Temperature (°F)	1987	1325	1858	1370	1132	1892	1143	1455
Lean Zone Exit Temperature (°F)	1699	1597	1864	1598	1597	1977	1527	1651
Dep. Probes 1 Gas Temp (°F)	1603	1453	1683	1489	1482	1780	1530	1640
Dep. Probes 2 Gas Temp (°F)	1712	1767	1755	1699	1878	1827	1813	1879
Dep. Probes 1 Metal Temp (°F)	5674	5730	5754	5716	5686	5756	5654	5784
Dep. Probes 2 Metal Temp (°F)	5685	5633	5665	5651	5633	5703	5615	5694
SO ₂ -A {lean} (ppm)	257.2	268.6	310.7	286.4	303.5	314	239.8	255.2
SO ₂ -B {rich} (ppm)	60.24	2.71	77.67	83.44	62.79	62.21	14.8	18.67
NO _x (ppm)	208.5	250.8	241.6	292.6	191.8	297.4	215.6	215.9
SO ₂ (mol%)	8.32	9.31	9.63	9.44	8.61	10.87	8.42	9.32
CO (ppm)	1211	350.7	1094	135.7	2327	78.27	1787	528.2
O ₂ -A {lean} (mol%)	12.15	10.89	10.48	10.24	10.76	8.559	11	11.86
O ₂ -B {rich} (mol%)	1.12	2.20	0.001	0.39	0	0.014	0.22	0.075
NO _x @ 15% O ₂	141	148	137	163	112	143	129	141
Rich Zone Comb Efficiency (%)	69.1	65.7	74.7	81.4	83.0	65.5	74.2	79.8
Lean Zone Comb Efficiency (%)	96.8	98.6	97.7	99.5	95.0	99.8	96.8	98.4
Rich Zone Carbon Burnout (%)	77.7	82.2	83.0	95.7	66.2	72.9	84.2	85.6
Lean Zone Carbon Burnout (%)	97.8	97.9	97.3	98.7	94.5	99.3	96.8	96.2
Cyclone Ash Cyclone Burnout (%)	98.55	ND	99.9	98.27	97.08	ND	97.14	99.75

ND Not Determined

Tests 13 & 15 could not sustain a stable flame.

Figure 13. Typical Operating Conditions from a Short Residence Time Combustion Test (46-7) Using 20-Micron Kemmerer Subbituminous Coal/Water Fuel.

from the low combustion air temperature and poor atomization from a low atomizer pressure ratio due to the low atomizing air-to-fuel ratio and high combustor pressure.

Figures 14 and 15 plot the particulate sample carbon burnout against atomizing air-to-fuel ratio and combustion air temperature, respectively. Figures 16 and 17 show the cyclone ash carbon burnout as functions of atomizing air-to-fuel ratio and combustion air temperature. The wider spread in the data for the Otisca fuel indicates that the bituminous fuel appeared to be more sensitive to the atomizing air-to-fuel ratio and combustion air temperature.

Table 31 shows GC analyses of selected gas samples taken from the rich combustion zone of the turbine simulator. As expected, the gases major combustible constituents are CO and H₂ with traces of methane, ethane, ethylene and propylene also being present. In general, no clear trend was observed with the molar ratios of the product gas as a function of the rich zone equivalence ratio. This unexpected result is probably due to some of the secondary flowing back into the rich combustion zone. This results in an actual equivalence ratio lower than that calculated from the fuel and air flow rates. The calculated heat content of the combustion gases ranged from approximately 20 up to 40 Btu/scf of product gas.

The gas analysis from the 10-micron Kemmerer fuel test (45-3) indicates some of the secondary air was probably being pulled into the rich combustion

Figure 14. Plot of Carbon Burnout Against Atomizing Air-to-Fuel Ratio for Parametric Combustion Tests 43-47.

Figure 15. Graph of Carbon Burnout as a Function of Combustion Air Temperature for Parametric Combustion Tests 43-47.

Figure 16. Plot of Cyclone Ash Carbon Burnout Against Atomizing Air-to-Fuel Ratio for Parametric Tests 43-47.

Figure 17. Graph of Cyclone Ash Carbon Burnout as a Function of Combustion Air Temperature for Parametric Tests 43-47.

TABLE 31
NORMALIZED GAS CHROMATOGRAPH ANALYSES OF RICH ZONE GAS SAMPLES
FROM SIMILAR TEST CONDITIONS

Test No.	43-3	44-3	45-3	46-3	47-3
Eq. Ratio	1.47	1.36	1.35	1.36	1.33
H ₂	5.59	1.23	3.26	5.96	3.71
CO ₂	13.58	16.51	11.54	15.34	16.19
C ₂ H _n	2.8e-3	0.00	4.3e-3	0.019	7.0e-3
C ₃ H _n	6.7e-3	0.00	0.026	0.046	0.041
O ₂	0.98	0.98	6.51	0.96	0.99
N ₂	72.61	74.75	72.80	71.33	73.02
CH ₄	0.19	0.00	0.29	0.34	0.22
CO	7.03	6.53	5.57	6.00	5.83
Total	100.00	100.00	100.00	100.00	100.00
Calculated Heat. Val (Btu/scf)	40.0	24.4	30.2	40.2	32.0

zone. Also, the higher O₂ levels detected by the on-line oxygen analyzer and the higher combustion temperatures in the rich zone indicates that more oxygen was present in the rich zone than the equivalence ratio indicates. The equivalence ratio calculated for the rich zone should have resulted in significantly higher CO, H₂ and CO₂ emissions.

4.3.2.3 Statistical Analysis of Parametric Tests 43 through 47

A statistical analysis of parametric combustion tests 43 through 47 was completed. Since not all test conditions were able to be achieved, one statistical analysis was performed on tests 44 and 46 which were two complete 2⁴ factorial designs.

These analyses were also run on all the successful tests in tests 43 through 47 even though all of these tests were not complete 2⁴ test matrices. The main variables examined were fuel type (X0), atomizing air-to-fuel ratio (X3), combustion air temperature (X7), combustor pressure (X8), and fuel firing rate (X29). The measured responses were lean zone carbon burnout as calculated from the particulate sample, and the cyclone ash carbon burnout. One-way statistical analyses looked at the effects of the main variables on the responses while the two-way analyses looked at the main variables and the interactions between these variables. Two-way analyses provided higher R-squares with the same number of model variables so these analyses are reported here. Two variable interactions are noted by a - symbol between the number of each variable (e.g., X0-7 is the interaction between the fuel type and the combustion air temperature). Input values were coded to provide input numbers that ranged between -1 and 1. Coded variables were calculated using the equation:

$$\text{Coded } X = (X - CP)/(X_h - CP) \quad (2)$$

where X = measured variable
 Xh = highest measured variable
 CP = variable center point = $(X_h + X_l)/2$
 Xl = lowest measured variable

This allows the magnitude of parameter estimate to indicate the relative importance of the statistically significant variables.

Table 32 indicates that fuel type (X0) and the fuel type/combustion air temperature interaction (X0-7) were always statistically significant and the fuel type/fuel firing rate interaction (X0-29) was statistically significant in the cyclone ash carbon burnout. R-squared ranged from about 0.67 for the lean zone ash carbon burnout measurements to approximately 0.81 for the cyclone ash carbon burnout meaning approximately 67 to 81 percent of the data can be predicted using two or three simple parameters. Converting the coded variables back to the original data results in the following models for predicting carbon burnout (CB):

$$\text{Lean Zone CB} = 98.2355 - 25.406 * X_0 + 0.03046 * X_{0-7} \quad (3)$$

$$\text{Cyclone Ash CB} = 99.5833 - 41.7465 * X_0 + 0.02284 * X_{0-7} + 2.104E-5 * X_{0-29} \quad (4)$$

where X0 = fuel type, Otisca = 1, Kemmerer = 0;
 X7 = combustion air temperature, (°F);
 X29 = fuel firing rate, (Btu/hr);
 X0-7 = fuel type/combustion air temp interaction, $X_0 * X_7$;
 X0-29 = fuel type/fuel firing rate interaction $X_0 * X_{29}$;

TABLE 32
 TWO-WAY INTERACTIONS FOR PARAMETRIC TESTS 44 AND 46

Lean Zone Carbon Burnout

Variable	Parameter Estimate	Standard Error	Type II Sum of Squares	F	Prob>F
INTERCEP	98.23555	0.83588	173704.0387	13811.6	0.0001
X0	-6.17146	1.22923	317.0110	25.21	0.0001
X0-7	7.08161	1.28269	383.3407	30.48	0.0001

Model R-Square = 0.6741

Cyclone Ash Carbon Burnout

Variable	Parameter Estimate	Standard Error	Type II Sum of Squares	F	Prob>F
INTERCEP	99.58333	0.71634	178503.12500	19325.4	0.0001
X0	-9.16260	1.06175	687.87585	74.47	0.0001
X0-7	5.30939	1.12268	206.58103	22.37	0.0001
X0-29	4.80100	1.15547	159.46437	17.26	0.0002

Model R-Square = 0.8121

This model indicates that the Kemmerer fuel resulted in a significant increase in the carbon burnout under otherwise comparable operating conditions (especially at lower combustion air temperatures and lower fuel firing rates). It should be remembered that this model is only valid between the ranges studied for the combustion air temperature (400 to 800°F) and fuel firing rate (0.7 to 1.0MM Btu/hr). The carbon burnout for the Kemmerer fuel was not affected by the combustion air temperature and fuel firing rate in these operating ranges while the Otisca bituminous fuel showed some increase in carbon burnout with increasing combustion air temperature or fuel firing rate.

Table 33 displays the important data from a statistical analysis of tests 43 through 47 even though not all test matrices were complete.

Table 33 indicates that the model R-square has dropped approximately 15 to 20% by performing the regression on all of the successful test periods. This drop in R-square is partially due to analyzing incomplete test matrices. The lean zone carbon burnout can be estimated from the variables fuel type (X0), and the fuel type/combustion air temperature interaction (X0-7). The significant variables for the cyclone ash carbon burnout are again fuel type (X0), the fuel type/combustion air temperature interaction (X0-7), and the fuel type/fuel firing rate interaction (X0-29). The models for estimating the carbon burnout (CB) as calculated using uncoded data are as follows:

TABLE 33

TWO-WAY INTERACTIONS FOR PARAMETRIC TESTS 43 THROUGH 47

Lean Zone Carbon Burnout

Variable	Parameter Estimate	Standard Error	Type II Sum of Squares	F	Prob>F
INTERCEP	97.43790	0.54074	408248.26578	32469.3	0.0001
X0	-4.39296	0.90934	293.43283	23.34	0.0001
X0-7	5.26065	1.02112	333.71445	26.54	0.0001

R-Square = 0.4677

Cyclone Ash Carbon Burnout

Variable	Parameter Estimate	Standard Error	Type II Sum of Squares	F	Prob>F
INTERCEP	98.67883	0.49214	418713.05525	40202.5	0.0001
X0	-7.33964	0.84056	794.09003	76.24	0.0001
X0-7	4.64148	0.95814	244.40577	23.47	0.0001
X0-29	3.82021	0.98285	157.34616	15.11	0.0002

R-Square = 0.6783

NOTE: The model was not of full rank. A full rank subset of the model was chosen.

$$\text{Lean Zone CB} = 97.4379 - 18.6816 * X0 + .022626 * X0-7 \quad (5)$$

$$\begin{aligned} \text{Cyclone Ash CB} = 98.6788 - 34.3989 * X0 + \\ 0.01996 * X0-7 + 1.674E-5 * X0-29 \end{aligned} \quad (6)$$

where X0 = fuel type, Otisca = 1, Kemmerer = 0, Beulah-Zap = 0;
 X7 = combustion air temperature, (°F);
 X29 = fuel firing rate, (Btu/hr);
 X0-7 = fuel type/combustion air temp interaction, X0 * X7;
 X0-29 = fuel type/fuel firing rate interaction X0 * X29;

These models again indicate that fuel type has a significant effect on the measured carbon burnout. The LRC fuels have high carbon burnouts, 97.5 to 98.7%, and appear to be relatively unaffected by other operating parameters (i.e., all interactions go to zero), however, the bituminous fuel was significantly affected by combustion air temperature and fuel firing rate. In both models, bituminous fuel carbon burnouts comparable to LRC fuels can be achieved but only under the most optimum conditions.

4.3.3 Ash and Slag Deposit Analysis

As might be expected with the relatively high ash in the Beulah-Zap coal and repeated reports from other coal-fired gas turbine researchers, significant ash deposition and slagging occurred in the turbine simulator. Four samples of combustion ash were collected during each of these slurry combustion tests in the turbine simulator. These samples were comprised of slag taken from the refractory-lined wall in the rich zone; a slag sample taken from the quench zone; a sample of ash taken off the refractory-lined wall of the lean zone, a sample of ash collected in the cyclone after the back pressure control valve, and sometimes a sample was collected off the deposition probes if an adequate sample could be obtained. Tables 34 through 40 show the chemical composition of the coal ash and slag or fly ash samples from the cyclone for the combustion tests completed during the shakedown testing.

Table 34 indicates that the Taggart-seam bituminous coal ash was originally high in Quartz (SiO_3), Alumina (Al_2O_3), and Iron (Fe_2O_3). In general, the collected ash samples from the LRC fuel tests were low in SO_3 indicating its release as SO_2 into the combustion gases. The bituminous fuel ash (especially the cyclone ash) contained significant quantities of SO_3 , primarily due to the large quantity of unburnt carbon still in the fly ash. The composition of the other constituents does not indicate the preferential deposition of any component in a single area of the turbine. The X-ray diffraction mineralogy shown in Table 34 again indicates that the ash's major constituents were not concentrated in a particular area of the turbine simulator.

Figures 18 and 19 are pictures showing deposits that formed in the rich zone and immediately after the quench zone, respectively, for turbine test 34 using the Otisca Bituminous coal/water fuel.

Figures 20 and 21 are pictures showing similar deposits formed in the rich zone and immediately after the quench zone, respectively, for turbine test 35 using the Beulah-Zap lignite coal/water fuel. When compared to the pictures from the bituminous fuel it is obvious deposition and slagging are more of a problem with the low-rank fuels.

Figures 22 and 23 are pictures showing deposits formed in the rich zone and immediately after the quench zone, respectively, for turbine test 37 using the Otisca Bituminous coal/water fuel.

Figures 24 through 27 are pictures showing deposits formed in the rich zone and immediately after the quench zone, respectively, for turbine tests 38 and 40 using the Kemmerer subbituminous coal/water fuel.

These analyses indicate the rich zone ash samples from the combustion test using Otisca and Beulah-Zap fuels were concentrated in alumina oxide, possibly due to contamination from the refractory while combustion tests using Kemmerer fuel showed a small concentration of quartz in the rich and quench zones. The ash samples from the short residence time combustion test (test 35) using the AMAX-cleaned Beulah-Zap lignite slurry indicate a small concentration of quartz in the ash while the iron concentration remains relatively constant. XRD analysis suggests that the residual magnetite from the physical cleaning process remains as magnetite in the reducing atmosphere of the rich zone but is converted to hematite when it reaches the highly oxidizing atmosphere encountered in the lean combustion zone. As indicated by these photographs, the low-rank slurries had significantly larger deposits than the Otisca slurry, primarily due to its high ash content and lower ash fusion temperatures.

TABLE 34
CHEMICAL COMPOSITION OF OTISCA COAL ASH AND SELECTED ASH SAMPLES
FOR COMBUSTION TEST 34

	Wt% SO ₃ Free Otisca	Rich Slag	Depos. Probe	Cyclone Ash
SiO ₂	35.0	40.5	37.3	37.2
Al ₂ O ₃	25.3	40.7	28.7	33.8
Fe ₂ O ₃	18.8	10.1	20.5	17.6
TiO ₃	3.8	2.2	4.2	3.4
P ₂ O ₅	0.4	0.1	0.0	0.4
CaO	11.8	4.2	6.3	4.8
MgO	2.5	1.4	1.7	1.5
Na ₂ O	0.8	0.0	0.0	0.0
K ₂ O	1.6	0.7	1.2	1.3
TOTAL	100.0	99.9	99.9	100.0

X-Ray Diffraction Analysis

Coal Ash: Gypsum/Anhydrite and Quartz (Major)

Rich Zone Slag: Sillimanite and Mullite (Major), Corundum (Minor), Unknown (trace)

Deposition Probe Ash: Albite and Iron Oxide (major)

Cyclone Fly Ash: Hematite (Major), Corundum and Powellite (Minor), Mullite (Trace)

TABLE 35

CHEMICAL COMPOSITION OF BEULAH-ZAP COAL ASH AND SELECTED ASH SAMPLES
FOR COMBUSTION TEST 35

	Wt% SO ₃ Free Beulah- Zap	Rich Slag	Quench Slag	Lean Ash	Depos. Probe	Cyclone Ash
SiO ₂	21.9	28.0	25.5	27.7	16.3	25.2
Al ₂ O ₃	7.5	7.2	6.8	13.0	8.0	6.3
Fe ₂ O ₃	65.7	60.7	63.6	53.1	70.6	64.2
TiO ₂	2.1	2.0	2.1	2.6	2.4	2.0
P ₂ O ₅	0.0	0.0	0.0	0.0	0.0	0.0
CaO	2.1	1.7	1.6	2.8	2.2	1.8
MgO	0.0	0.0	0.0	0.1	0.0	0.0
Na ₂ O	0.0	0.0	0.0	0.0	0.0	0.0
K ₂ O	0.5	0.5	0.4	0.6	0.5	0.4
TOTAL	99.8	100.1	100.0	99.9	100.0	99.9

XRD Analysis

Coal Ash: Magnetite (major), Quartz (minor)

Rich Zone Slag: Magnetite (major), Hematite and Quartz (minor), Noselite (trace)

Quench Zone Slag: Magnetite (major), Hematite (minor), unknown (trace)

Lean Zone Ash: Hematite (major), Quartz (minor), magnetite (trace)

Deposition Probe Ash: Hematite (major), Calcium Aluminum Ortho Silicate (trace)

Cyclone Fly Ash: Hematite (major), Quartz and Magnetite (minor), Noselite (trace)

TABLE 36
CHEMICAL COMPOSITION OF BEULAH-ZAP COAL ASH AND SELECTED ASH SAMPLES
FOR COMBUSTION TEST 36

	Wt% SO ₃ Free Beulah- Zap	Rich Slag	Quench Slag	Lean Ash	Depos. Probe	Cyclone Ash
SiO ₂	40.0	36.6	42.0	35.6	34.8	42.3
Al ₂ O ₃	14.9	18.4	10.1	12.5	10.2	11.8
Fe ₂ O ₃	36.5	39.9	42.5	46.8	49.8	40.4
TiO ₂	3.1	2.0	3.2	2.6	2.8	3.0
P ₂ O ₅	0.0	0.0	0.0	0.0	0.0	0.0
CaO	2.8	2.2	1.8	1.9	2.0	1.8
MgO	0.5	0.3	0.0	0.1	0.0	0.3
Na ₂ O	0.0	0.0	0.0	0.0	0.0	0.0
K ₂ O	0.6	0.4	0.4	0.4	0.4	0.4
TOTAL	100.1	99.8	100.0	99.9	100.0	100.0

TABLE 37
CHEMICAL COMPOSITION OF OTISCA COAL ASH AND SELECTED ASH SAMPLES
FOR COMBUSTION TEST 37

	Wt% SO ₃ Free Beulah- Zap	Rich Slag	Quench Slag	Lean Ash	Depos. Probe	Cyclone Ash
SiO ₂	35.0	22.0	38.3	29.6	30.9	34.5
Al ₂ O ₃	25.3	54.2	27.9	23.5	24.2	27.4
Fe ₂ O ₃	18.8	13.5	20.9	24.4	16.9	22.1
TiO ₂	3.8	1.0	3.7	3.7	4.0	3.9
P ₂ O ₅	0.4	0.0	0.0	0.4	0.2	0.2
CaO	11.8	7.0	6.0	15.9	20.9	9.3
MgO	2.5	2.0	1.5	1.4	1.5	1.4
Na ₂ O	0.8	0.0	0.0	0.0	0.0	0.0
K ₂ O	1.6	0.3	1.8	1.1	1.2	1.5
TOTAL	100.0	100.0	100.1	100.0	99.8	100.3

TABLE 38

CHEMICAL COMPOSITION OF KEMMERER COAL ASH AND SELECTED ASH SAMPLES
FOR COMBUSTION TEST 38

	<u>Wt% SO₃ Free Kremmerer</u>	<u>Rich Slag</u>	<u>Quench Slag</u>	<u>Lean Ash</u>	<u>Depos. Probe</u>	<u>Cyclone Ash</u>
SiO ₂	60.7	74.6	67.6	56.3	56.6	59.6
Al ₂ O ₃	19.8	12.6	16.8	23.6	23.2	21.2
Fe ₂ O ₃	9.0	6.2	7.5	9.1	9.0	8.7
TiO ₂	1.3	0.9	1.1	1.6	1.5	1.4
P ₂ O ₅	0.4	0.2	0.2	0.1	0.2	0.1
CaO	5.8	3.6	4.6	6.2	6.5	6.2
MgO	2.6	1.5	1.9	2.5	2.5	2.3
Na ₂ O	0.0	0.0	0.0	0.0	0.0	0.0
K ₂ O	0.5	0.3	0.3	0.5	0.4	0.4
TOTAL	100.1	99.9	100.0	99.9	99.9	99.9

TABLE 39

CHEMICAL COMPOSITION OF KEMMERER COAL ASH AND SELECTED ASH SAMPLES
FOR COMBUSTION TEST 39

	<u>Wt% SO₃ Free Kemmerer</u>	<u>Rich Slag</u>	<u>Quench Slag</u>	<u>Lean Ash</u>	<u>Depos. Probe</u>	<u>Cyclone Ash</u>
SiO ₂	60.7	74.4	68.6	66.3	ND	60.9
Al ₂ O ₃	19.8	12.3	15.1	17.0	ND	19.8
Fe ₂ O ₃	9.0	7.1	8.5	8.3	ND	9.3
TiO ₂	1.3	0.9	1.1	1.3	ND	1.4
P ₂ O ₅	0.4	0.2	0.2	0.1	ND	0.2
CaO	5.8	3.4	4.3	4.8	ND	5.7
MgO	2.6	1.3	1.9	1.7	ND	2.1
Na ₂ O	0.0	0.0	0.0	0.0	ND	0.0
K ₂ O	0.5	0.3	0.3	0.4	ND	0.4
TOTAL	100.1	99.9	100.0	99.9	ND	99.8

ND Not Determined

TABLE 40

CHEMICAL COMPOSITION OF KEMMERER COAL ASH AND SELECTED ASH SAMPLES
FOR COMBUSTION TEST 40

	<u>Wt% SO₃ Free Kemmerer</u>	<u>Rich Slag</u>	<u>Quench Slag</u>	<u>Lean Ash</u>	<u>Depos. Probe</u>	<u>Cyclone Ash</u>
SiO ₂	60.7	44.2	62.8	59.1	ND	60.7
Al ₂ O ₃	19.8	40.0	18.5	20.9	ND	19.6
Fe ₂ O ₃	9.0	9.3	9.6	9.6	ND	10.1
TiO ₂	1.3	0.8	1.2	1.4	ND	1.4
P ₂ O ₅	0.4	0.0	0.1	0.2	ND	0.1
CaO	5.8	3.9	5.3	6.1	ND	5.6
MgO	2.6	1.6	2.1	2.3	ND	2.1
Na ₂ O	0.0	0.0	0.0	0.0	ND	0.0
K ₂ O	0.5	0.3	0.4	0.5	ND	0.5
TOTAL	100.1	99.8	100.0	100.1	ND	100.1

ND Not Determined

Figure 18. Photograph of Rich Zone Deposits for Combustion Test 34 Using Otisca Bituminous CWF.

Figure 19. Photograph of Quench Zone Deposits for Combustion Test 34 Using Otisca Bituminous CWF.

Figure 20. Photograph of Rich Zone Deposits for Combustion Test 35 Using Beulah-Zap Lignite CWF.

Figure 21. Photograph of Quench Zone Deposits for Combustion Test 35 Using Beulah-Zap Lignite CWF.

Figure 22. Photograph of Rich Zone Deposits for Combustion Test 37 Using Otisca Bituminous CWF.

Figure 23. Photograph of Quench Zone Deposits for Combustion Test 37 Using Otisca Bituminous CWF.

Figure 24. Photograph of Rich Zone Deposits for Combustion Test 38 Using Kemmerer Subbituminous CWF.

Figure 25. Photograph of Quench Zone Deposits for Combustion Test 38 Using Kemmerer Subbituminous CWF.

Figure 26. Photograph of Rich Zone Deposits for Combustion Test 40 Using Kemmerer Subbituminous CWF.

Figure 27. Photograph of Quench Zone Deposits for Combustion Test 40 Using Kemmerer Subbituminous CWF.

Tables 41 through 44 show the chemical composition of the ash samples collected from the parametric test matrices run in tests 44 through 47. The concentration of alumina in the rich zone ash from test 44 is probably due to contamination of the slag with the wall refractory. The composition of the other constituents does not indicate the preferential deposition of any component in a single area of the turbine.

Figures 28 through 35 are photographs of the rich zone looking toward the quench zone and pictures looking at the first deposition probe for turbine tests 44, 45, 46 and 47, respectively. As can be seen, the bituminous fuel test had some deposition around the quench zone but the rich zone was relatively free of slag. The deposition probe from this test was relatively clean of deposits but did show some signs of erosion. The two subbituminous fuel tests (tests 45 and 46) had significant slag deposits in the rich and quench zones and also had some deposits around the first deposition probe. The Beulah-Zap lignite fuel test had very large slag deposits in the rich and quench zones. The deposition probe in this test was not visible due to a deposit completely covering the probe and blocking off half of the flow area around the probe.

In Table 45, the weight of ash in was calculated from the total weight of slurry feed to the turbine at the measured solids loading and ash content. Weights of rich zone slag used to calculate the percentage of ash recovered in that zone were typically contaminated with some refractory, giving inflated percentages of retained ash. Table 45 indicates that the Beulah-Zap lignite fuel had a much higher deposition potential as indicated by high levels of ash

TABLE 41
CHEMICAL COMPOSITION OF OTISCA COAL ASH AND SELECTED ASH SAMPLES
FOR COMBUSTION TEST 44

	Wt% SO ₃ Free Otisca	Rich Slag	Quench Slag	Lean Ash	Depos. Probe	Cyclone Ash
SiO ₂	37.0	17.2	37.0	39.9	40.8	36.8
Al ₂ O ₃	28.8	66.1	29.9	45.2	37.9	33.0
Fe ₂ O ₃	20.1	8.4	21.5	5.8	10.9	19.4
TiO ₂	4.4	1.3	3.9	2.8	2.9	3.7
P ₂ O ₅	0.4	0.0	0.0	0.3	0.3	0.2
CaO	5.7	4.7	5.1	3.3	4.1	4.2
MgO	1.6	2.0	1.3	1.6	1.6	1.3
Na ₂ O	0.0	0.0	0.0	0.0	0.0	0.0
K ₂ O	1.8	0.4	1.3	1.0	1.3	1.4
TOTAL	99.8	100.1	100.0	99.9	99.8	100.0

TABLE 42

CHEMICAL COMPOSITION OF KEMMERER COAL ASH AND SELECTED ASH SAMPLES
FOR COMBUSTION TEST 45

	<u>Wt% SO₃ Free Kemmerer</u>	<u>Rich Slag</u>	<u>Quench Slag</u>	<u>Lean Ash</u>	<u>Depos. Probe</u>	<u>Cyclone Ash</u>
SiO ₂	49.0	57.5	56.3	48.8	48.9	51.4
Al ₂ O ₃	22.0	24.5	18.8	25.9	22.7	22.1
Fe ₂ O ₃	14.5	11.0	15.4	14.0	16.2	15.2
TiO ₂	1.2	0.8	1.2	1.5	1.2	1.2
P ₂ O ₅	0.4	0.0	0.0	0.0	0.0	0.0
CaO	9.1	4.4	6.0	6.9	7.9	7.1
MgO	3.5	1.7	2.0	2.4	3.0	2.8
Na ₂ O	0.0	0.0	0.0	0.0	0.0	0.0
K ₂ O	0.2	0.1	0.2	0.3	0.2	0.2
TOTAL	99.9	100.0	99.9	99.8	100.1	100.0

TABLE 43

CHEMICAL COMPOSITION OF KEMMERER COAL ASH AND SELECTED ASH SAMPLES
FOR COMBUSTION TEST 46

	<u>Wt% SO₃ Free Kemmerer</u>	<u>Rich Slag</u>	<u>Quench Slag</u>	<u>Lean Ash</u>	<u>Depos. Probe</u>	<u>Cyclone Ash</u>
SiO ₂	49.0	57.3	53.5	54.6	47.0	43.7
Al ₂ O ₃	22.0	19.1	20.0	20.1	23.9	24.5
Fe ₂ O ₃	14.5	13.6	15.6	14.0	15.3	18.0
TiO ₂	1.2	1.0	1.1	1.1	1.3	1.3
P ₂ O ₅	0.4	0.0	0.0	0.0	0.0	0.0
CaO	9.1	6.5	7.0	7.3	8.9	9.1
MgO	3.5	2.4	2.5	2.7	3.4	3.3
Na ₂ O	0.0	0.0	0.0	0.0	0.0	0.0
K ₂ O	0.2	0.1	0.2	0.2	0.2	0.2
TOTAL	99.9	100.0	99.9	100.0	100.0	100.1

TABLE 44

CHEMICAL COMPOSITION OF BEULAH-ZAP COAL ASH AND SELECTED ASH SAMPLES
FOR COMBUSTION TEST 47

	Wt% SO ₃ Free Beulah-Zap	Rich Slag	Quench Slag	Lean Ash	Depos. Probe	Cyclone Ash
SiO ₂	25.2	30.9	33.7	29.9	23.9	25.6
Al ₂ O ₃	20.5	24.5	18.5	21.9	20.9	19.0
Fe ₂ O ₃	29.2	29.9	32.3	31.6	33.7	37.5
TiO ₂	1.8	1.4	1.5	1.6	1.6	1.6
P ₂ O ₅	1.5	0.3	0.3	0.3	0.8	0.4
CaO	16.3	11.0	11.1	11.9	14.0	12.8
MgO	4.8	2.1	2.5	2.6	4.2	3.0
Na ₂ O	0.0	0.0	0.0	0.0	0.9	0.0
K ₂ O	0.7	0.1	0.1	0.2	0.0	0.2
TOTAL	100.0	100.2	100.0	100.0	100.0	100.1

Figure 28. Photograph of Rich and Quench Zone Deposits for Combustion Test 44 Using 4.3-Micron Otisca Bituminous CWF.

Figure 29. Photograph of Deposition Probe #1 Deposits for Combustion Test 44 Using 4.3-Micron Otisca Bituminous CWF.

Figure 30. Photograph of Rich and Quench Zone Deposits for Combustion Test 45 Using 10-Micron Kemmerer Subbituminous CWF.

Figure 31. Photograph of Deposition Probe #1 Deposits for Combustion Test 45 Using 10-Micron Kemmerer Subbituminous CWF.

Figure 32. Photograph of Rich and Quench Zone Deposits for Combustion Test 46 Using 20-Micron Kemmerer Subbituminous CWF.

Figure 33. Photograph of Deposition Probe #1 Deposits for Combustion Test 46 Using 20-Micron Kemmerer Subbituminous CWF.

Figure 34. Photograph of Rich and Quench Zone Deposits for Combustion Test 47 Using 15-Micron Beulah-Zap Lignite CWF.

Figure 35. Photograph of Deposition Probe #1 Deposits for Combustion Test 47 Using 15-Micron Beulah-Zap Lignite CWF.

TABLE 45

ASH MATERIAL BALANCE CALCULATIONS FOR THE TURBINE SIMULATOR
TESTS 43 THROUGH 47

Test No.	43	44	45	46	47
Fuel Name	Otisca	Otisca	Kemmerer	Kemmerer	Beulah
Wt. Ash In (gm)	<u>1078</u>	<u>2137</u>	<u>4763</u>	<u>7615</u>	<u>6928</u>
Percent of Ash In:					
Rich Zone Ash (%)	0.35	7.8	4.4	4.5	33.2
Quench Zone Ash (%)	1.00	0.14	0.06	0.43	0.39
Lean Zone Ash (%)	1.00	0.21	7.8	8.3	36.0
Depos. Sect. Ash (%)	ND	0.16	0.09	0.19	0.78
Cyclone Ash (%)	40.1	40.9	20.5	23.5	13.5
Ash Closure (%)	42.45	49.21	32.85	36.92	83.87

recovered in the rich and lean zones and the overall high ash closure. The Kemmerer also showed higher deposition levels than the Otisca fuel, especially in the lean zone area. Most of the recovered Otisca ash was recovered in the cyclone pot. This is probably the result of the cyclone ash containing high levels of carbon (70% or greater), thus a large percentage of the fine mineral grains is still tied up in the char cenospheres and has not been released from the char particle where it could contact internal surfaces to form deposits. In addition, the agglomerating nature of the bituminous fuel tends to increase the efficiency of the cyclone on the exhaust of the turbine simulator, thereby collecting a higher percentage of particulate entering the cyclone.

4.4 Design and Construction of a Pressurized Atomization Spray Chamber

It has been proposed to modify an existing pressure vessel to include observation ports to perform atomization studies under typical turbine operating pressures and air flows. The main objective of this work is to determine if differences in atomization quality account for the improvements in carbon burnout experienced with LRC fuels. The design of the spray chamber involves an existing 11.25-in ID pressure vessel that will be modified to provide optical access perpendicular to the direction of the atomized spray. The optical access consists of two diametrically opposite 3"-sight ports for the use of high speed photography. In addition, a 2"-sight port opposite a 1"-NPT port, through which a sight pipe can be inserted is also planned. The use of a sight pipe reduces the length of spray the Malvern 2600 laser beam must pass through and eliminates the potential for vignetting that could occur if the beam were to pass through the complete spray cone. A honey comb catalyst support will be used as a flow straightener to provide a laminar flow of air around the atomizing nozzle. The height of the atomizer in relationship to the optical ports will be adjustable from outside the pressure vessel thus allowing the atomizer position to be changed during a single atomization test.

The atomized slurry will be collected in a funnel at the bottom of the spray chamber where it will be drained off periodically through a hand valve. Pneumatic control valves will be used to control the air flow rate and to back pressure the spray chamber. High speed photography will be accomplished using a high speed strobe to back light the slurry droplets during atomization. The use of high speed photography will allow droplet sizes larger than 564-microns (the top size for a Malvern particle size analyzer with a 300mm lens) to be detected and will also provide information about the spray angle obtained under a given set of operating conditions.

4.5 Design and Construction of a Pressurized Drop-Tube furnace

The emergence of advanced coal combustion technologies such as coal slurry-fired gas turbines requires fundamental knowledge of the fuel combustion processes at elevated pressures. Of critical importance are the basic combustion kinetics and the fate of coal mineral matter in such systems. To address these issues, a pressurized drop-tube furnace is being constructed. The pressurized drop-tube furnace (PDTF) will be capable of operating under the following conditions:

Temperature: ambient to 1500°C
Pressure: ambient to 20.4 atm

Oxygen: 0 - 20 mol%
Gas Flow: 0 to 20 l/min at 20 atm
Residence Time: 0 to .50 sec
- Optical access at any residence time
- Provision for char and ash collection
- Provision for ash deposition studies

The design of the PDTF incorporates several novel features that will allow the design goals to be met. A drawing of the PDTF facility is given in Figure 36. The entire PDTF will be constructed of standard 24"- and 6"-flanged pipe sections. The large pressure vessel contains the furnace sections of the PDTF. The walls of the vessel are water-cooled to dissipate the heat from the furnaces. There will be a preheater and two furnace sections located above the optical sight ports and one furnace after the optical sight ports to reduce the temperature gradient across the optical access section. Optical access is provided by four 3"-diameter ports in the pressure vessel. Electrical power is supplied to the furnaces by electrical feedthroughs in the bottom blind flange of the pressure vessel.

Above the large pressure vessel containing the furnace is the injector section containing the injector assembly. The injector is a one inch diameter water cooled probe sheathed in high temperature insulation. Above the injector section is the translating mechanism for raising and lowering the injector into the ceramic tube inside the furnace assembly. The injector may be retracted completely out of the furnace when not in use or may be lowered into the furnace to give the desired residence time between 0 and 0.5 second. Small viewports in the pipe crosses at the bottom and top of the injector section allow visual inspection of the probe and sample feeding behavior.

Below the large pressure vessel is a similar collection assembly and translation mechanism. The collector may be raised to the level of the optical access ports and retracted completely from the furnace for the removal of sample deposits or when not in use. Two pipe crosses with small sight ports allow inspection of the collection probe operation and the removal of a blind flange provides access for the removal of sample deposits. Cooling water and sampling connections are carried inside the translation rods that move the injector and collector assemblies. Both assemblies are interchangeable to allow for specific fuel types or collection tasks.

The sample feeder assembly is a blank flanged 6" pipe cross-pressurized to slightly above the furnace pressure with gas connections to the furnace assembly. The design allows the actual sample feeder to be constructed of light weight material since it does not have to withstand more than slight pressure differentials. A small sight port allows inspection of the feeder operation, and removal of a blind flange gives access to the vessel for filling or adjustment of the feeder. The light weight feeder can then rest on a load cell in the pressure vessel to a continuous record of the sample feed rates. The gas composition and flow rate of gas into the PDTF is controlled by oxygen and nitrogen mass flow controllers. Gas composition can be controlled between 0-20 mol% at flow rates up to 20 lit/min. The furnace pressure is controlled by a let-down control valve at the exit of the furnace.

Figure 36. Schematic of the Pressurized Drop-Tube Furnace and Facilities.

A major expansion of the drop-tube furnace facility to provide more space for the PDTF has been completed. The furnace assembly, which is the item with the longest lead time, has been ordered. All of the materials for the construction of the pressure vessels have arrived and construction of the major components is proceeding as the availability of certified welders allows.

5.0 CONCLUSIONS AND FUTURE PLANS

The future plans for this project involve atomization testing of low-rank coal water slurries to determine if their superior burnout is the result of higher reactivity or just better atomization than bituminous fuels. In this next quarter, construction of a pressurized drop-tube furnace will be completed. This pressurized drop-tube furnace will be used to study the mineral matter transformations of various beneficiated LRC fuels. This work will lead to a better understanding of the role various beneficiation processes play on the ash composition and its chemistry under high temperature conditions. Next year's work will also include hot-gas cleanup work to finish evaluating the effects of sorbent addition on SO₂ control and to evaluate potential hot gas cleanup techniques for the control of particulate emissions.

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1. Program/Project Identification No. DE-FC21-86MC10637	2. Program/Project Title Turbine Combustion Phenomena (3.1)	3. Reporting Period 4/1/88 through 6/30/89
4. Name and Address University of North Dakota, Energy and Environmental Research Center, Box 8213, University Station, Grand Forks, ND 58202		5. Program/Project Start Date 4/1/86
		6. Completion Date 3/31/92

11. Major Milestone Status	Units Planned	
	Units Complete	
a. Technology and Market Assessment	P	
	C	Completed in Year 1.
	P	
	C	
b. Reactivity of Fuel	P	3▲
	C	
	P	
	C	
c. Gas Turbine Simulation	P	3▲ 4▲
	C	
	P	
	C	
d. Hot Gas Cleanup	P	
	C	3, 4 & 5 moved to APP4 year.
	P	
	C	
	P	
	C	
	P	
	C	
	P	
	C	
	P	
	C	
	P	
	C	
	P	
	C	
	P	
	C	
	P	
	C	
	P	
	C	

12. Remarks

13. Signature of Recipient and Date

14. Signature of DOE Reviewing Representative and Date

U.S. DEPARTMENT OF ENERGY
FEDERAL ASSISTANCE MANAGEMENT SUMMARY REPORT

Page ____ of ____

1. Program/Project Identification No. DE-FC21-86MC10637		2. Program/Project Title Turbine Combustion Phenemena (3.1)		3. Reporting Period 4/1/88 through 6/30/89	
4. Name and Address University of North Dakota, Energy and Environmental Research Center, Box 8213, University Station, Grand Forks, ND 58202				5. Program/Project Start Date 4/1/86	
				Completion Date 3/31/92	
Milestone ID, No.	Description	Planned Completion Date	Actual Completion Date	Comments	
b.1	Reactivity tests of LRC slurries in combustion bomb	2/28/89	5/31/89		
b.2	Correlate results from reactivity tests to gas turbine simulator performance	3/31/89	6/30/89	In Diesel Utiliza tion Annual Repor	
b.3	Correlate results from reactivity test to fuel properties	4/30/89	6/30/89	In Diesel Utiliza tion Annual Repor	
c.1	Screening tests on baseline LRC slurry fuel using fractional factorial test plan	1/31/89	1/89		
c.2	Test bituminous slurries in turbine simulator investigating important parameters	3/31/89	3/31/89		
c.3	Test LRC slurries in turbine simulator investigating important parameters	5/31/89	6/30/89		
c.4	Correlate combustion, emission, deposition data to fuel properties	6/30/89	7/30/89		
d.1	Install high pressure sorbent feeding equipment		11/88		
d.2	Test sorbent addition in slurry, rich zone and lean zone on SO ₂ control and particulate emissions	3/01/89		Unsuccessful feeding problems	
d.3	Build HPHT filtration device	In next App			
d.4	Test selected HPHT filtration device for particulate removal efficiency	In next App			
d.5	Test integrated sorbent addition and HPHT filtration device for total SO ₂ and particulate control	In next App			

10/1/21

3.2 Combustion Inorganic Transformation

COMBUSTION INORGANIC TRANSFORMATIONS

Final Technical Report for the period
April 1, 1988 through June 30, 1989
Including the Thirteenth Quarterly-Interim
for the period April 1, 1989 through June 30, 1989

by:

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TABLE OF CONTENTS

	<u>Page</u>
EXECUTIVE SUMMARY.....	1
TASK 3.2A: LIFS PROJECT.....	1
TASK 3.2B: DROP-TUBE FURNACE PROJECT.....	2
1.0 GOALS AND OBJECTIVES.....	5
TASK 3.2A: LIFS PROJECT.....	6
TASK 3.B: DROP-TUBE FURNACE PROJECT.....	6
2.0 TASK 3.2A: LIFS PROJECT.....	7
2.1 Introduction.....	7
2.2 Experimental.....	8
2.2.1 Laser-Induced Fluorescence Spectrometer.....	8
2.2.2 Sample Introduction.....	9
2.2.2 Solid Preparation.....	14
2.2.4 Char Analysis.....	14
2.3 Calculations.....	17
2.4 Results and Discussion.....	19
2.4.1 Solution Studies.....	19
2.4.2 Solids Feeders.....	24
2.4.3 Solids.....	26
2.4.3.1 The Low Sodium-Releasing Solids.....	32
2.4.3.2 The Moderate Sodium-Releasing Solids.....	32
2.4.3.3 The High Sodium-Releasing Solids.....	38
2.4.3.4 Summary of Solids Data.....	42
2.4.4 Char Analysis.....	44
2.4.5 Other Solid Studies.....	48
2.5 Conclusions.....	50
2.6 Future Work.....	53
3.0 TASK 3.2B: DROP-TUBE FURNACE PROJECT.....	53
3.1 Introduction.....	53
3.2 Equipment and Procedures.....	53
3.2.1 Drop-Tube Furnace System.....	53
3.2.2 Characterization of Coal, Char, and Fly Ash.....	58
3.2.3 Production and Characterization of Chars.....	60
3.2.4 Production of Fly Ash.....	62
4.0 RESULTS AND DISCUSSION.....	64
4.1 Characterization of Eagle Butte Coal, Char, and Fly Ash....	64
4.1.1 Eagle Butte Coal Characterization.....	64
4.1.2 Eagle Butte Char Characterization.....	70
4.1.3 Eagle Butte Char and Ash Droplet Morphology.....	78
4.1.4 Eagle Butte Fly Ash Characterization.....	84
4.2 Characterization of Upper Freeport Coal, Char, and Fly Ash.....	86
4.2.1 Upper Freeport Coal Characterization.....	86
4.2.2 Upper Freeport Char Characterization.....	89

TABLE OF CONTENTS (continued)

	<u>Page</u>
4.2.3 Upper Freeport Char and Ash Droplet Morphology	89
4.2.4 Upper Freeport Fly Ash Characterization.....	101
4.3 Characterization of Robinson Coal, Char, and Fly Ash.....	101
4.3.1 Robinson Coal Characterization.....	101
4.3.2 Robinson Coal Char Characterization.....	105
4.3.3 Discussion of Inorganic Transformation.....	108
4.3.4 Kaolinite Transformation.....	108
4.3.5 Quartz Transformations.....	110
4.3.6 Gypsum Transformation.....	113
4.3.7 Formation of New Inorganic Phases.....	113
4.3.8 Robinson Char and Ash Droplet Morphology.....	115
4.3.9 Characterization of Robinson Fly Ash.....	118
4.4 Characterization of Beulah Coal, Char, and Fly Ash.....	118
4.4.1 Beulah Coal Characterization.....	118
4.4.2 Beulah Char Characterization.....	125
4.4.3 Discussion of Inorganic Transformations.....	129
4.4.4 Beulah Fly Ash Characterization.....	131
4.4.5 Surface Analysis of Beulah Multicyclone Fly Ash.....	136
4.5 Characterization of Monticello Coal, Char, and Fly Ash.....	138
4.5.1 Monticello Coal Characterization.....	138
4.5.2 Characterization of Monticello Char.....	146
4.5.3 Characterization of Monticello Fly Ash.....	148
4.5.4 Discussion of Inorganic Transformations for Monticello.....	150
4.5.5 Fly Ash Particle Size Distributions as a Function of Different Combustion Temperatures and Coal Sizes.....	150
4.5.6 fly Ash Classification Scheme.....	152
5.0 CONCLUSIONS.....	164
6.0 REFERENCES.....	171

LIST OF FIGURES

<u>Figure</u>	<u>Page</u>
1 Initial optical layout of the laser-induced fluorescence spectroscopy system. PMT = photomultiplier tube in amplifier/socket assembly, bs = beamsplitter.....	10
2 Final optical layout of the laser-induced fluorescence spectroscopy system. PMT = photomultiplier tube in amplifier/socket assembly, bs = beamsplitter.....	10
3 Sodium Analysis System.....	11
4 Burner design for the introduction of solids or solutions into a flame.....	12
5 Horizontal temperature profile of methane/oxygen/argon flame at 0.415 and 1.915 inches above the burner.....	13
6 Horizontal temperature profile of methane/oxygen/argon flame at 0.415 and 1.915 inches above the burner.....	13
7 Collection Probe.....	16
8 Saturation profile for Phase-R laser using a 1500- μ g Na/ml sodium chloride solution.....	20
9 Saturation profile for the Candela laser using a 1500- μ g Na/ml sodium benzoate solution.....	20
10 Horizontal fluorescence profile of a 1500- μ g Na/ml sodium benzoate solution.....	22
11 Horizontal fluorescence profile of a 1500- μ g/ml sodium benzoate solution at 1.915 inches above the burner. The N_{ta} value at the flame center was 1.4×10^{11} atoms/mm.....	22
12 Horizontal fluorescence profile of a 3000- μ g Na/ml sodium chloride solution.....	23
13 Concentration curve for sodium chloride solutions.....	23
14 Spouting Bed Feeder.....	25
15 Mass flow rate for the spouting bed solids feeder. The feeder was only partially filled with solid.....	27
16 Mass flow rate for the spouting bed solids feeder when it was full.....	27

LIST OF FIGURES (continued)

<u>Figure</u>	<u>Page</u>
17 Stirring feeder.....	28
18 Spinning spouter feeder.....	29
19 Mass flow rate for the spinning spouter solids feeder.....	30
20 Horizontal fluorescence profile of solid sodium benzoate.....	31
21 Horizontal fluorescence profile of solid sodium montmorillonite.....	33
22 Horizontal fluorescence profile of solid sodium chloride, obtained using the Phase-R laser at a vertical position of 0.415 inches above the burner.....	33
23 Horizontal fluorescence profile of solid sodium chloride, obtained using the Cendela laser at a vertical position of 0.415 inches above the burner.....	34
24 Horizontal fluorescence profile of solid sodium carbonate at a vertical position of 0.415 inches above the burner head.....	36
25 Horizontal fluorescence profile of solid sodium sulfate.....	36
26 Horizontal fluorescence profile of solid sodium carbonate at a vertical position of 1.915 inches above the burner.....	37
27 Horizontal fluorescence profile of solid sodium sulfate at a vertical position of 1.915 inches above the burner.....	37
28 Horizontal fluorescence profile of Beulah lignite at a vertical position of 0.415 inches above the burner.....	39
29 Horizontal fluorescence profile of Beulah lignite at a vertical position of 1.915 inches above the burner.....	39
30 Horizontal fluorescence profile of demineralized Beulah lignite loaded with sodium.....	40
31 Horizontal fluorescence profile of demineralized Beulah lignite at 0.415 inches above the burner.....	40
32 Horizontal fluorescence profile of demineralized Beulah lignite at a vertical position of 1.915 inches above the burner.....	41
33 Horizontal fluorescence profile of sodium-loaded decolorizing carbon at a vertical position of 0.415 inches above the burner.....	42

LIST OF FIGURES (continued)

<u>Figure</u>	<u>Page</u>
34 Horizontal fluorescence profile of sodium-loaded decolorizing carbon at a vertical position of 1.915 inches above the burner..	42
35 Peak R_{fa} values for horizontal profiles of each solid taken at a vertical position of 0.415 inches above the burner.....	43
36 Concentration curve for Beulah lignite solid samples.....	45
37 Horizontal fluorescence profile of solid sodium benzoate mixed with elemental sulfur.....	49
38 Horizontal fluorescence profile of sodium benzoate solution at a vertical position of 0.415 inches above the burner head.....	51
39 Horizontal fluorescence profile of decoloring carbon with sodium benzoate deposited upon it in the methane/oxygen/argon/carbon dioxide flame.....	52
40 Horizontal fluorescence profile of decolorizing carbon with sodium benzoate deposited upon it in the methane/oxygen/argon/carbon dioxide flame.....	52
41 Drop-tube furnace laboratory.....	55
42 Cross-sectional diagram of the drop-tube furnace.....	56
43 Drop-tube furnace coal feeder assembly.....	57
44 Fly ash-quenching probe assembly for drop-tube furnace.....	57
45 Short-residence-time-probe for drop-tube furnace.....	59
46 Distribution of quartz in Eagle Butte bulk coal and sized coal fractions.....	71
47 Distribution of kaolinite in Eagle Butte bulk coal and sized coal fractions.....	71
48 Particle size distribution for all minerals in the Eagle Butte bulk coal and sized coal fractions.....	72
49 Particle size distribution of inorganic phases detected by CCSEM in Eagle Butte chars and original coal.....	73
50 Major inorganic phases and minerals in Eagle Butte original coal and successive chars.....	74

LIST OF FIGURES (continued)

<u>Figure</u>	<u>Page</u>
51 Transformation of quartz particle size distribution in Eagle Butte coal and chars.....	77
52 Transformation of kaolinite particle size distribution in Eagle Butte coal and chars.....	77
53 Transformation of CaO particle size distribution in Eagle Butte coal and chars.....	78
54 Production and transformation of ca-silicate particle size distribution in Eagle Butte chars (no Ca-silicate was detected in the coal).....	79
55 SEM micrograph of 0.05-second Eagle Butte char particle with compositions of selected areas.....	80
56 Thermal gravimetric analysis of Eagle Butte chars.....	81
57 SEM micrograph of 0.2-second Eagle Butte char particle with composition of selected areas.....	82
58 SEM micrograph of 0.5-second Eagle Butte char particle showing reaction between CaO and quartz (silica).....	83
59 Upper Freeport coal and char mineral/phase particle size distributions.....	93
60 Upper Freeport coal and char mineral/phase contents as a function of residence time.....	93
61 TGA analysis of Upper Freeport 53-74- μ M coal.....	94
62 Upper Freeport .05-second char (scanning electron micrograph and EDS data).....	95
63 Upper Freeport 0.1-second char (scanning electron micrograph and EDS data).....	96
64 Upper Freeport 0.5-second char (scanning electron micrograph obtained using backscattered electron imaging).....	97
65 Upper Freeport 0.8-second char (scanning electron micrograph obtained using backscattered electron imaging).....	97
66 Particle size distribution of Robinson coal minerals and char inorganic phases as determined by CCSEM.....	109

LIST OF FIGURES (continued)

<u>Figure</u>		<u>Page</u>
67	Distribution of kaolinite or aluminosilicate in the Robinson coal and chars.....	110
68	Individual kaolinite or halloysite spherules separated by organic coal matrix.....	111
69	Aggregates of kaolinite or halloysite spherules in a coal particle.....	111
70	Distribution of quartz in the Robinson coal and chars.....	112
71	Distribution of quartz and calcium silicate as a function of residence time in the drop-tube furnace.....	112
72	Distribution of gypsum and anhydrite in Robinson coal and chars.....	114
73	Concentrations of major phases produced during combustion as a function of residence time.....	116
74	SEM micrograph of a 0.8-second char particle showing association of inorganic ash particles and char matrix.....	116
75	SEM micrograph showing char burnout of particle and the formation of fly ash on surface (0.5 sec RT).....	117
76	SEM micrographs of Robinson 0.2-second char showing abundant uncombusted char particles.....	119
77	SEM micrograph of small 1-3- μ m inorganic ash particles lining coal char structures in the Robinson 0.2-second char.....	119
78	SEM micrograph of Robinson 0.1-second char particles.....	120
79	SEM micrograph of minute (<1 μ m) inorganic ash droplets that formed on the surface of a char particle.....	120
80	Mineral and other inorganic phases present in original Beulah coal and chars at set residence times.....	130
81	Particle size distribution of total minerals in original Beulah lignite and in successive chars produced at set residence times.....	130
82	Distribution of quartz in Beulah coal and chars.....	132

LIST OF FIGURES (continued)

<u>Figure</u>	<u>Page</u>
83 Distribution of aluminosilicate in Beulah coal and chars.....	132
84 Distribution of Ca-Aluminosilicate in Beulah coal and chars.....	133
85 Distribution of inorganic phases in each stage of the multicyclone for Beulah fly ash.....	134
86 Comparison of quartz content as a function of particle size for Beulah coal using CCSEM, and for Beulah fly ash using SEMPC.....	134
87 Comparison of kaolinite content as a function of particle size for Beulah coal using CCSEM, and for Beulah fly ash using SEMPC.....	135
88 Comparison of iron oxide and pyrite content as a function of particle size for Beulah coal using CCSEM, and for Beulah fly ash using SEMPC.....	135
89 Surface composition determined by XPS of Beulah fly ash collected in each stage of the multicyclone.....	137
90 XPS analysis of Beulah fly ash multicyclone stages: A) analysis for C, O, Al, and Si, and B) analysis for Na, S, Ca, Fe, and Ba.....	140
91 XPS analysis of Beulah fly ash multicyclone stages (carbon free): 1) analysis for C, O, Al, and Si, and B) analysis for Na, S, Ca, Fe, and Ba.....	141
92 SIMS profiles of six elements in Beulah multicyclone fly ash samples.....	143
93 Monticello char particle produced at 0.5-second residence time at 1300°C.....	147
94 Monticello char particle produced at 0.5-second residence time, showing inorganic ash droplets on surface.....	148
95 Fly ash particle size distributions for multicyclone and impactor runs as a function of coal size (38-53- μ m coal).....	151
96 Fly ash particle size distribution for multicyclone and impactor runs as a function of coal size (53-74- μ m coal).....	153
97 Fly ash particle size distribution for multicyclone and impactor runs as a function of coal size (74-106- μ m coal).....	154

LIST OF FIGURES (continued)

<u>Figure</u>	<u>Page</u>
98 Eagle Butte fly ash particle distribution as a function of temperature.....	155
99 Upper Freeport fly ash particle size distribution as a function of temperature.....	155
100 Beulah fly ash particle size distribution as a function of temperature.....	156
101 Robinson fly ash particle size distribution as a function of temperature.....	156
102 Monticello fly ash particle size distribution as a function of temperature.....	157
103 Secondary electron images of fly ash particles produced from Beulah lignite.....	158
104 Secondary electron images of char and fly ash particles produced from Beulah lignite.....	160
105 Secondary electron images of Upper Freeport fly ash particles found in Stage 1 of the multicyclone ($>11\text{ }\mu\text{m}$), (A) 1300°C , (B) 1400°C , and (C) 1500°C	162
106 Secondary electron image of Upper Freeport char and fly ash produced at 1300°C	163
107 Secondary electron image of Upper Freeport fly ash produced at 1400°C	165
108 Secondary electron image of Upper Freeport fly ash from stage 5 of the multicyclone produced at 1400°C	166
109 Secondary electron image of Upper Freeport fly ash from Stage 1 produced at 1500°C	167

LIST OF TABLES

<u>Table</u>	<u>Page</u>
1 Solid Sodium Salt Mixtures.....	15
2 X-ray Fluorescence Analysis of Sodium Montmorillonite.....	15
3 Analysis of Beulah Lignite by Atomic Absorption.....	16
4 Distribution of Sodium in the Flame.....	24
5 Particle Size Analyses of Solids.....	31
6 Distribution of Sodium From Sodium Montmorillonite.....	34
7 Distribution of Sodium From Sodium Chloride.....	35
8 Gaseous and Condensed Species for the Thermodynamic Calculations of Sodium Chloride.....	35
9 Distribution of Sodium from Sodium Benzoate.....	38
10 Chemical Fractionation Results for Beulah 53-74- μ m Lignite.....	45
11 Analyses of Beulah Lignite Char.....	46
12 Summary of Thermogravimetric Data for the Solids of the Sodium Benzoate Char Analysis.....	47
13 Analyses of Solid Sodium Benzoate Chars.....	47
14 A Comparison of N_{tt} and H_{tf}	49
15 Percentages of the Major Flame Constituents as Predicted by Solvamix at 1830 K.....	51
16 Drop-Tube Furnace Run Conditions Used to Produce Chars from the Monticello Lignite.....	61
17 Drop-Tube Furnace Run Conditions Used to Produce Chars from the Beulah Lignite.....	61
18 Drop-Tube Furnace Run Conditions Used to Produce Char from Robinson Coal (74-106- μ m).....	62
19 Drop-Tube Furnace Run Conditions Used to Produce Char from Upper Freeport Coal (53-74 μ m).....	63

LIST OF TABLES (continued)

<u>Table</u>	<u>Page</u>
20 Drop-Tube Furnace Run Conditions for Char Formation from Eagle Butte Coal (53-74 μm).....	63
21 Drop-Tube Furnace Run Conditions for the Formation of Fly Ash from Coal Size Fractions.....	64
22 Drop-Tube Furnace Run Conditions for Middle Size Cuts at Three Different Temperatures.....	64
23 Ash Composition of Eagle Butte Coal and Sized Fractions (Normalized Oxide Wt%).....	65
24 Chemical Fractionation Results for Eagle Butte Coal Sized Fractions.....	66
25 Mineral Content for Eagle Butte Coal Size Fractions (Wt% Mineral Basis).....	67
26 Mineral Size Distribution in Eagle Butte Bulk and Sized Fractions (WT% Mineral Basis).....	68
27 Composition of Crandallite Minerals in Eagle Butte Coal (Wt%)...	72
28 Particle Size Distribution for Individual Inorganic Phases in Eagle Butte Chars at Different Residence Time (Area % by CCSEM).....	74
29 Phases Detected by SEMPC for Eagle Butte Fly Ash.....	85
30 Comparison of Eagle Butte ASTM and >11- μm Multicyclone Fly Ash.....	86
31 Composition of ASTM Ashes and Distribution of Crystalline Species in the LTA Ashes Produced From Upper Freeport Coal.....	87
32 Mineral Distribution Data for Upper Freeport Size Fractions.....	88
33 Distribution of Inorganic Phases in Upper Freeport Chars.....	90
34 Mineral Distribution for Upper Freeport 53-74 μm Coal.....	92
35 Composition of Selected Inorganic Particles in Upper Freeport Chars.....	95

LIST OF TABLES (continued)

<u>Table</u>	<u>Page</u>
36 Composition of Illite and K-Aluminosilicate in Upper Freeport Coal and Char.....	98
37 Phases detected by SEMPC for Upper Freeport 0.05-Second Char....	99
38 Comparison of SEMPC and XRF Chemical Composition for Upper Freeport.....	100
39 Comparison of Selected Upper Freeport 0.05-Second Char Phases and Coal Minerals for >11- μ m Size Range.....	100
40 Phases Detected by SEMPC for Upper Freeport Fly Ash.....	102
41 Chemical Fractionation Results for Robinson Coal.....	103
42 Results of Robinson Coal and Ash Analysis.....	103
43 Mineral Distribution Data for Robinson Size Fractions.....	104
44 Distribution of Inorganic Phases in the Robinson Chars.....	106
45 Mineral Distribution Data for Robinson 74-106- μ m Coal Size Fraction.....	109
46 Selected Inorganic Phase Compositions for Robinson Char.....	114
47 Composition of Representative Inorganic Ash Particle and the Formation of Fly Ash on Surface.....	117
48 Phases Detected by SEMPC for Robinson Fly Ash.....	121
49 Composition of ASTM and LTA Ashes from Beulah Coal Using XRF and XRD.....	122
50 Chemical Fractionation Results for Beulah Coal.....	122
51 Chemical Fractionization Results for Beulah 53-74- μ m Coal.....	123
52 Mineral Distribution Data for Beulah Size Fractions (Wt%).....	124
53 Mineral Grains Present as Extraneous, Inherent, and Associated with Other Minerals in the 53-74-Micrometer Size Fraction of Beulah Lignite.....	126
54 Distribution of Inorganic Phases in the Beulah Chars.....	127

LIST OF TABLES (continued)

<u>Table</u>	<u>Page</u>
55 SEMPC Results for Beulah Fly Ash Multicyclone Size Fractions....	133
56 Chemical Species Identified in Beulah Fly Ash Using XPS Analysis.....	137
57 XPS Results on Beulah Ash from Multicyclone Stages.....	139
58 XPS Results on Beulah Ash from Multicyclone Stages, Carbon-Free Calculation (Wt%).....	139
59 XPS Binding Energies from Detailed Scans of Beulah Fly Ash.....	142
60 Chemical Fractionation Results for Monticello Coal.....	144
61 Results of Monticello Coal and Ash Analysis.....	144
62 Mineral Distribution Data for Monticello Size Fractions (Wt%)...	145
63 Composition of Representative Inorganic Ash Particles and Char Matrix in Monticello Chars.....	147
64 Phases Detected by SEMPC for Monticello Fly Ash.....	149
65 EDS Analysis of Fly Ash Types.....	160
66 EDS Analysis of Calcium-Rich Particles.....	161
67 Analysis of Particles in Figure 106, Weight Percent Expressed As Equivalent Oxide.....	163
68 Analysis of Selected Particles in Figure 107, Weight Percent Expressed As Equivalent Oxide.....	165
69 Analysis of Selected Particles in Figure 108, Weight Percent Expressed as Equivalent Oxide.....	166
70 Analysis of Selected Particles in Figure 109, Weight Percent Expressed as Equivalent Oxide.....	167

COMBUSTION INORGANIC TRANSFORMATIONS

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EXECUTIVE SUMMARY (LIFS)

TASK 3.2A: LIFS PROJECT

The goal of this project is to define the variables that affect the release of sodium atoms from coals and model compounds at temperatures similar to those produced in full-scale boilers. Laser-induced fluorescence spectroscopy (LIFS) was chosen for this task due to its high sensitivity for the detection of gas-phase atoms. This task complements the drop-tube furnace project (3.2B) in that the gas-phase species are examined as opposed to the solid and liquid products.

Difficulties with feeding solid sodium salts were solved with the construction of a spinning spouter solid feeder. This feeder was used to feed all solids.

The system was moved from the University of North Dakota Chemistry Department to the University of North Dakota Energy and Mineral Research Center.

A study of the effect of sodium concentration on the fluorescence was completed. At the leading edge of the flame the fluorescence signal was found to be linearly dependent on the concentration of sodium.

Horizontal fluorescence profiles were obtained for a number of pure sodium salts: benzoate, chloride, montmorillonite, sulfate, and carbonate. Sodium benzoate, sulfate, and carbonate gave fluorescence signals similar to those for solutions. Sodium chloride and sodium montmorillonite gave signals much smaller than those for solutions.

Horizontal fluorescence profiles were obtained for a series of Beulah lignites: plain Beulah lignite, demineralized Beulah lignite, and demineralized Beulah reloaded with sodium. The fluorescence signals were much higher for these solids than for sodium solutions and, at the leading edge of the flame, were linearly dependent on the concentration of the sodium fed into the flame.

Horizontal fluorescence profiles were obtained for a solid with sodium deposited upon it. Like the lignites, this solid gave a fluorescence signal much higher than that for sodium solutions.

The effect of sulfur and carbon dioxide on the sodium atom densities in the flame was studied. For the conditions used, no significant differences in the fluorescence signals were found.

Chars from Beulah lignite and solid sodium benzoate were analyzed to determine the percent of sodium in the solids that was vaporized. Both solids had some sodium remaining in their chars.

TASK 3.2B: DROP-TUBE FURNACE PROJECT

As part of the interim period research, original inorganic constituents, char, and ash combustion products from the drop-tube furnace (DTF) were examined for the Eagle Butte subbituminous coal from Wyoming. The purpose of the research was to observe and characterize the inorganic transformations that occurred during combustion under carefully controlled conditions.

Three size fractions and a bulk sample of Eagle Butte coal were analyzed for mineral content using computer controlled scanning electron microscopy (CCSEM). The major mineral phases observed were quartz, aluminosilicate, a calcium-aluminum-phosphorus mineral (crandallite?), gypsum, and calcite. Minor contents of apatite, K and Ca aluminosilicates and barite were also observed. X-ray fluorescence analysis revealed high CaO contents in all of the Eagle Butte coal size fractions, ranging from 23%-27% CaO. Chemical fractionation revealed that most of the calcium was organically bound or in a finely sized carbonate or phosphate form, for all three size fractions of the Eagle Butte coal.

The most abundant phases observed in the Eagle Butte fly ash multicyclone samples were calcium oxide followed by quartz and gehlinite. Fly ash that was classified as less than 6.0 microns in the multicyclone showed very low amounts of crystalline or chemically ordered phases. The amount of unclassifiable amorphous species seems to decrease with decreasing size of fly ash. Iron in the Eagle Butte fly ash was more concentrated in the smaller size fraction most likely because iron was associated in the coal as finely dispersed carbonate or organically bound cations, or because iron particles in the largest fly ash size fraction were being coated with calcium aluminosilicates or other materials that mask the identity of an iron-bearing core material. Other trends noticed were that Fe_2O_3 and SO_3 contents increased with decreasing particle size, and SiO_2 increased with increasing particle size. The SiO_2 and Al_2O_3 contents in the fly ash follow trends observed with the other test coals.

Chars produced from the Eagle Butte 53-74- μm coal were all very high in CaO. Other major phases produced during the combustion process were calcium silicate, calcium aluminate, and calcium aluminosilicate. Quartz was drastically reduced in content in the chars due to reaction with calcium aluminosilicate and CaO. Submicron calcium-rich minerals or organically bound calcium is the source for ubiquitous CaO-rich inorganic ash droplets that appear on the surface of early-stage chars. By 0.8 seconds of combustion, 95% carbon burnout had been achieved. The early-stage chars show greater quantities of discrete phases that are 1.2-8.0 μm in size, which is evidence for initial fragmentation of mineral grains. By 0.8 seconds, the char shows greater quantities of discrete phases or particles that are >8.0 μm in size, which is evidence for coalescence of fly ash particles.

The major phases observed in the Upper Freeport coal by CCSEM were quartz, mixed aluminosilicate (illite), kaolinite, and pyrite. Minor amounts of calcite and gypsum were also noted. The quartz grains were evenly

distributed in the various size ranges except for the 74-106- μm coal size fractions, where there was a high level of >11- μm quartz. Illite and pyrite were found most frequently in the >11- μm size fraction. The chars were collected in the DTF at five different residence times for the Upper Freeport coal. The general form of the mineral/phase particle size distribution remained the same through 0.8 seconds of combustion. The coal mineral and the char inorganic phases were bimodally distributed. Upper Freeport char morphologies were examined using the scanning electron microscope (SEM) and qualitative analyses were performed on selected particles to determine their relative elemental compositions. Thermal gravimetric analysis (TGA) was performed on the chars to monitor carbon burnout. Many of the Fe-rich particles showed significant quantities of aluminosilicate in their composition and illite-derived particles commonly had high Fe_2O_3 contents. Illite in the coal had lower Si/Al ratios than the illite-derived material in the char. The data suggest that a depletion of Si in association with Al occurred during the combustion process.

An additional DTF run was made to collect Upper Freeport 0.05-second char, whereby the char was quenched using the short residence time probe and then collected in the multicyclone. The major phases present in the Upper Freeport 0.05-second char were montmorillonite, illite, kaolinite, calcite or calcium oxide, anhydrite, plagioclase (anorthite-albite), quartz, and unclassified material. When compared to the coal, the char revealed a depletion of calcite, mixed aluminosilicate, illite, and pyrite; most likely because of melting and interaction with other liquid- or gas-phase inorganic components. The char showed an enrichment of quartz and kaolinite as compared to the coal.

Upper Freeport fly ash was generated from a 53-74- μm coal size fraction and analyzed for inorganic phases using SEMPC. Illite-derived was the most abundant phase recognized by SEMPC. Illite-derived is an amorphous K-aluminosilicate derived from the clay mineral illite.

Analysis of Robinson coal size fractions by CCSEM indicated that quartz, kaolinite, Ca-clay (montmorillonite) and pyrite were the most abundant mineral grains. Quartz was found to be most abundant in the larger size categories (>11- μm). The size distribution of pyrite and kaolinite was variable. Overall, the majority of the mineral grains were greater than 11 μm .

Short residence time combustion tests were conducted to produce chars from the Robinson 74-106- μm coal. It appeared that after 0.2 seconds of combustion, extensive fragmentation of larger sized mineral grains occurred. The mechanism for the fragmentation phenomenon in the first 0.2 seconds of combustion was based on the break-up of aggregates of aluminosilicate clays. At longer residence times of 0.5 and 0.8 seconds there was successive coalescence of finer sized inorganic phases. It is proposed that CaO, which was very abundant in the organic fraction of the coal, reacted with aluminosilicate clays that were abundant as discrete minerals. Calcium silicate formed as a result of the assimilation of vapor or liquid-phase CaO into the partially molten surface of quartz grains. Robinson char displays initial inorganic ash droplet formation within the first 100 ms of combustion at 1300°C. The smallest sized inorganic ash particles that begin to form on the surface of the coal char range from 0.1 to 3 microns in size. These initial combustion products are high in Ca and some contain significant amounts of Na. Robinson fly ash produced from the 53-74- μm coal had major phases of

quartz, amorphous kaolinite-derived, iron oxide, anhydrite, melilite, and plagioclase. Melilite and anhydrite were concentrated in the smaller sized fraction of the fly ash while iron oxide and quartz were concentrated in larger size fractions. Kaolinite-derived phases were distributed evenly in all size fractions. Average chemical compositions of the fly ash size fractions showed greater CaO, Na₂O, and SO₃ in the smaller sized fractions.

A 53-74- μ m sieve fraction of Beulah lignite was analyzed for inorganic transformations. The major minerals identified in the initial coal were kaolinite and quartz. Minor amounts of gypsum and Ca-aluminosilicate were also observed. Quartz, kaolinite, and gypsum were most abundant in the 4.4 to 8.0- μ m size range, while Ca-aluminosilicate was more concentrated in the 2.1 to 4.4- μ m range. Chars were produced for this lignite in the drop-tube furnace and analyzed using CCSEM. The most common phases identified in the chars were Ca-aluminosilicate, quartz, aluminosilicate, gypsum, and iron oxide. Pyrite virtually disappeared from the chars after 200 milliseconds of coal particulate residence time.

Distributions of major inorganic components in the chars and their comparisons to similar components in the original coal revealed some interesting trends. The overall area percent distribution of the inorganic phases showed a general decrease in material with combustion residence time in the lower size ranges (<8.0- μ m) and an increase in material with time in the higher size ranges (>8.0- μ m). Quartz and kaolinite decreased in concentration with residence time, and Ca-aluminosilicate increased dramatically with time. The above data may be indicative of coalescence of finer-grained minerals and interaction of organically bound inorganic constituents to form larger fly ash grains. In the case of kaolinite (or aluminosilicate) particles, there is strong evidence to suggest that these particles are undergoing a chemical transformation from kaolinite to Ca-aluminosilicate particles of nearly the same size. This inorganic transformation results in Ca-aluminosilicate particles having nearly the same size distribution as the kaolinite particles (4.4 - 8.0- μ m). The infusion of calcium from organically bound sites, with the mineral form of kaolinite, may have been the mechanism by which Ca-aluminosilicate was formed.

The variation in composition and distribution of phases as a function of particle size was determined for Beulah lignite fly ash. Each stage of the multicyclone was analyzed using the SEMPC technique. The iron oxide and quartz-derived particles were found in the larger sizes. Kaolinite-derived particles were found evenly distributed in Stages 2 through 5. Sodium calcium sulfate was concentrated in Stage 6 (<1.2 μ m).

The most abundant minerals found in the Monticello lignite consisted of quartz, kaolinite, Ca-clay and mixed aluminosilicate. Very little pyrite was found. Quartz, kaolinite, and Ca-clay had grain sizes that were largely in the >11- μ m range for the 38-53- μ m and 74-106- μ m fractions. Some of the aluminosilicate clays occurred as aggregates of 1-3- μ m particles.

Comparisons between original mineral matter, inorganic phases in early stage chars, and final fly ash show a progressive reaction of organically bound Ca with quartz and aluminosilicate species derived from kaolinite.

Inorganic ash droplets on the surface of Monticello short-residence-time char particles were very rich in CaO and consistently showed an aluminosilicate component with an Al/Si ratio of 1:1. These particles were generally 1-3 μm in average diameter and were often rich in Fe_2O_3 .

Fly ash particle size distributions (PSD) were determined using the multicyclone and impactor for Monticello, Beulah, Robinson, Upper Freeport, and Eagle Butte ashes produced in the drop-tube furnace. The PSD data was interpreted to note trends between original coal size and fly ash particle sizes for the five coals of varying ranks.

A fly ash particle classification scheme is being developed based on particle morphology and composition. Four general types of particles have been initially classified for Beulah and Upper Freeport. Type 1 particles are spherical with a relatively smooth surface and are usually composed of Fe-, Ca-, and Na-rich aluminosilicates. Type 2 particles display complex crystalline patterns at the particle surface, and are composed primarily of Fe with minor amounts of Ca and Na. Type 3 particles are aluminosilicates with Al/Si ratios similar to kaolinite and have irregular surfaces. Type 4 particles have angular shapes and are rich in Si.

Electron spectroscopy for chemical analysis (ESCA) was used to determine the form of selected elements and the composition of the surfaces of particles in the multicyclone size cuts for the Beulah Zap lignite ash produced in the drop-tube furnace. The highest level of sodium was found on the surfaces of the particles in Stage 6 (<1.2- μm). Aluminum and silicon levels were relatively constant but dropped off in Stage 6. Sulfur levels increased with decreasing particle size. The forms of sodium, calcium, and sulfur were determined for each stage of the multicyclone. Sodium was in a silicate form in Stages 1 to 5 and a sulfate form in Stage 6 (<1.2- μm). Calcium was found to be in a silicate form in Stage 1 and a sulfate form in Stages 3 through 6.

1.0 GOALS AND OBJECTIVES

The overall goal is to develop a unified picture of the physical and chemical changes that occur in coal inorganic matter during combustion. The research is centered on two main tasks. Task 3.2A deals with the use of laser-induced fluorescence spectroscopy (LIFS) to study the release of sodium from various model compounds and coal during combustion in a flame. The vaporized or released sodium is considered to be an important factor in the formation of ash-fouling deposits in full-scale utility boilers. Task 3.2B will study changes in the morphology and chemical associations of inorganic components in coals during combustion in a drop-tube furnace designed to simulate the time-temperature profile of a pulverized coal-fired utility boiler. The primary objectives of the drop-tube furnace task are to develop a means to predict the size and composition of the fly ash and to provide adequate information for development of ash deposition modeling efforts to effectively predict deposit growth. The important information with regard to ash deposition is the distribution of inorganic gases, liquids, and solids (intermediate material) as functions of residence time and temperature in a combustor. The partitioning of the inorganic components will influence the particle size distribution of the fly ash.

The composition of the ash particles is needed to predict the quantity of liquid phase present. In the initial stages of deposit growth (via the inertial impaction transport mechanism), the ability of a particle to stick is dependent upon the quantity and physical properties (viscosity and surface tension) of the liquid phase on and within the particle. The latter stages of deposit growth due to inertial impaction are primarily governed by the quantity of liquid phase present at the surface of the deposit.

Task 3.2A: LIFS Project

The specified objectives of the LIFS project during this year were to:

- 1) Develop a technique for obtaining constant and reproducible feed rates for sodium salts.
- 2) Integrate the detection system with a laser dedicated to LIFS and optimized for atomic fluorescence work.
- 3) Investigate the parameters affecting the ability of the system to quantitatively measure gas-phase atom concentrations, and define conditions under which a linear response could be expected using solution sources of sodium.
- 4) Complete the study of the model compounds (pure salts) to establish the effect of anion identity on degree of volatilization.
- 5) Establish the ability of the system to quantitatively measure varying sodium concentrations in a given solid matrix.
- 6) Study the volatilization of sodium from a lignite coal.
- 7) Develop a simple model system to probe effects of the carbon matrix on sodium release.
- 8) Determine the effect of sulfur and carbon dioxide on sodium release from the model salts.
- 9) Begin using char analysis to independently determine degree of sodium evolution from solids in the LIFS burner.

Task 3.2B: Drop-Tube Furnace Project

The specified objectives of the drop-tube furnace project during this year were to:

- 1) Determine mineral content (CCSEM analysis) for three size fractions of Beulah, Robinson, Monticello, Upper Freeport, and Eagle Butte coals.
- 2) Produce chars at short residence times in the drop-tube furnace using Beulah, Robinson, Upper Freeport, and Eagle Butte coals and analyze these chars using CCSEM.

- 3) Document the transformation of original minerals and organically bound inorganics with time during combustion in the drop-tube furnace for the five coals mentioned above.
- 4) Produce fly ash from the Beulah, Upper Freeport, and Eagle Butte coals and analyze for crystalline and amorphous species using SEMPC.
- 5) Determine the particle size distribution of fly ash produced in the drop-tube furnace for the five coals mentioned above using the multicyclone and impactor.
- 6) Determine speciation and surface chemistry of Beulah fly ash using Auger and ESCA techniques.

2.0 TASK 3.2A: LIFE PROJECT

2.1 Introduction

Ash fouling of heat transfer surfaces is the most serious operational problem in boilers fired on low-rank coals. Fouling can cause a serious loss of boiler efficiency and, in extreme cases, make it necessary to shut a boiler system down. The costs, therefore, associated with fouling are high. This has led to the call for much research in this area. It is the goal of the research presented here to add understanding to the mechanisms causing fouling.

Much has already been done to control fouling in the area of boiler design (1,2,3). By adding blowers inside the boilers, incorporating large furnace volumes, and carefully controlling the gas temperatures, the coal particle size and the gas composition inside the boiler, it is possible to minimize fouling (4).

Changing the design of the boilers, however, does not attack the root of the problem. Developing an understanding of mineral matter transformations should provide a basis for reducing fouling and corrosion in combustors. Some work has been done in this area. Gronhoyd et al., (5) performed a series of field tests, the results of which enabled relating fouling to the sodium content of the lignite used. Sondreal et al., (6) derived an expression for the fouling rate of a coal, but again the rate was found to be largely related to the sodium content of the coal. Tufte and coworkers (7) also found a correlation of fouling tendency with the sodium content of the ash. A possible explanation of these observed correlations lies in the flame behavior of sodium-containing species. Flame-volatilized alkalis can condense on the surfaces of entrained fly ash particles, forming low-melting layers that enhance the adhesion of ash particles to heat transfer surfaces (8, 9). Sodium sulfate particles were shown to form the initial layers of the fouling deposits (10).

More current research has focused on the use of additives to reduce fouling. Shadman and Punjak studied the use of additives to absorb vaporized sodium (11). Logan and Richards studied additives for their ability to reduce the sticking coefficient of coal and ash deposits (12). Decreased fouling has been related to the calcium content of a coal (7). However, Sondreal and coworkers (13) mixed calcium into a lignite but observed no decrease in fouling.

Although ash fouling has been related to the sodium content of a coal, much work needs to be done before an understanding of the mechanism of fouling is gained. It is believed that the volatilization of sodium is an important step in the fouling process. Since volatilized sodium has been shown to contribute to fouling, the work presented here focuses on factors effecting volatilization of sodium from solids.

Laser-induced fluorescence spectroscopy (LIFS) was the method chosen for the study. LIFS has several advantages over other methods for measuring volatilized sodium. First, it permits an in situ measurement of the gas-phase sodium, eliminating the need to infer the concentration of the volatilized sodium in the flame from the end products of the combustion reaction, as is typically done. It is highly selective and very sensitive. Calculations done by Daily (14) showed that it is possible to obtain detectability limits of down to 10^{-8} (mole fraction). LIFS is readily adaptable to high temperature systems such as flames and, since it provides good spatial and temporal resolution, LIFS permits the measurement of atom concentrations across the flame. Laminar-flow burners are typically used, but Wrobel and Pratt (15) measured laser-induced sodium fluorescence in turbulent flames. LIFS systems such as the one described below, which uses a flash lamp pumped-dye laser, are readily adapted to monitoring other species, both atomic and molecular. Winefordner, using a pulsed N_2 dye laser, obtained the best linear dynamic ranges and detectability limits obtained so far for a wide variety of species (16).

An LIFS system, however, sees only the single species it was set up to see. The current instrument can observe gaseous atomic sodium, but will miss any molecular or ionic forms of sodium. It is possible, too, that quenching reactions compete with fluorescence to such a degree that atomic fluorescence can not be monitored. The effect of chemical decay can be eliminated by using the leading edge of the flame and only the peak fluorescence values (17), and by saturating the fluorescence signal. Other potentially serious interference may come from molecular fluorescence of species formed in the flames by concomitants and flame gases, and by Rayleigh and Mie scattering (18).

The primary focus of this study is on the volatilization of sodium from solids. Before the solids studies were begun, a number of solution studies were done to characterize the LIFS system. After completing this work, the fluorescence signals from a series of solid sodium salts, three Beulah lignites, and one synthetic sodium solid were studied. The combustion products from two of these solids were collected and analyzed. Finally, the effect of sulfur and carbon dioxide gas on the fluorescence signals were also studied.

2.2 Experimental

2.2.1 Laser-Induced Fluorescence Spectrometer

The study was started using a Phase-R-DL2100b laser and continued with a Candela SLL-250. In order to narrow the band width of the laser light, each laser used a system of Schott prisms. The Candela laser also used an etalon tuned to 589.0 nm. The bandpass of the Candela laser is 0.2 to 0.4 Å with a power of 150-350 mJ, and that of the Phase-R laser's is 2 to 3 Å with a power of approximately 1 J. For the fluorescence measurements the lasers were tuned to 589.0 nm, one of the sodium D lines. The output of the Phase-R laser was

already largely horizontally polarized. To obtain horizontally polarized light from the Candela laser, the laser was turned on its side.

Diagrams of the optical layouts used with the two lasers are shown in Figures 1 and 2. In each case the layout consisted of a focusing lens, beam splitter, photodiode trigger, sample path, and a reference path. The focusing lens focused the laser beam down to a diameter of 2 mm in the region above the burner head. The beam splitter, a CaCO_3 polarizing beam splitter (Ealing no. 34-5595), directed the vertically polarized light to the reference path and passed the horizontally polarized light through the flame across the burner head. For the Phase-R laser, the ratio of the intensities of the horizontally polarized light to the vertically polarized was estimated to be 1000:1. The sample path is made up of two focusing lenses, a polarizer, a neutral density filter, a monochromator, and a photomultiplier tube (Hamamatsu no. R374) in an amplifier/socket assembly. The focusing lenses give a solid angle of collection of 0.14 sr. The reference path is made up of a series of neutral density filters and a photomultiplier tube (Hamamatsu no. R374) in an amplifier/socket assembly. The photodiode trigger was used to trigger the electronic system, a diagram of which is shown in Figure 3. A Stanford Research Systems' SRS gated integrator and boxcar averager (SRS 250) was used to collect the signal from each optical path. The sample and reference signals were transferred to an IBM PC/XT computer via an SRS 245 computer interface.

The monochromator (Oriel model 77250) was set at 589.3 nm, and its slits were set to a height of 1 mm (front) and 12 mm (back) and widths of 1.400 mm (front and back). These slits gave a band width of 8.8 nm and allowed the collection of emission from both of the sodium D lines. The monochromator was turned on its side so that the slit height was parallel to the laser beam.

For all of the solution measurements the polarizer was set to pass horizontally polarized light. For solids measurements the polarizer was set to pass vertically polarized light, except for the sodium benzoate and sodium chloride solid studies. For the latter studies it was set to pass horizontally polarized light. Neutral-density filters were placed in front of the monochromator as necessary to keep from saturating the photomultiplier tube with light.

2.2.2 Sample Introduction

The burner set-up is shown in Figure 4. It consisted of a 0.5-inch diameter capillary burner head, of the type described by K.M. Aldous and coworkers, mounted in a Perkin Elmer stainless steel burner body (19). The capillary head is made up of 75, 1/32-inch capillary tubes. A propeller was glued under the capillary tubes of the burner head to distribute the solids more evenly throughout the flame. Better results were obtained when the propeller was placed lower in the burner body than when it was closer to the capillaries. With one exception, the same reducing methane/oxygen flame sheathed in argon gas was used for the collection of all data. The components for this flame were methane, oxygen, and argon supplied at gas flow rates of 1.23, 1.96, and 3.65 L/min respectively. Argon gas flowing at a rate of 2.39 L/min was used to sheath the flame. For the work done with carbon dioxide, the flame components were methane, oxygen, and 70% Ar/30% CO_2 (Linde Speciality Gases), which were supplied at gas flow rates of 1.23, 1.96, and 1.55 L/min, respectively. Horizontal temperature profiles of these flames

Figure 1. Initial optical layout of the laser-induced fluorescence spectroscopy system. PMT = photomultiplier tube in amplifier/socket assembly, bs = beamsplitter.

Figure 2. Final optical layout of the laser-induced fluorescence spectroscopy system. PMT = photomultiplier tube in amplifier/socket assembly, bs = beamsplitter.

Figure 3. Sodium Analysis System.

Figure 4. Burner design for the introduction of solids or solutions into a flame.

were obtained using a Pt/Pt-10% Rh thermocouple with a 0.03-inch diameter. No correction for radiative heat loss was made. Figures 5 and 6 show the horizontal temperature profiles of these flames at 0.415 and 1.915 inches above the burner head, the vertical positions used when horizontal fluorescence profiles were obtained. The corresponding residence times for these vertical positions are 0.008 and 0.035 seconds.

Solutions were aspirated into the burner using a Perkin-Elmer adjustable nebulizer. The flow rate of solution into the nebulizer was typically between 1 to 3 mL/min, and 6.1% of the nebulized solution was actually introduced into the flame. Solids were fed into the burner using a spinning spouter solids feeder described in the section on solid feeder design. The exit tube from the feeder was connected to the 1/8-inch-diameter stainless steel tube fitted up into the bottom of the burner. Measurement of the solid accumulated in the burner body demonstrated a 70% to 98% efficiency of solids delivery to the flame, depending on the solid introduced.

Solution studies used water as a blank. When a background signal for solids was measured, it was done by detuning the laser to approximately 580 nm (a shorter wavelength, out of resonance with the sodium absorption line) and collecting the light scattered by the flame when it was illuminated by pulses of the same intensity used to generate sodium emission signals.

For the horizontal fluorescence profiles taken initially--the solid sodium benzoate, one of the solid sodium chlorides, and the sodium benzoate and sulfur solid mixture--each point on a graph is the average of five laser shots. For those done after these, the number of shots was increased to 10 to 15 in order to increase our confidence in the data.

Figure 5. Horizontal temperature profile of methane/oxygen/argon flame at 0.415 and 1.915 inches above the burner.

Figure 6. Horizontal temperature profiles of methane/oxygen/argon/carbon dioxide flame at 0.415 and 1.915 inches above the burner.

2.2.3 Solid Preparation

Solid samples with particle sizes between 200 and 325 mesh (45-75- μ m in diameter) were prepared by grinding and sieving the solid salts. The pure solids were mixed with decolorizing carbon of the same size fraction to improve their feeding characteristics, and then dried over night. Table 1 shows the percent salt by weight and the percent sodium by weight for the salts used. For the sample of solid sodium benzoate mixed with sulfur, the sized salt was mixed with elemental sulfur that had been ground and sized and with sized decolorizing carbon so that the solid mixture was 1.7% sodium by weight, 10.5% salt by weight, and 6.7% sulfur by weight.

The demineralized coal was prepared by stirring 25 g Beulah lignite with 100 ml of concentrated HCl for 1 hour at 50°C. The suspension was filtered using a Millipore vacuum filtration apparatus with HVLP filter paper. The filtrate was discarded and the residue washed once with 100 ml of distilled water. The residue was then stirred with 100 ml of concentrated HF for 1 hour at 50°C. The suspension was filtered as before. The resulting residue was stirred with 100 ml of concentrated HCl for 1 hour at 50°C, filtered, and washed with 100 ml washes of distilled water until a test of the filtrate with pH paper indicated that no residual HCl was present. The resulting solid was either air dried or dried under mild vacuum in a vacuum desiccator.

To prepare the sodium-loaded coal, 50 g of the demineralized Beulah lignite was placed in a plastic beaker with 5 ml of 0.100 M sodium acetate and sufficient water to permit easy stirring, and stirred over night. The slurry was vacuum filtered. The resulting solid was dried in a heated vacuum desiccator for 24 hours.

The sodium-loaded decolorizing carbon was prepared by stirring 50 g decolorizing carbon of the desired size range (45- μ m to 75- μ m) with 1.75 L of a solution of 11.4 mM sodium benzoate in ethanol over night. The suspension was then filtered using a Buchner funnel and dried in a vacuum desiccator.

The sodium content of the sodium montmorillonite was analyzed using X-ray fluorescence (see Table 2). The sodium contents of the three coals, the sodium benzoate loaded on to the decolorizing carbon, and of the chars were analyzed by atomic absorption. Table 3 shows the results of the atomic absorption analysis of the Beulah lignite. The sodium content of the demineralized Beulah lignite and the sodium-loaded Beulah lignite were measured to be 100 and 1400 μ g/g respectively. The sodium-loaded decolorizing carbon contained 2400 μ g/g sodium.

2.2.4 Char Analysis

For the study of the Beulah lignite and the solid sodium benzoate char, char was collected using a water cooled, nitrogen quench probe designed by McCollor (20). The probe consists of a series of four concentric steel tubes in a ceramic sheath (Figure 7). The outer shell is for introducing the quench gas, the innermost shell removes the combustion gases and the char, and the remaining shells carry the cooling water. The probe is lowered over the flame so that the flame is quenched at the desired residence time. Char was collected with a heated cyclone. To estimate the percentage of carbon matter lost, both the original sample and the char were analyzed using thermogravimetric analysis (TGA). The sodium content of the original sample and the char were measured by atomic absorption.

TABLE 1
SOLID SODIUM SALT MIXTURES

<u>Sodium Salt</u>	<u>Percent of salt by weight</u>	<u>Percent of sodium by weight</u>
Benzoate	10.0	1.6
Chloride	4.1	1.6
Montmorillonite	77.8	1.7
Sulfate	5.2	1.7
Carbonate	3.1	1.7

TABLE 2
X-RAY FLUORESCENCE ANALYSIS OF SODIUM MONTMORILLONITE

<u>Oxide</u>	<u>% Elemental</u>	<u>% of Ash</u>	<u>% of Ash (Normalized)</u>	<u>% of Ash (Normalized) SO₃-Free</u>
Silica, SiO ₂	27.96	59.82	63.71	64.18
Aluminum Oxide, Al ₂ O ₃	11.37	21.48	22.88	23.05
Ferric Oxide, Fe ₂ O ₃	2.761	3.95	4.20	4.24
Titanium Oxide, TiO ₂	0.126	0.21	0.22	0.23
Phosph. Pentoxide, P ₂ O ₅	0.000	0.00	0.00	0.00
Calcium Oxide, CaO	1.083	1.52	1.61	1.63
Magnesium Oxide, MgO	1.772	2.94	3.13	3.15
Sodium Oxide, Na ₂ O	1.988	2.68	2.85	2.88
Potassium Oxide, K ₂ O	0.502	0.60	0.64	0.65
Sulfur Trioxide, SO ₃	0.277	0.69	0.74	0.00
Totals	<u>47.84</u>	<u>93.89</u>	<u>100.00</u>	<u>100.00</u>

TABLE 3
ANALYSIS OF BEULAH LIGNITE BY ATOMIC ABSORPTION

<u>Element</u>	<u>($\mu\text{g/g}$)</u>
Sodium	5700
Calcium	9700
Potassium	100
Iron	6000
Magnesium	2600
Aluminum	3500

Figure 7. Collection Probe.

2.3 Calculations

Equation 1 was used to calculate the total sodium densities (gas, liquid, and solid) in the sample region of the flame from the solution aspiration rates. This equation was reported by Winefordner and Vickers (21) and used by Smith et al. (22).

$$N_{ta} = \frac{C N_{298} B \emptyset E T_{RT} K}{N_T T Q} \quad (1)$$

N_{ta} = the total atom density in the flame (atoms/mm³)

C = the concentration of sodium in the aspirated solution ($\mu\text{g Na/ml}$) or the weight percent of sodium in the solid ($\mu\text{g Na/g}$)

$\emptyset$ = the aspiration rate of the solution (ml/min) or the feed rate for the solid (g/min)

Q = the flow rate of unburned gases (L/min) at the introduction temperature (25°C)

E = the sample introduction efficiency = 1.0

B = the reactivity/ionization coefficient = 1.0

N_{298} = the moles of flame components at the introduction temperature (moles/min)

N_T = the moles of combustion products at T (moles/min)

T_{RT} = room temperature (K)

T = the flame temperature (K)

K = a constant of conversion = $2.619 \times 10^{34} \frac{\mu\text{g atoms Na mm}^3}{\text{g}^2 \text{ L}^1}$

The sample introduction efficiency is a measurement of the efficiency of the drop desolvation for solution in the flame. This was assumed to equal 1.0 (100% efficiency) based on the results of Winefordner et al., (23) who showed 100% efficiencies for all aspiration rates at or below 0.15 ml/min. Decreased efficiencies were not reported until the aspiration rate was increased to 0.5 ml/min. The aspiration rate used for the present solution studies was 0.076 to 0.18 ml/min. The sample introduction efficiency was left as 1.00 for the solids.

The reactivity/ionization constant is the parameter used to adjust for reactions or ionization of sodium atoms after excitation by the laser pulse. Such phenomena would decrease the fluorescence intensity measured from a given initial concentration of sodium atoms. Muller et al., (24) reported that the ionization of excited-state sodium atoms is not fast enough to significantly decrease atomic fluorescence in a hydrogen/oxygen/nitrogen flame. They also reported that reactions of sodium atoms with H₂O may be significant. In the present study, this coefficient was assumed to be unity.

The SOLGASMIX computer code was used with the NaSSi data base to calculate the percentage of atomic sodium of the sodium introduced into the flame. This program is designed to calculate the distribution of compounds in multi-component systems by free energy minimization. The values so calculated will be referred to as R_{th} values.

The gas-phase sodium atom densities can be calculated (14) from the fluorescence measurements through the use of Equation 2. This equation is valid for a three-level system in which saturation has been achieved. Equation 2 was modified (25) to allow the calculation of the sodium atom density from the total intensity of fluoresced light, producing Equation 3. The Einstein coefficient for spontaneous emission was assumed to be the same for both the $^2P_{1/2}$ and $^2P_{3/2}$ energy levels (14).

$$N_{tf} = (1 + (g_1/g_3)) \frac{I_3}{h\nu (A_3/4\pi)\Omega_C V_C} + \frac{I_2}{h\nu (A_2/4\pi)\Omega_C V_C} \quad (2)$$

$$N_{tf} = (1 + (g_1/g_3)) \frac{0.67I_t}{h\nu (A_3/4\pi)\Omega_C V_C} + \frac{0.33I_t}{h\nu (A_2/4\pi)\Omega_C V_C} \quad (3)$$

The equation symbols and employed values are listed below.

g_1 = the degeneracy of the $2S_{1/2} = 2$

g_2 = the degeneracy of the $2P_{1/2} = 2$

g_3 = the degeneracy of the $2P_{3/2} = 4$

I_3 = the fluorescence intensity of $2P_{3/2}$ level

I_2 = the fluorescence intensity of $2P_{1/2}$ level

I_t = $I_2 + I_3$

h = Plank's constant = 6.63×10^{-34} Js

ν = the frequency = 5.09×10^{14} s⁻¹

$A_3=A_2$ = Einstein coefficient for spontaneous emission = 6.28×10^7 s⁻¹

Ω_C = the solid angle cut by the collection optics = 0.14 sr

V_C = the sample volume (mm³)

N_{tf} = the atom density calculated from fluorescence (atom/mm)

Four values were calculated for each solid: N_{ta} , N_{tf} , R_{fa} , R_{th} . The N_{ta} value is a calculation of the total sodium density (gas, liquid, and solid) in the sample region. The N_{tf} value is a measurement of the concentration of gas-phase atoms. Dividing N_{tf} by N_{ta} yields R_{fa} , the mole fraction of total sodium present as gas-phase atoms. The R_{th} value is this same fraction calculated using SOLGASMIX for a condition when all species have equilibrated.

Note that the symbolism for the various calculated and derived values used in this report differs slightly from that used previously. What was formerly called N_{tf}/N_{ta} is now referred to by one symbol: R_{fa} (ratio of fluorescing sodium to aspirated sodium). For consistency, the fraction of gas-phase atoms predicted by calculations is now referred to as R_{th} (thermodynamic ratio, formerly N_{tt}). The symbol N_{tt} is now reserved for atom concentrations projected from N_{ta} and calculated R_{th} values (see Section 2.4.4).

For the study of the chars from Beulah lignite, the percent sodium lost and the carbon lost from the Beulah lignite was calculated from Equations 4 and 5, respectively. Ash is used as a tracer. McCollor used Equation 4 in his study of the coal chars (20).

$$1 - \frac{RC}{OC} \frac{OA}{RA} \times 100 = \%C \quad (4)$$

$$1 - \frac{RNa}{ONa} \frac{OA}{RA} \times 100 = \%Na \quad (5)$$

Where

OA = % Ash in original sample

RA = % Ash in the residual sample

OC = % original carbon

RC = % residual carbon

ONa = % original sodium

RNa = % residual sodium

2.4 Results and Discussion

2.4.1 Solution Studies

After optimizing the optical alignment and the laser output, work with solutions was started. The first question to be addressed was whether it was possible to achieve saturation with our system, since there are several advantages in operating under saturated conditions. Saturation occurs when the upper state density, N_k , is related to the lower state density by the factor g_l/g_k , where g_n is the degeneracy for the state. For a two-level system at saturation, the fluorescence intensity is independent of the quenching rates and the laser intensity (26). Here the quenching rates are those for collision deactivation and for chemical reactions. Figures 8 and 9 show the fluorescence signal of sodium benzoate solution minus a blank, water, versus the reference reading in volts (which is a measure of the relative laser intensity) for the Phase-R and Candela systems. In the case of the Phase-R laser, saturation occurred around 3.0 volts, and for the Candela laser, around 0.5 volts.

Figure 8. Saturation profile for Phase-R laser using a 1500- μ g Na/ml sodium chloride solution. The N_{ta} value at the center of the flame was 7.5×10^{10} atoms/mm³. The horizontal position was 0.000 inches (0.000 inches corresponds to the center of the burner); the vertical position was 0.415 inches above the burner.

Figure 9. Saturation profile for the Candela laser using a 1500- μ g Na/ml sodium benzoate solution. The N_{ta} value at the flame center was 1.2×10^{11} atoms/mm³. The horizontal position was 0.300 inches (0.000 inches corresponds to the center of the burner); the vertical position was 0.415 inches above the burner.

Next, horizontal fluorescence profiles of sodium solutions were studied. Figures 10 and 11 show the results obtained using a 1500- μg Na/ml sodium benzoate solution at vertical positions of 0.415 and 1.915 inches above the burner. The results are reported in terms of $R_{fa} = N_{tf}/N_{ta}$, where N_{tf} is the measured gas-phase sodium atom density and N_{ta} is the total sodium density (gas, liquid, and solid) in the same region. This value gives the ratio of the fluorescing sodium atoms to the total sodium introduced, and corrects for slight differences in the introduction rates.

To determine the fraction of the total signal that was due to scattered and reflected light, the signal for water was measured and subtracted. This was done for all solution studies. In order to determine if water was an appropriate background, the signals from a solution of potassium chloride and water were compared. No significant differences were observed.

In order to decrease the amount of scattering in our signal we adopted the technique used by Daily (25). The laser light was horizontally polarized by the series of Schott prisms. Since the laser light was polarized, the scattered light is horizontally polarized and lower in intensity than what would be scattered from an unpolarized laser beam. The fluorescence, however, is not polarized. By placing a polarizer in the sample path such that it passes vertical light, it is possible to decrease the ratio of scattered light to fluorescence light that is collected by the monochromator, since the scattered light is effectively totally cut out by the polarizer while the unpolarized fluorescence light is reduced by 50%. Daily achieved a fluorescence signal of 2×10^{-7} times that of the scattered signal (25). For the LIFS system, the fluorescence signal for a 1500- μg /ml solution was typically 10 to 15 times that of the signal for water.

A horizontal fluorescence profile for a 3000- μg Na/ml sodium chloride solution (Figure 12) differs little from that for the sodium benzoate. This result is in agreement with the work of Sweeney and coworkers (27), who had measured the fluorescence from five differing sodium solutions (NaCl , Na_2CO_3 , $\text{Na}_2\text{C}_2\text{O}_4$, $\text{Na}_2\text{S}_2\text{O}_3$, $\text{NaCO}_2\text{C}_6\text{H}_5$, and NaOH) using an LIFS system. They found that fluorescence intensity was independent of the sodium source when using solutions.

These curves, along with all of the fluorescence profiles done so far, show a high degree of asymmetry about the flame center. This is attributed to self-absorption. As is expected, the solution of higher concentration shows a greater slump on the far side of the flame--the side opposite the optics. (See Figures 10 and 12). This is consistent with the work of Daily and Chan (17). As a result, only measurements taken from the flame center out to a horizontal position of 0.30 inches can be used for quantitative calculations.

To determine the effect of self-absorption on the fluorescence, the fluorescence signal was measured for a series of solutions with differing sodium concentrations. The concentrations selected were those that would give total sodium concentrations in the flame close to those we would obtain from the solids. Figure 13 shows the results of this work. It is clear from this graph that in the region of 1.0×10^{17} to 3.0×10^{17} atoms/ cm^3 , that N_{tf} is linearly related to N_{ta} . It is also clear that at these concentrations, N_{tf} has fallen off from that of lower concentrations. However, as long as a calibration curve like Figure 13 is available it is possible to obtain quantitative data from an LIFS system.

Figure 10. Horizontal fluorescence profile of a 1500- μg Na/ml sodium benzoate solution. The N_{ta} value at the flame center was 1.0×10^{11} atoms/mm. A horizontal position of 0.000 inches corresponds to the center of the burner; the vertical position was 0.415 inches above the burner.

Figure 11. Horizontal fluorescence profile of a 1500- μg /ml sodium benzoate solution at 1.915 inches above the burner. The N_{ta} value at the flame center was 1.4×10^{11} atoms/mm.

Figure 12. Horizontal fluorescence profile of a 3000- $\mu\text{g Na/ml}$ sodium chloride solution. The N_{ta} value at the flame center was 2.4×10^{11} atoms/ mm^3 . A horizontal position of 0.000 inches corresponds to the center of the burner; the vertical position was 0.415 inches above the burner.

Figure 13. Concentration curve for sodium chloride solutions. A horizontal position of 0.290 inches was used (0.000 inches corresponds to the center of the burner); the vertical position was 0.415 inches above the burner.

The distribution of sodium species in the flame was calculated (28) using SOLGASMIX, which predicted that 39.8% of the sodium introduced would be present as atomic sodium. The measured value is, however, 7.0%. The results of the SOLGASMIX calculation are shown in Table 4. The temperature used for the calculation, 1548 K, is that seen at about 0.30 inches from the center of the burner.

Possible reasons for the difference between the predicted value and the measured value are:

1. The sample introduction efficiency is incorrect.
2. The data base for the calculation is incomplete or incorrect.
3. The system has not achieved a minimum free energy.
4. Not all of the necessary parameters have been accounted for in the equation for N_{tf} .

It is possible that the sample introduction efficiency is incorrect, since it was difficult to measure accurately because the introduction rates used are so low. The efficiency, however, is at most, double that used. It is also possible that the value calculated for N_{tf} is in error, since the efficiency of the photomultiplier tubes were not calibrated; instead the response was calculated from the equations and graphs supplied by Hamamatsu in their catalogue. However, the most likely cause of the difference is that the flame has not reached a thermodynamic minimum.

2.4.2 Solids feeders

Before any solids work could be done, a reliable solids feeder had to be built. Several models were built and tested before one was settled upon. The first model was a spouting bed feeder (Figure 14). This feeder consisted of a sealed cone with a circulation pump attached to it. The pump pulled the circulating gas, which was argon, out of the top of the feeder into the bottom, where some of the gas was sent through the bed of solid and the rest was sent

TABLE 4
DISTRIBUTION OF SODIUM IN THE FLAME

Compound	Mole %
Na(g)	39.8
NaH(g)	0.1
Na ₂ (g)	2.7×10^{-5}
NaOH(g)	60.1

Figure 14. Spouting Bed Feeder.

up a pipe through the center of the cone. This gas would carry the solid out the exit tube on the side of the feeder. This feeder would feed solids evenly but not for the times needed for this study. As Figure 15 shows, when the solids feeder had just been filled, the feed rate was relatively slow and even, but as it emptied out, the feed rate decreased. Also, in order to get it to feed solids that were difficult to feed, it was necessary to place a vibrating rod against it. It was possible to get the feeder to feed fairly evenly for a long period of time by filling it very full (Figure 16). However, since this feeder required a vibrating rod to run properly, which made it very noisy and annoying to use, and since it needed many grams of sample to fill it, the use of this feeder was abandoned.

The second feeder built is shown in Figure 17. It consisted of a plastic cone with a tube, which was turned by a stepper motor at the top of the cone, down the center of the cone. Attached to the tube was a series of stirring wires and, inserted into the bottom of the tube was another tube with holes cut into it. The solid would be agitated by the stirring wires and fall into the holes in the bottom tube. A carrier gas fed into the top of the feeder would flow down the center tube and pick up any solid in the tube, and exit out the bottom of the feeder. This feeder fed solids relatively evenly for a long period of time, but not over short periods of time, since for every step turn of the motor it fed a pulse of solid. This meant that a microsecond laser shot might miss the pulse altogether.

The third feeder (Figure 18) built was the one used for all of the solids work. Again, the solids feeder consisted of a plastic cone with a metal tube, which was turned by a stepper motor, down its center. A series of propellers for stirring the solid was attached to the center tube, and another tube with three holes cut into it was inserted into the bottom of the center tube. Attached to this bottom tube was a solids trap and the gas line for the carrier gas. The gas would carry any solid that had fallen into the bottom tube out of the top of the center tube, where it would create a cloud of solid in the top of the feeder. The gas with entrained solid would then exit out of the exit tube in the side of the feeder. Solid feed rates obtained from this feeder are usually between 0.010 and 0.050 g/min. Figure 19 shows how the feed rate for this feeder typically varies with time. When this feeder was used to obtain a fluorescence profile for a solid, the feed rate was checked before and after the profile was taken to increase our confidence in the measured feed rate for that profile. If any change in feed rate was measured, the fluorescence profile was repeated.

2.4.3 Solids

Nine different solids were studied including a series of solid sodium salts, a mixture of a solid sodium salt and elemental sulfur, a series of three lignites, and a sample of decolorizing carbon with sodium deposited upon it. Horizontal fluorescence profiles were taken for all of the solids at 0.415 inches above the burner top, and for a few of the solids, profiles were also taken at 1.915 inches above the burner top. Because the optical system was sensitive to small changes, before a horizontal fluorescence profile was taken for a given solid, the system was calibrated by measuring the horizontal fluorescence profile of a 1500- μ g Na/ml solution of sodium benzoate.

Figure 15. Mass flow rate for the spouting bed solids feeder. The feeder was only partially filled with solid.

Figure 16. Mass flow rate for the spouting bed solids feeder when it was full.

Figure 17. Stirring Feeder.

Figure 18. Spinning Spouter Feeder.

Figure 19. Mass flow rate for the spinning spouter solids feeder.

As was discussed in the section on solids preparation (2.2.3), all of the solids were sized by grinding and sieving. The resulting particle sizes were determined with a Malvern laser scattering apparatus. Table 5 shows the analysis results.

In these solids studies background signals can be measured by detuning the laser to shorter wavelengths, out of resonance with the sodium absorption line. However, even when the laser was detuned four nanometers it was found that a large portion of the background signal was fluorescence caused by continuum emission of the laser. For example, the off-resonance (continuum-induced) signal for a 1000- μ g Na/ml sodium benzoate solution was 143% and 170% of that for deionized water at -0.145 and 0.145 inches from the geometric center of the burner, respectively, and 0.415 inches from the top of the burner. Under these circumstances, it is difficult to estimate the true background (from scattering and reflection). The lack of a background measurement is acceptable as long as the fluorescence signal is significantly larger than the signal due to reflection and scattering, as is usually the case. Figure 20 shows the fluorescence and background signal for solid sodium benzoate. The sodium benzoate curve shown here is typical of the solids. Background signals were measured for all of the solids except the sodium carbonate, sodium sulfate, and sodium benzoate deposited on decolorizing carbon. However, since a significant amount of off-resonance (continuum-induced) fluorescence occurred for sodium solutions, and since the background is small relative to the fluorescence signal, the horizontal fluorescence profiles of the solids are all graphed here without subtracting a background signal.

TABLE 5
PARTICLE SIZE ANALYSES OF SOLIDS

Solid	Mean Particle Size (μm)	Range (μm)
Sodium benzoate	68	20-250
Sodium chloride	79	60-115
Sodium carbonate	26	6-62
Sodium montmorillonite	69	5-100
Sodium sulfate	40	10-80
Plain Beulah lignite	20	6-60
Demineralized Beulah lignite	40	10-80
Sodium-loaded, demineralized Beulah lignite	40	8-112

Figure 20. Horizontal fluorescence profile of solid sodium benzoate. [] is the fluorescence signal and + is the background signal. The vertical position was 0.415 inches above the burner head. The N_{ta} at the flame center was 1.2×10^{11} atoms/mm³.

The solids can be divided into three groups: those that give high sodium atom densities in the flame, those that give densities similar to that of solutions, and those that gave a density much lower than that for solutions.

2.4.3.1 The Low Sodium-Releasing Solids

In this last group were two solids: sodium montmorillonite and solid sodium chloride. Figure 21 is a horizontal fluorescence profile of solid sodium montmorillonite. As Table 3 shows, this salt is siliconaceous in content. The solid sodium chloride is the only simple salt solid in this group. A horizontal fluorescence profile for solid sodium chloride was first done with the Phase-R laser (see Figure 22). Because this was the only salt that behaved in this manner, it was decided to repeat this profile using the new system (see Figure 23). Again, the R_{fa} for solid sodium chloride was significantly lower than that for the sodium benzoate solution.

The fluorescence measurements agree qualitatively with the thermodynamic calculations done for the solid montmorillonite and sodium chloride. The results from thermodynamic calculations for these solids are shown in Tables 6 and 7. The SOLGASMIX calculation for the sodium montmorillonite used the NaAlSSi data base and the temperature was 1821 K (28). SOLGASMIX was modified for the calculation of the distribution of the sodium from the solid sodium chloride by adding chloride species likely to be in the flame to the data base and deleting sulfur and silica species. The chloride species included were the same as those used by Wibberly and Wall (8). The data base used to make this calculation is listed in Table 8.

For both solids the percentage of gas-phase atomic sodium is predicted to be lower than that for the sodium benzoate solution (See Tables 4, 6 and 7). For the sodium benzoate solution, the predicted percentage of gas-phase sodium was 40% of the total sodium. The percentage of sodium predicted to be present in the flame as gas-phase atoms was 7.4% for the sodium montmorillonite and only a trace percentage for the sodium chloride. Sodium chloride was predicted to be present almost entirely as sodium chloride gas. The calculations were also done for two other temperatures (1225 and 1925 K); the results differed little from those obtained at 1821 K (Table 7).

2.4.3.2. The Moderate Sodium-Releasing Solids

The solids that gave sodium atom densities similar to solutions were the other simple sodium salts. Figures 24 and 25 are horizontal fluorescence profiles for solid sodium carbonate and sulfate taken 0.415 inches above the burner head. Also included in this group is the solid sodium benzoate (Figure 20). All of these salts have R_{fa} peaks around 0.050. Figures 26 and 27 show horizontal fluorescence profiles for solid sodium carbonate and sulfate at 1.915 inches above the burner head. These profiles have R_{fa} peaks roughly the same as those lower in the flame.

The distribution of sodium calculated from SOLGASMIX (29) for the sodium benzoate was nearly identical to that calculated for the sodium benzoate solution. The NaSSi data base was used and the temperature used was 1821 K. The results of this calculation are shown in Table 9.

Figure 21. Horizontal fluorescence profile of solid sodium montmorillonite. The N_{ta} value at the flame center was 2.4×10^{11} atoms/mm³. A horizontal position of 0.000 inches corresponds to the center of the burner; the vertical position was 0.415 inches above the burner.

Figure 22. Horizontal fluorescence profile of solid sodium chloride, obtained using the Phase-R laser at a vertical position of 0.415 inches above the burner. The N_{ta} value at the center was 2.0×10^{11} atoms/mm³.

Figure 23. Horizontal fluorescence profile of solid sodium chloride, obtained using the Candela laser at a vertical position of 0.415 inches above the burner. The N_{ta} value at the center was 1.9×10^{11} atoms/mm³.

TABLE 6
DISTRIBUTION OF SODIUM FROM SODIUM MONTMORILLONITE

Compound	Mole %
Na(g)	7.4
NaH(g)	0.02
NaOH(g)	11.2
NaOH(l)	0.2
Na ₂ Si ₂ O ₅ (l)	81.2
Na ₂ SiO ₃	0.09

TABLE 7
DISTRIBUTION OF SODIUM FROM SODIUM CHLORIDE

<u>Compound</u>	<u>Mole %</u>
Na(g)	3.87×10^{-3}
NaH(g)	1.42×10^{-5}
Na ₂ Cl(g)	1.60×10^{-10}
NaCl(g)	~100
NaOH(g)	1.38×10^{-3}

TABLE 8
GASEOUS AND CONDENSED SPECIES FOR THE
THERMODYNAMIC CALCULATIONS ON SODIUM CHLORIDE

<u>Gaseous</u>
Cl, ClO, ClO ₂ , CO, CO ₂ , H, H ₂ , HCl, H ₂ O, Na, NaH, Na ₂ , NaOH, NaCl, O, O ₂ , OH
<u>Liquid</u>
NaOH, NaCl, Na ₂ O
<u>Solid</u>
Na, Cl, C

Figure 24. Horizontal fluorescence profile of solid sodium carbonate at a vertical position of 0.415 inches above the burner head. The N_{ta} value at the center was 3.1×10^{11} atoms/mm³.

Figure 25. Horizontal fluorescence profile of solid sodium sulfate. The N_{ta} value at the flame center was 2.7×10^{11} atoms/mm³. A horizontal position of 0.000 inches corresponds to the center of the burner; the vertical position was 0.415 inches above the burner.

Figure 26. Horizontal fluorescence profile of solid sodium carbonate at a vertical position of 1.915 inches above the burner. The N_{ta} value at the center was 3.7×10^{11} atoms/mm.

Figure 27. Horizontal fluorescence profile of solid sodium sulfate at a vertical position of 1.915 inches above the burner. The N_{ta} value at the center was 3.6×10^{11} atoms/mm. A horizontal position of 0.000 inches corresponds to the center of the burner.

TABLE 9
DISTRIBUTION OF SODIUM FROM SODIUM BENZOATE

<u>Compound</u>	<u>Mole %</u>
Na(g)	39.5
NaH(g)	0.1
Na ₂ (g)	4.3×10^{-5}
NaOH(g)	60.5

2.4.3.3 The High Sodium-Releasing Solids

The group of solids that gave high sodium atom densities in the flame includes the lignites and the decolorizing carbon with the sodium deposited upon it. Figures 28 through 32 are horizontal fluorescence profiles for the solids: plain Beulah lignite, demineralized Beulah lignite, and demineralized Beulah lignite loaded with sodium acetate. Figures 33 and 34 are horizontal fluorescence profiles of the decolorizing carbon with sodium deposited upon it at 0.415 and 1.915 inches above the burner. These solids give a greater percentage of atomic sodium in the flame. The fact that they have the ability to generate a reducing environment around the vaporizing sodium may explain these larger percentages. The mole fraction of atomic gaseous sodium has been previously predicted (30) to be 0.82 from thermo-dynamic calculations on a Beulah lignite using SOLGASMIX. Note that this is approximately twice as much as calculated for solution sources or for solid sodium benzoate (see Table 4 and 9).

The Beulah lignite and the decolorizing carbon with the sodium benzoate deposited upon it were the only two solids that gave R_{fa} values at 1.915 inches significantly different from those at 0.415 inches above the burner. The change in temperature, which decreases approximately 200°C going from 0.415 to 1.915 inches above the burner, is not responsible for this decrease, since no similar decrease is seen for the simple solid salts, and SOLGASMIX does not predict such a significant drop for a decrease in temperature of 200°C at these temperatures. Instead, the difference is likely due to the differences in the solid matrix. For the Beulah lignite at 1.915 inches (a residence time of 35 msec) approximately 73% of the combustible material has burned away, but 70% of the sodium originally in the solid is still present. At 1.00 inches (a residence time of 17 msec), 67% of the combustible material has burned away, but 65% of the sodium originally in the solid is still present. (See Section 2.4.4 on the analysis of the char from Beulah lignite). The difference, then, between the Beulah lignite at 0.415 inches and 1.915 inches is in the reducing environment present around the solid at 0.415 inches. This reducing environment is responsible for the high concentration of sodium at 0.415 inches. At 1.915 inches, the bulk of the combustible material has burned away and the sodium environment approaches that of the low sodium-releasing solids. Sodium benzoate and organically bound sodium are

Figure 28. Horizontal fluorescence profile of Beulah lignite at a vertical position of 0.415 inches above the burner. The N_{ta} value at the center was 5.9×10^{18} atoms/mm³. A horizontal position of 0.000 inches corresponds to the center of the burner.

Figure 29. Horizontal fluorescence profile of Beulah lignite at a vertical position of 1.915 inches above the burner. The N_{ta} value at the center was 3.4×10^{18} atoms/mm³.

Figure 30. Horizontal fluorescence profile of demineralized Beulah lignite loaded with sodium. The N_{ta} value at the center was 1.6×10^{18} atoms/mm³. A horizontal position of 0.000 inches corresponds to the center of the burner; the vertical position was 0.415 inches above the burner.

Figure 31. Horizontal fluorescence profile of demineralized Beulah lignite at 0.415 inches above the burner. N_{ta} value at the center was 5.5×10^{18} atoms/mm³. A horizontal position of 0.000 inches corresponds to the center of the burner.

Figure 32. Horizontal fluorescence profile of demineralized Beulah lignite at a vertical position of 1.915 inches above the burner. The N_{ta} value at the center of the flame is 5.2×10^8 atoms/mm³.

Figure 33. Horizontal fluorescence profile of sodium-loaded decolorizing carbon at a vertical position of 0.415 inches above the burner. The N_{ta} value at the center was 4.5×10^8 atoms/mm³.

Figure 34. Horizontal fluorescence profile of sodium-loaded decolorizing carbon at a vertical position of 1.915 inches above the burner. The N_{ta} value at the center was 4.5×10^{10} atoms/mm³.

thought to decompose in a flame by similar mechanisms (31). That the sodium atom concentrations at 1.915 inches are not like those of the simple solid sodium benzoate, but more similar to the solid sodium chloride and sodium montmorillonite, suggests that the form of the sodium has changed; i.e., the sodium is no longer present as sodium benzoate or organically bound sodium. This is not an unreasonable proposition since the form of sodium in sodium benzoate itself changes during the combustion process. (See the discussion of the analysis of char from sodium benzoate in Section 2.4.4).

2.4.3.4 Summary of Solids Data

Figure 35 is a summary of the horizontal fluorescence profiles for solids. What is immediately apparent from this graph is that the matrix supporting the sodium is important in determining the amount of the gaseous atomic sodium measured. The solids with the sodium in contact with a carbon matrix (the Beulah lignites and the decolorizing carbon with the sodium benzoate deposited upon it) gave the highest R_{fa} values. The sodium montmorillonite, which has its sodium in an inorganic matrix, gave the lowest signal. It is unlikely, then, that sodium bound in clay matter is responsible for the fouling or for volatilized sodium in utility boilers. In general, the simple sodium salts all gave R_{fa} values close to those of the solutions. The one exception is the solid sodium chloride, which gave a signal much lower than that for a solution.

Figure 35. Peak R_{fa} values for horizontal profiles of each solid taken at a vertical position of 0.415 inches above the burner.

The solids, unlike solutions, show an anion effect; that is, a particle size effect. (Consider the sodium chloride solution and solid). How large is the sphere of influence of a particle? Note that calculations show that for the feed rates used, four percent of a particle is in the sample volume during one shot of the laser. This suggests that a gaseous environment is being observed for the solids, just as it is for solutions. This leads us to ask how much must the particle sizes be reduced before no anion effect is observed.

The reaction of potassium carbonate with a supporting carbon matrix also clearly shows a matrix effect (32). Potassium carbonate was deposited on two different carbon matrices--carbon black and graphite; then heated. On the carbon black, the potassium was found to decompose to potassium oxide and carbon dioxide, as in Reaction 6.

The potassium oxide reacted with the carbon matrix to form metallic potassium on the surface of the carbon black. The metallic potassium was found to migrate in to the carbon black matrix and was stabilized against evaporation. The potassium carbonate on the graphite decomposed to metallic potassium and carbon monoxide. However, the metallic potassium was not stabilized against evaporation and did not migrate into the graphite carbon matrix.

The fluorescence signal measured for the Beulah lignites was linearly related to the amount of sodium in the solid (see Figure 36). This is of interest since all of these solids have the same carbon matrix, although it is not clear that the form of the sodium is the same for all three coals, nor is the mineral content the same in all three lignites, since some of the minerals in the demineralized lignites were most likely washed away when the lignite was washed with hydrochloric acid. The amount of sodium present as atomic gas in the flame is determined by the carbon matrix and not by any mineral matter present in the solid. Calcium and magnesium, two minerals which at times decrease fouling, originally in the lignite, should have been washed away. It appears, then, that the loss of the calcium and magnesium has not influenced the percentage of gas-phase atomic sodium in the flame.

Chemical fractionation of the Beulah lignite showed 26% of the sodium by weight was water soluble, 66% was extracted by NH_4OAc , and 1% was extracted by HCl (see Table 10). The selective extraction of the minerals in the coal describes how the minerals are associated with the coal (33). The first extraction with water removes water-soluble elements, the second extraction with ammonium acetate removes elements that are associated as salts of organic acid groups, and the last extraction with hydrochloric acid removes organic coordination complexes, hydroxides, oxides, and carbonates. The inorganic components in the residue after all three extractions are assumed to be associated in the lignite with the insoluble clays, quartz, and pyrite minerals.

Chemical fractionation was not done on the demineralized lignite loaded with sodium. The sodium in the solid is either associated with the anionic sites on the lignite or present as a thin layer of sodium acetate on the surface of the solid (sodium acetate, since that was the salt used to reload the coal). The little sodium that remains in the demineralized Beulah lignite is most likely tied up in inert mineral matter.

Again, the fluorescence signal measured for the Beulah lignites was linearly related to the amount of sodium in the solid (See Figure 36). This is of interest since all of these solids have the same carbon matrix, although it is not clear that the form of the sodium is the same for all three coals, nor is the mineral content the same in all three lignites. The fact that a non-zero response was observed from the demineralized material demonstrates the sensitivity of the LIFS measurements.

2.4.4 Char Analysis

As is frequently done with most coal studies, we too found it beneficial to analyze the products from the combustion in the LIFS burner. To date, the chars from two solids have been studied.

The results of the char analysis for plain Beulah lignite are shown in Table 11. It is clear from these results that the sodium is not completely released from either solid for the residence times used. The percent sodium released from the Beulah lignite is 30%. For this calculation it was assumed that none of the ash residue in the original sample was lost when it was burned in the LIFS burner. In order to estimate the amount of carbon matter lost during the combustion process, the ash content of the original sample and the char were measured by thermogravimetric analysis, and the percentage ash was used as a tracer for the amount of carbon matter lost during the combustion process (see equations 4 and 5).

Figure 36. Concentration curve for Beulah lignite solid samples. The graph was made from peak R_{fa} values from each solid. The vertical position was 0.415 inches above the burner.

TABLE 10
CHEMICAL FRACTIONATION RESULTS FOR BEULAH 53-74- μ m LIGNITE

	<u>Wt% Extracted by Each Solvent</u>				<u>Wt% Remaining</u>
	<u>Initial μg/g</u>	<u>H₂O</u>	<u>NH₄OAc</u>	<u>HCl</u>	
Na	6900	26	66	1	7
Mg	3870	1	73	22	4
Al	9460	1	0	10	89
Si	15400	1	2	1	96
K	168	16	53	3	28
Ca	14200	1	45	22	32
Fe	11500	0	0	22	78

TABLE 11
ANALYSES OF BEULAH LIGNITE CHAR

Residence Time (sec)	% OA	% OC	% ONa	% RA	% RC	% RNa	% Combust. Loss	% Na Loss
0	13.10	78.10	0.55	---	---	---	---	---
17	13.10	78.10	0.55	27.87	55.56	0.765	66.6	34.6
35	13.10	78.10	0.55	33.46	54.26	0.985	72.8	29.9

OA = % Ash in original sample
RA = % Ash in the residual sample
OC = % original carbon
RC = % residual carbon
ONa = % original sodium
RNa = % residual sodium

The results from the char analysis of the simple salt, sodium benzoate, proved more difficult to interpret than those for the lignite. A comparison of our results to those of Stewart and Chakrabarti (31), who analyzed the thermal decomposition of sodium benzoate by thermogravimetric analysis (TGA) and differential thermal analysis (DTA), provides some insight into the reactions of the solid sodium benzoate in the flame. Stewart and Chakrabarti showed that the solid sodium benzoate decomposes when heated, according to Reaction 8 (31).

The resulting sodium carbonate decomposed analogously to the potassium carbonate in Reaction 7. Their data showed weight loss in two regions: 450°-550°C and 750°-900°C. The region between 550° and 750°C was shown to correspond to the stable product sodium carbonate. TGA analysis of our solid sodium benzoate mixture also showed two weight loss regions: one at 418°-762°C and the other above 900°C. Neither the char collected at 1.915 inches above the burner nor the char collected at 1.00 inches above the burner showed a weight loss between 450°-550°C. TGA analysis of plain, unburned decolorizing carbon was also done. It showed a weight loss beginning at 532°C. Therefore, the sodium that remained in the char is likely not present as sodium benzoate. Table 12 summarizes the TGA data for these solids.

In an attempt to calculate the amount of sodium and combustible matter lost from the sodium benzoate, the same equations used to calculate the percent sodium vaporized and the percent combustibles lost for the Beulah lignite were applied. This, however, gives rather peculiar results. The percent sodium lost is 70% to 85% and the percent combustibles lost is -33% to -34%; this means that the solid gained carbon matter during the combustion process. But it is unclear whether the assumption that no ash is lost during

the combustion process is valid for this pure salt. The ash residue from the TGA analysis of the sodium benzoate solid is most likely similar to the ash of the decolorizing carbon, sodium benzoate, and sodium carbonate. But the sodium benzoate and sodium carbonate are vaporized in the flame. Table 13 shows the results of the calculation for the percent vaporized sodium and lost combustibles for the sodium benzoate, without using ash as a tracer. About 67 to 81% of the sodium is thought to be vaporized.

TABLE 12
SUMMARY OF THERMOGRAVIMETRIC DATA FOR THE SOLIDS
OF THE SODIUM BENZOATE CHAR ANALYSIS

% WEIGHT LOST BY:				
Loss Type	Sodium Benzoate -Carbon Mix	Decolorizing Carbon	Char at 1.00 inches	Char at 1.915 inches
Water	2.81	4.88	2.93	2.97
Volatile matter	12.14 ^a	10.45 ^b	6.60	5.00
Combustible matter	78.85	81.38	85.51	86.92
Residue	6.19	3.28	5.03	5.08

^a Temperature range was 418°-763°C

^b Temperature range was 532°-891°C

TABLE 13
ANALYSES OF SOLID SODIUM BENZOATE CHARs

Residence Time (sec)	% OA	% OC	% ONa	% RA	% RC	% RNa	% Combust. Loss	% Na Loss
0	6.19	78.85	1.74	--	--	--	--	--
17	6.19	78.85	1.74	5.03	85.51	0.570	-8.4	67
35	6.19	78.85	1.47	5.08	86.91	0.320	-10	82

OA = % Ash in original sample
RA = % Ash in the residual sample
OC = % original carbon
RC = % residual carbon
ONa = % original sodium
RNa = % residual sodium

These results could account for some of the difference between the sodium atom ratio calculated from the fluorescence measurement, R_{fa} , and the sodium atom ratio calculated using SOLGASMIX, R_{th} . Using the value calculated from the char analysis for the percentage of sodium vaporized, a new density for sodium atoms in the flame can be calculated:

$$N_{tt} = R_{th} \times N_{ta} \times (\text{fraction lost}) \quad (9)$$

where the fraction lost is 100 times the % Na resulting from Equation 5. For example, for the Beulah lignite, since the maximum amount of sodium lost is $0.3 \times N_{ta}$, and the SOLGASMIX calculations typically predict that 80% of the sodium released is present as sodium gas, the maximum sodium atom density, N_{tt} , in the flame is predicted to be $0.24 \times N_{ta}$. Table 14 shows the results of such a calculation for Beulah lignite and for the solid sodium benzoate. Table 14 also shows the corresponding N_{tf} peaks for the N_{tts} . For the Beulah lignite, the agreement is quite good between N_{tt} and N_{tf} , but for the sodium benzoate solid it is not. In any case the char analysis has shown that the R_{th} values are 30 to 70% in error, since the mole fraction values input to calculate R_{th} are that much in error.

It is significant that more sodium was vaporized from the solid sodium benzoate than from the Beulah lignite, but a higher R_{fa} value was measured for the Beulah lignite than for the sodium benzoate; that is, the Beulah lignite has a greater ability to reduce the sodium to its atomic form, although the sodium is not as readily released from the lignite as it is from the organic solid salt. Note that the chemical fractionation results suggest that 8% of the sodium in the Beulah is present in inert mineral matter, which is not expected to release sodium readily.

2.4.5 Other Solid Studies

The effect of other flame constituents on the release of sodium was also studied, the first of which was sulfur. It was hoped some understanding of the interaction of sodium and sulfur would be gained, since sodium sulfate is often a major constituent in ash deposits in boilers, along with calcium sulfate and eutectics of calcium, sodium and sulfate (13, 34). Sulfur in coal, both organic and pyritic, is thought to be released as SO_2 , which reacts with alkaline constituents in the fly ash at lower temperatures (34). To determine the effect of sulfur on the release of sodium from sodium benzoate, solid elemental sulfur was mixed with solid sodium benzoate, and again with decolorizing carbon to enhance the feed characteristics of the solid. (Solid sulfur was used instead of sulfur dioxide gas because the LIFS system is not equipped to handle toxic materials such as sulfur dioxide. However, it is expected (35) that the sulfur does react with the oxygen in the flame to form sulfur dioxide.) Little difference was observed between the solid sodium benzoate and solid sodium benzoate mixed with sulfur (see Figure 37).

This is in agreement with the thermodynamic calculations done on the system using SOLGASMIX. The calculations show that for the concentrations of the sulfur used (0.005% of the total gas stream) the gaseous sodium atom concentration was not significantly affected until the temperature dropped to lower than 927°C. Temperatures lower than 927°C are only produced at the extreme outer edges of the flame where comparison of the data is difficult (36). If we are to observe an effect on the sodium atom concentration by

TABLE 14
A COMPARISON OF N_{tt} AND N_{tf}

Solid	N_{ta} (atoms/mm ³)	N_{tt} (atoms/mm ³)	N_{tf} (atoms/mm ³)
Beulah Lignite	7.9×10^{10}	1.9×10^{10}	7.6×10^9
Sodium Benzoate	1.5×10^{11}	4.2×10^{10}	7.38×10^9

Figure 37. Horizontal fluorescence profile of solid sodium benzoate mixed with elemental sulfur. The profile was taken at a vertical position of 0.415 inches above the burner head. The N_{ta} value at the center is 1.0×10^{11} atoms/mm³.

sulfur, it is likely that a new flame would have to be characterized and used. It was not practical to explore the effect of increasing the sulfur concentration.

Carbon dioxide is postulated to inhibit the release of sodium from sodium carboxylates. Chakrabarti found that decomposition of alkali carbonates occurred at 300°C higher in an atmosphere of carbon dioxide than in air (37). Carbon dioxide was added as a flame constituent in order to see if it would have any effect on the amount of sodium vaporized. In selecting a flame for

this study, gas flow rates were selected that would minimize changes in the flame. The gas flow rates of methane and oxygen were kept constant, and flow rate of the argon-30% carbon dioxide was adjusted so that a steady flame was achieved. A temperature profile of this flame is shown in Figure 6. Horizontal profiles of a standard sodium benzoate solution were obtained before and after changing the flame. The first profile was for checking the optical alignment, as is always done before taking a horizontal fluorescence profile of a solid; the second was for checking the effect of changing the flame on a well characterized system. Although there is some difference in the predicted major flame constituents (as Table 15 shows), the horizontal fluorescence profile for the sodium benzoate solution differs little from that taken using the standard flame. This result is in agreement with SOLGASMIX calculations, which predict the mole fraction of gaseous atomic sodium in the standard flame and the flame with the added carbon dioxide to be 0.0035 and 0.0031, respectively. Figure 38 shows the horizontal fluorescence profile for the solution at 0.415 inches from the burner. Figures 39 and 40 show the horizontal fluorescence profiles for decolorizing carbon with sodium deposited upon it in the new flame.

2.5 Conclusions

Laser-induced fluorescence spectroscopy is a valuable tool in the study of sodium volatilization from solids in flames. With an LIFS system, sodium fluorescence can be observed from solids. Different solids did give different sodium atom densities in the flame. This difference is related to the matrix supporting the sodium. The solids that gave low sodium-atom densities in the flame include sodium montmorillonite and sodium chloride. The montmorillonite results suggest that sodium tied up in aluminosilicates is not responsible for fouling in boilers. Solids that gave high sodium-atom densities were those which had their sodium supported by a carbon matrix, including the Beulah lignites and the sodium benzoate on decolorizing carbon.

The sodium released from the Beulah lignites was linearly related to the sodium atom densities resulting in the flame from sodium benzoate and the sodium benzoate on decolorizing carbon.

The addition of elemental sulfur and carbon dioxide had no effect on the sodium atom densities resulting in the flame from sodium benzoate and the sodium benzoate on decolorizing carbon.

The analysis of the char resulting from burning a solid in the LIFS burner also proved to be a valuable technique for analyzing the fluorescence data. The Beulah lignite was found to release approximately 30% of its sodium, while the solid sodium benzoate released 70%. These results emphasize the importance of the carbon matrix in reducing sodium to its atomic state.

With an LIFS system, it is possible to observe differing sodium atom concentrations in a flame. This LIFS study has shown the effect of different supporting matrices on the concentration of gaseous atomic sodium observed in a flame.

TABLE 15
PERCENTAGES OF THE MAJOR FLAME CONSTITUENTS
AS PREDICTED BY SOLGASMIX AT 1830 K

Flame	Ar(g)	CO(g)	CO ₂ (g)	H ₂ (g)	H ₂ O(g)
Standard	49.8	7.6	9.1	5.8	27.7
With CO ₂ Added	35.0	10.1	21.57	3.4	29.7

Figure 38. Horizontal fluorescence profile of sodium benzoate solution at a vertical position of 0.415 inches above the burner head. The N_{ta} value at the center is 1.2×10^{11} atoms/mm³. The methane/oxygen/argon-30% carbon dioxide flame was used.

Figure 39. Horizontal fluorescence profile of decolorizing carbon with sodium benzoate deposited upon it in the methane/oxygen/argon/carbon dioxide flame. The vertical position used was 0.415 inches above the flame. The N_{ta} value at the center of the flame was 6.6×10^{10} atoms/mm³.

Figure 40. Horizontal fluorescence profile of decolorizing carbon with sodium benzoate deposited upon it in the methane/oxygen/argon/carbon dioxide flame. The vertical position was 1.915 inches above the burner top. The N_{ta} value at the center was 6.6×10^{10} atoms/mm³.

2.6 Future Work

Future work for this project includes further studies into the effects of the matrix supporting the sodium species. Further studies like the study of the decolorizing carbon with the sodium benzoate deposited upon it will be done. Srinivasacher et al. (39) proposed the following reaction for sodium chloride:

If such a reaction occurs, the signal from a solid of sodium chloride deposited on some sort of carbon matrix should give an enhanced signal over that for the simple solid sodium chloride.

In order to gain some understanding of what sodium is vaporized, a Beulah lignite char is being prepared in a drop-tube furnace so that it would have approximately the same percent volatiles as a char prepared from burning the lignite in the LIFS burner. This char will be sent through the burner in order to see if additional sodium volatilization can be observed from the char.

3.0 TASK 3.2B: DROP-TUBE FURNACE PROJECT

3.1 Introduction

Coals contain a complex suite of inorganic species that include significant quantities of both organically associated cations and discrete minerals. Problems associated with inorganic constituents in coal combustion systems include ash deposition, fine particulate formation, and corrosion and erosion of boiler parts. Of specific interest are the interactions between those inorganic constituents that result in the formation of low melting-point phases during combustion and gas cooling. These phases are often the cause of ash deposition problems on boiler heat transfer surfaces. The formation of these low melting-point phases is a result of a combination of complex physical and chemical transformation of inorganic components associated in and with the coal during the combustion process. This task will study changes in the morphology and chemical associations of inorganic components in coals during combustion in a drop-tube furnace designed to simulate the time-temperature profile of a pulverized coal-fired utility boiler. The chemical and physical transformations of the inorganic constituents depend upon their association in the coal and upon combustion conditions. Volatilization and condensation of sodium is one of the key transformations that the drop-tube furnace project is investigating to gain insight into the formation of liquid phases in and on the surfaces of entrained ash particles. The primary objectives of the drop-tube furnace task are to determine the factors that affect the size and composition of the fly ash.

3.2 Equipment and Procedures

3.2.1 Drop-Tube Furnace System

The drop-tube furnace is a laboratory-scale, entrained-flow tube furnace with the ability to combust coal and produce ash under closely controlled conditions. Combustion parameters such as initial hot zone temperature, residence time, and gas cooling rate can be closely controlled and monitored.

The furnace system is housed in a three-floor laboratory specifically designed for clean and efficient operation of the system, as shown in Figure 41. The furnaces are mounted on furnace bars extending through all three levels. The furnaces can be moved to accommodate specific applications. The adjoining control room provides a clean, climate-controlled environment for the electronic equipment associated with the drop-tube system.

The furnace assembly consists of a series of vertically oriented tube furnaces illustrated in Figure 42. These furnaces possess a total of five independently controlled, electrically heated zones. Each of these furnaces can be used separately or in conjunction with the other furnaces. This allows for maximum flexibility and precise control over combustion conditions.

Coal, primary air, and secondary air are introduced into the furnace system by means of a preheat injector. This system injects ambient temperature primary air and coal into the furnace from a water-cooled probe assembly at the center of the tube. Secondary air is typically heated to 1000°C and introduced into the furnace through a mullite flow straightener. Thus, the material to be combusted is introduced into the top of the furnace along with preheated secondary air, and travels down the length of the furnace in a laminar-flow regime.

The coal feed system is designed to feed particles of various sizes at rates of 0.1 to 0.5 grams per minute and at primary carrier gas rates of approximately 1 liter per minute. The basic apparatus shown in Figure 43 consists of a pressurized plastic cone, a stepper motor, and a feed tube. The cone acts as the coal hopper. As the motor rotates the feed tube, the coal falls through the small holes in the tube and is carried out by the gas into the injector.

Fly ash is cooled by means of a fly ash-quenching probe shown in Figure 44. This system is reliable and versatile. Several collection devices can be added to the probe to collect the fly ash.

Size-segregating methods of fly ash collection are being employed. The Environmental Protection Agency Southern Research Institute Five-Stage Cyclone (EPAFSC) is being used on a routine basis to collect fly ash. The EPAFSC is designed to make five equally spaced particle size cuts (D50) on a logarithmic scale within the range of 0.1-10 micrometers. The advantage of this system is its capability of collecting the relatively large sample amounts needed for subsequent chemical and morphological analyses.

In addition to the EPAFSC, the University of Washington Mark 5 Source Test Cascade Impactor (STCI) is used during selected combustion tests. The STCI was developed as a means of measuring the size distribution of particles in stacks and ducts at air pollution emission sources. The Mark 5 impactor produces even-size cuts of fly ash particles by inertial separation. These data will be used for comparison with the EPAFSC data, and to provide more detailed information concerning the effects of combustion conditions on the size distribution of the fly ashes.

A short-residence-time probe was designed and constructed to collect ash samples at any residence time. The probe consists of a series of four concentric, water-cooled, steel tubes. The outer shell is for introducing the

Figure 41. Drop-tube furnace laboratory.

Figure 42. Cross-sectional diagram of the drop-tube furnace.

Figure 43. Drop-tube furnace coal feeder assembly.

Figure 44. Fly ash-quenching probe assembly for drop-tube furnace.

quench gas at the top of the probe. The innermost shell removes the combustion gases and the remaining shells carry the cooling water. The probe is covered with an alumina insulating cylinder two inches in outside diameter. This probe is illustrated in Figure 45.

The probe is inserted in the bottom of the furnace a set distance that is calculated from the desired residence time. The quench gas and the vacuum are turned on. The coal is fed through the preheat injector and collected with a cyclone or with the multicyclones. The samples collected are analyzed by SEM.

3.2.2 Characterization of Coal, Char, and Fly Ash

The coals are carefully sized using a sonic sieving device into three size cuts and characterized. These cuts include 38-53, 53-74, and 74-106 micrometers. Once sized, the coals are characterized by a variety of techniques to determine the abundance, size, and association of their constituents. In addition to conventional ashing followed by determination of the ash components, chemical fractionation and computer-controlled scanning electron microscopy are used to determine abundance and distribution of inorganic components as well as the size and type of mineral grains.

Chemical fractionation (1) is used to selectively extract elements from the coals based on how they are associated in the coal. Briefly, the technique involves extracting the coal with water to remove elements that are water soluble, followed by extraction with 1 M ammonium acetate to remove elements that are associated as salts of organic acid groups. The residue from the ammonium acetate extraction is extracted with 1 M HCl to remove acid-soluble species in the form of organic coordination complexes, hydroxides, oxides, and carbonates. The inorganic components in the residue after all three extractions are assumed to be associated in the coal with the insoluble clays, quartz, and pyrite minerals.

Computer-controlled scanning electron microscopy (CCSEM) is being used to characterize coal, char, and ash samples and inorganic combustion products. A computer program is used to locate, size, and analyze particles. Because the analysis is automated, a large number of particles can be analyzed quickly and consistently. The main component of the CCSEM analysis system is an annular backscattered electron detector (BES). The BES system is used because the coefficient of backscatter (the fraction of the incoming beam that is back-scattered) is proportional to the square root of the atomic number of the scattering atoms. This permits a high degree of resolution between sample components based on their atomic numbers. This means that minerals can be easily discerned from the coal or char matrix, and fly ash particles can be easily discerned from epoxy in polished sections. Brightness and contrast controls are used to optimize threshold levels between the coal or char matrix and mineral grains or fly ash particles. When a video signal falls between these threshold values, a particle is discerned and the particle center is located. A set of eight diameters about the center of the particle is measured, and the particle's area, perimeter, and shape are calculated. The beam is then repositioned to the center of the particle and an X-ray spectrum is obtained. The information is then stored to a Lotus® transportable file for data reduction and manipulation. The CCSEM data provides quantitative information concerning the discrete mineral species or noncrystalline inorganic phases present, and their size and shape characteristics. Since the same analysis can be performed on the initial coal, char, and resultant fly ash, direct comparisons can be made and inorganic transformations inferred.

Figure 45. Short-residence-time probe for drop-tube furnace.

In addition to the CCSEM analysis of coals to determine size and type of minerals, the technique has recently been expanded to determine the juxtaposition of minerals; i.e., how minerals are associated with each other, and whether mineral grains are associated within coal particles (inherent) or associated extraneous to coal particles. This information is extremely important with respect to understanding the transformations of inorganic constituents during combustion. In order to perform such an analysis, each frame analyzed by CCSEM was photographed, and the coordinates of the particles were located. Inherent and extraneous associations, and associations with other minerals were determined by visually examining each photograph.

Characterization of fly ash was performed using scanning electron microscopy and electron microprobe analysis. A technique was developed at the Energy and Mineral Research Center to determine the relative abundance of phases present in ashes and deposits (2). The technique is called SEM point count or SEMPC. The method involves microprobe analysis of a large number of random points in a polished cross-section of a sample. The quantitative analysis of each point is transferred to a computer file for data base analysis. New fortran software is used to calculate molar and weight ratios for each point. Using these ratios, the points that have compositions of known phases (common to ashes and coal minerals) are identified and counted. The software then finds the relative number of unknown phases. The unknown phases are those for which there are no known phases corresponding to the chemical composition. For this study, it was assumed that these points were amorphous. In addition, the average chemical composition of all the points in the sample were calculated.

X-ray photoelectron spectroscopy (XPS) and Auger spectroscopy were used to characterize the surface of the fly ashes. The XPS technique determines the binding energy of an electron removed from the outer 50 angstroms of the surface due to the impingement of beam x-rays. The binding energy of the electrons is a function of the elements present and their electronic environment. Thus, XPS can be used to determine both the chemical composition of, and the chemical species present on a surface. The Auger technique uses the electron beam as the ionization source and the Auger electrons that come from the secondary electron emission are measured. This technique can provide chemical composition data for very small areas on the order of 1 square micrometer. Thus, the Auger technique can be used to examine the first 20- to 50-angstrom depths of surface layers of individual fly ash particles.

SIMS is a surface analysis and depth profiling technique that utilizes an ion beam to bombard the sample. This produces emission of positive and negative secondary ions from the surface. These ions, both individual and clusters of atoms, are mass-analyzed with an energy-filtered quadrupole mass spectrometer. The technique is used for trace impurity analysis and offers extremely high detection sensitivity for many elements, full elemental detection capability (including hydrogen detection), and the ability to provide isotopic and molecular information.

3.2.3 Production and Characterization of Chars

Short-residence-time combustion tests were conducted to produce chars from the Monticello, Beulah, Robinson, Upper Freeport and Eagle Butte coals. The short-residence-time probe was inserted in the bottom of the drop-tube furnace at a distance from the tip of the injector that would give the appropriate residence time. The chars were analyzed for inorganic phases using CCSEM. Three types of inorganic phases were included in the CCSEM output: discrete mineral phases; thermally altered mineral phases that lack crystalline mineral structure but hold true to chemical compositions of known minerals; amorphous phases that have a consistent chemistry such as amorphous calcium aluminosilicate; and unknown amorphous compounds that do not have a chemical composition that matches known phases. Comparisons were made between the original coal minerals and the inorganic phases in the chars on an area-percent basis.

The 74-106-micrometer size fraction of Monticello coal was subjected to the combustion conditions shown in Table 16. The selected residence times were 0.1, 0.2, 0.5, and 0.8 seconds. The length of each test was five to seven minutes. The collected char samples were submitted for morphological and chemical analysis.

The 53-74- μm size fraction of Beulah was subjected to the combustion conditions shown in Table 17. The selected residence times were 0.1, 0.2, 0.5, and 0.8 seconds. The length of each test was five to seven minutes. The collected char samples were submitted for morphological and chemical analysis using scanning electron microscopy and CCSEM, respectively.

A 74-106- μm size fraction of Robinson coal was subjected to the combustion conditions shown in Table 18 to produce four chars at 0.1, 0.2, 0.5, and 0.8-second residence times. The coal was combusted at an initial temperature of approximately 1300°C and the chars were quenched in the short-residence-time probe at about 1200°C.

TABLE 16

DROP-TUBE FURNACE RUN CONDITIONS USED TO PRODUCE CHARS
FROM THE MONTICELLO LIGNITE

Residence Time, sec	0.1	0.2	0.5	0.8
Coal Size, μm	74-106	74-106	74-106	74-106
Primary Air, L/min	1.0	1.0	1.0	1.0
Secondary Air, L/min	3.0	3.0	3.0	3.0
Collection Probe				
Quench Gas, L/min	23.6	23.6	23.6	23.6
Coal Feed Rate, g/min	0.313	0.138	0.136	0.470
Distance From Injector				
Tip To Quench Probe, cm	7.1	14.1	35.3	56.5
Secondary Air				
Temperature, $^{\circ}\text{C}$	956	956	976	976
Mullite Tube Temp., $^{\circ}\text{C}$				
T1 (14 cm)	1295	1302	1306	1302
T2 (28.6 cm)	1302	1311	1313	1312
T3 (43.2 cm)	1284	1280	1279	1270
T4 (61.6 cm)	1256	1249	1258	1222

* Distance from tip of the injector

TABLE 17

DROP-TUBE FURNACE RUN CONDITIONS USED TO
PRODUCE CHARS FROM THE BEULAH LIGNITE

Residence Time, sec	0.1	0.2	0.5	0.8
Coal Size, μm	53-74	53-74	53-74	53-74
Primary Air, l/min	1.0	1.0	1.0	1.0
Secondary Air, l/min	4.0	4.0	4.0	4.0
Collection Probe				
Quench Gas, l/min	3.0	3.0	3.0	3.0
Coal Feed Rate, g/min	0.131	0.168	0.119	0.429
Secondary Air				
Temperature, $^{\circ}\text{C}$	1000	1000	1000	1000
Mullite Tube Temp., $^{\circ}\text{C}$				
T1 (6.35 cm)*	1500	1405	1423	1498
T2 (21.6 cm)	1444	1445	1460	1488
T3 (34.9 cm)	1465	1461	1471	1486

* Distance from tip of injector

TABLE 18
DROP-TUBE FURNACE RUN CONDITIONS USED TO PRODUCE
CHAR FROM ROBINSON COAL (74-106- μ m)

Residence Time, sec	0.1	0.2	0.5	0.8
Coal Size, μ m	74-106	74-106	74-106	74-106
Primary Air, L/min	1.2	1.2	1.2	1.2
Secondary Air, L/min	3.0	3.0	3.0	3.0
Collection Probe				
Quench Gas, L/min	23.6	23.6	23.6	23.6
Coal Feed Rate, g/min	0.14	0.24	0.33	0.25
Secondary Air				
Temperature, °C	928	952	976	974
Mullite Tube Temp., °C				
T1 (6.35 cm)	1310	1307	1308	1321
T2 (21.6 cm)	1327	1320	1313	1310
T3 (34.3 cm)	1320	1312	1294	1285
T4 (58.4 cm)	----	1296	1277	1248

* Distance from tip of injector.

Chars were produced using a 53-74- μ m sonically sieved fraction of Upper Freeport coal. The chars were produced in the UNDEMRC drop-tube furnace at five residence times under the conditions described in Table 19. The gas temperature was approximately 1500°C and the chars were quenched at approximately 1200°C. Thermal gravimetric analysis (TGA) was performed on the chars to monitor carbon burnout with time.

Eagle Butte short-residence-time chars were produced under the conditions shown in Table 20. The initial combustion temperature was 1500°C and the chars were quenched at approximately 1200°C. The 53-74- μ m coal size fraction was used for the char production. The chars were also analyzed using a TGA to determine carbon burnout at each residence time.

3.2.4 Production of Fly Ash

Fly ash was formed in the drop-tube furnace and size-classified using the multicyclone and impactor for Beulah, Robinson, Monticello, Upper Freeport, and Eagle Butte coals. Three coal size fractions were combusted, with particle sizes of 38-53 μ m, 53-74 μ m, and 74-106 μ m. The combustion temperature was approximately 1500°C and quench temperatures were about 1100°C. The residence time for the combusting particles was approximately 1 second. Table 21 summarizes the drop-tube furnace run conditions for the five test coals.

Fly ash was produced from the 53-74- μ m size fraction of coal at three different temperatures for the Beulah, Upper Freeport, and Eagle Butte coals. The different temperatures used were 1300, 1400, and 1500°C. The Robinson and Monticello 53-74- μ m coals were combusted at 1300°C and 1500°C. Fly ash from these test runs was size-segregated using the multicyclone and impactor. The run conditions for these tests are given in Table 22.

TABLE 19

DROP-TUBE FURNACE RUN CONDITIONS USED TO PRODUCE
CHAR FROM UPPER FREEPORT COAL (53-74 μm)

Residence Time, sec	0.05	0.10	0.20	0.50	0.80
Coal Size, μm	53-74	53-74	53-74	53-74	53-74
Primary Air, L/min	1.2	1.2	1.2	2.0	1.2
Secondary Air, L/min	3.0	3.5	3.5	2.5	3.0
Collection Probe					
Quench Gas, L/min	5.0	5.0	5.0	5.0	5.0
Coal Feed Rate, g/min	---	0.064	---	0.048	0.059
Secondary Air					
Temperature, $^{\circ}\text{C}$	982	982	983	982	992
Mullite Tube Temp., $^{\circ}\text{C}$					
T1 (6.35 cm)	1502	1498	1497	1503	1499
T2 (21.6 cm)	1567	1565	1565	1564	1562
T3 (34.3 cm)	1572	1570	1563	1552	1545
T4 (58.4 cm)	1567	1568	1562	1547	1531

* Distance from tip of injector.

TABLE 20

DROP-TUBE FURNACE RUN CONDITIONS FOR CHAR FORMATION
FROM EAGLE BUTTE COAL (53-74 μm)

Residence Time, sec	0.05	0.1	0.2	0.5	0.8
Coal Size, μm	53-74	53-74	53-74	53-74	53-74
Primary Air, L/min	1.0	1.0	1.0	1.0	1.0
Secondary Air, L/min	3.0	3.0	3.0	3.0	3.0
Collection Probe					
Quench Gas, L/min	4.0	4.0	4.0	4.0	4.0
Coal Feed Rate, g/min	0.25	0.18	0.31	0.31	0.095
Secondary Air					
Temperature, $^{\circ}\text{C}$	960	960	960	960	960
Mullite Tube Temp., $^{\circ}\text{C}$					
T1 (6.35 cm)	1503	1505	1506	1503	1507

* Distance from tip of injector.

TABLE 21
DROP-TUBE FURNACE RUN CONDITIONS FOR THE FORMATION OF FLY ASH
FROM COAL SIZE FRACTIONS

Coal Size, μm	38-53	53-74	74-106
Primary Air, L/min	1.0	1.0	1.0
Secondary Air, L/min	4.0	4.0	4.0
Collection Probe			
Quench Gas, L/min	3.0	3.0	3.0
Coal Feed Rate, g/min	0.183	0.316	0.13
Secondary Air			
Temperature, $^{\circ}\text{C}$	840	849	1000
Mullite Tube Temp., $^{\circ}\text{C}$			
T1 (14 cm*)	1498	1507	1498
T2 (28.6 cm)	1514	1521	1515
T3 (57.8 cm)	1513	1521	1533

* Distance from tip of the injector.

TABLE 22
DROP-TUBE FURNACE RUN CONDITIONS FOR MIDDLE SIZE CUTS
AT THREE DIFFERENT TEMPERATURES

Coal Size, μm	53-74	53-74	53-74
Primary Air, L/min	1.0	1.0	1.0
Secondary Air, L/min	3.0	3.0	3.0
Quench Gas, L/min	3.0	3.0	3.0
Coal Feed Rate, g/min	0.291	0.451	0.314
Secondary Air			
Temperature, $^{\circ}\text{C}$	933	930	930
Furnace Temperature, $^{\circ}\text{C}$	1300	1400	1500

4.0 RESULTS AND DISCUSSION

4.1 Characterization of Eagle Butte Coal, Char, and Fly Ash

4.1.1 Eagle Butte Coal Characterization

Three coal size fractions, including the 38-53- μm , 53-74- μm , and 74-106- μm fractions of Eagle Butte coal were characterized using XRF, XRD, chemical fractionation and CCSEM. The different size fractions are very similar in bulk ash composition. Composition of the ASTM ashes for the size fractions reveal high CaO and SO_3 levels, as shown in Table 23. Sodium content was fairly low at 0.9% in the bulk ash. Ash concentrations were determined for the samples and are listed in Table 23. The average ash content for the three size fractions (5.96%) is almost identical to the bulk coal ash content (5.99%).

TABLE 23
ASH COMPOSITION OF EAGLE BUTTE COAL AND SIZED FRACTIONS
(NORMALIZED OXIDE WT%)

Elemental Composition	Bulk Coal	38-53 μm	53-74 μm	74-106 μm
SiO_2	26.1	28.9	24.8	21.6
Al_2O_3	13.3	13.3	13.5	13.8
Fe_2O_3	5.7	5.4	5.8	6.1
TiO_2	1.3	1.3	1.2	1.2
P_2O_5	1.3	1.2	1.3	1.3
CaO	24.4	23.8	24.9	26.6
MgO	5.7	5.6	5.6	6.3
Na_2O	0.9	1.6	1.2	1.2
K_2O	0.10	0.20	0.1	0.1
SO_3	21.30	18.70	21.7	21.7
% Ash	5.99	6.46	5.86	5.55

Chemical fractionation results show similar values for all three size fractions (Table 24). A high level of calcium is associated in the coal as a carbonate, since close to 60% was dissolved in HCl. A significant portion, however, is also organically bound (34%-37%). Fairly high amounts of Fe and Al were removed by HCl. This suggests that the elements are associated either as a coordination complex or an acid-soluble mineral. These may be, in part, associated with a calcium aluminum phosphate compound, possibly crandallite, which was observed using CCSEM. The small amounts of Na in all size fractions were either organically bound or associated as water-soluble salts.

The major mineral phases observed using CCSEM in the three size fractions and the bulk coal were quartz, aluminosilicate, a calcium aluminum phosphorus mineral (crandallite), gypsum, and calcite. Minor contents of apatite, K- and Ca-aluminosilicates, and barite were also observed (Table 25).

Table 26 summarizes the size distribution of the minerals for the four coal size fractions. The bulk fraction shows a fairly even distribution of quartz and kaolinite (aluminosilicate) in all of the size categories except for the <1.2- μm range. Crandallite is most abundant in the 2.1-4.4- μm category for this size fraction. Overall, the 2.1-4.4- μm category shows the highest amount of mineral matter, with total mineral content equaling 1.64 wt% of the coal.

The 38-53- μm fraction showed a bimodal distribution of quartz. Most of the quartz was either >11 μm or between 2.1-4.4 μm in diameter. No kaolinite mineral grains were observed in the >11- μm range. The total mineral size distribution was also bimodal due to the distribution of the dominant quartz content, and the mineral content was 2.82 wt% of the coal.

TABLE 24
CHEMICAL FRACTIONATION RESULTS FOR EAGLE BUTTE COAL SIZED FRACTIONS

Eagle Butte 74-106- μ m Coal					
	Initial (μ g/g mf coal)	Removed by H ₂ O (%)	Removed by NH ₄ OAc (%)	Removed by HCl (%)	Unextracted (%)
Silica	10100	0	0	0	100
Aluminum	6800	0	0	37	63
Iron	4000	3	0	83	15
Calcium	17900	7	34	58	2
Magnesium	3500	11	57	26	6
Sodium	900	67	33	0	0
Potassium	200	50	0	0	50
Eagle Butte 53-74- μ m Coal					
	Initial (μ g/g mf coal)	Removed by H ₂ O (%)	Removed by NH ₄ OAc (%)	Removed by HCl (%)	Unextracted (%)
Silica	10500	0	0	0	100
Aluminum	6700	0	0	37	63
Iron	4000	8	0	78	15
Calcium	17700	7	34	58	2
Magnesium	3300	9	55	30	6
Sodium	1000	60	40	0	0
Potassium	400	75	25	0	0
Eagle Butte 38-53- μ m Coal					
	Initial (μ g/g mf coal)	Removed by H ₂ O (%)	Removed by NH ₄ OAc (%)	Removed by HCl (%)	Unextracted (%)
Silica	13500	0	0	0	100
Aluminum	7700	7	0	22	71
Iron	4200	5	0	79	2
Calcium	18600	5	37	57	2
Magnesium	3700	8	60	24	8
Sodium	800	13	88	0	0
Potassium	100	0	100	0	0
Sulfur	9900	16	20	62	2

TABLE 25
MINERAL CONTENT FOR EAGLE BUTTE COAL SIZE FRACTIONS
(Wt% Mineral Basis)

<u>Wt% Mineral-Basis</u>	<u>Bulk Coal</u>	<u>38-53 μm</u>	<u>53-74 μm</u>	<u>74-106 μm</u>
Quartz	39.54	49.16	46.88	44.21
Aluminosilicate	27.83	14.81	26.28	19.95
Fe-Aluminosilicate	0.15	0.23	0.44	0.01
K-Aluminosilicate	1.40	3.28	1.88	1.07
Ca-Aluminosilicate	1.35	2.12	2.16	2.68
Iron Oxide	0.65	0.34	2.44	4.68
Alumina	0.00	0.00	0.00	0.00
Pyrite	1.75	2.68	2.24	6.11
Gypsum/Barite	1.08	0.90	1.02	1.00
Calcite	2.16	3.22	1.51	0.73
Rutile	0.35	1.74	0.54	2.50
Barite	1.96	1.11	1.62	1.49
Gypsum	4.83	2.62	3.33	0.63
Apatite	1.62	0.21	0.00	0.30
Crandallite	10.64	8.00	3.32	8.84
Al-Sil/Gyp	0.08	0.67	0.37	0.21
Ankerite	0.03	0.22	0.03	2.16
Unknown	4.59	8.75	5.94	3.42
Wt% Total Minerals (Coal Basis)	1.64	2.82	1.36	1.93

TABLE 26
MINERAL SIZE DISTRIBUTION IN EAGLE BUTTE BULK AND SIZED FRACTIONS
(WT% MINERAL BASIS)

Mineral/Phase	Eagle Butte Bulk Coal Particle Size Categories (microns)						Total Area %
	<1.2	1.2-2.1	2.1-4.4	4.4-8.0	8.0-11	>11	
Quartz	0.84	4.18	10.50	8.36	6.73	8.30	38.90
Aluminosilicate	0.56	3.15	7.15	5.23	6.71	4.58	27.38
Fe-aluminosilicate	0.00	0.10	0.05	0.00	0.00	0.00	0.15
K-aluminosilicate	0.04	0.24	1.09	0.00	0.00	0.00	1.37
Ca-aluminosilicate	0.21	0.68	0.13	0.30	0.00	0.00	1.32
Iron Oxide	0.11	0.17	0.36	0.00	0.00	0.00	0.64
Alumina	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Pyrite	0.10	0.15	0.62	1.42	0.00	0.00	2.28
Gypsum/Barite	0.21	0.71	0.14	0.00	0.00	0.00	1.06
Calcite	0.12	0.92	0.86	0.21	0.00	0.00	2.12
Rutile	0.06	0.18	0.11	0.00	0.00	0.00	0.35
Barite	0.23	1.59	0.75	0.00	0.00	0.00	2.57
Gypsum	0.01	0.27	0.29	0.93	0.00	3.25	4.75
Apatite	0.00	0.19	0.61	0.79	0.00	0.00	1.59
Crandallite	0.16	1.89	6.06	2.14	0.00	0.00	10.25
Aluminosilicate/Gypsum	0.06	0.02	0.00	0.00	0.00	0.00	0.08
Ankerite	0.00	0.03	0.00	0.00	0.00	0.00	0.03
Unknown	0.48	1.95	1.92	0.80	0.00	0.00	5.15
Total (and PSD)*	3.19	16.42	30.64	20.18	13.44	16.12	100.00

Mineral/Phase	38-53 μ m Coal Particle Size Categories (microns)						Total Area %
	<1.2	1.2-2.1	2.1-4.4	4.4-8.0	8.0-11	>11	
Quartz	0.43	4.17	9.49	10.16	1.03	22.78	48.06
Aluminosilicate	0.32	2.28	4.30	4.86	2.72	0.00	14.48
Fe-aluminosilicate	0.01	0.14	0.07	0.00	0.00	0.00	0.23
K-aluminosilicate	0.06	0.39	0.82	1.20	0.74	0.00	3.21
Ca-aluminosilicate	0.15	1.05	0.86	0.00	0.00	0.00	2.07
Iron Oxide	0.00	0.14	0.19	0.00	0.00	0.00	0.33
Alumina	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Pyrite	0.00	0.24	0.11	3.13	0.00	0.00	3.48
Gypsum/Barite	0.00	0.42	0.46	0.00	0.00	0.00	0.88
Calcite	0.01	0.77	2.37	0.00	0.00	0.00	3.14
Rutile	0.00	0.13	0.44	1.13	0.00	0.00	1.70
Barite	0.02	0.75	0.09	0.59	0.00	0.00	1.44
Gypsum	0.00	0.10	0.50	0.00	0.00	1.92	2.52
Apatite	0.00	0.09	0.11	0.00	0.00	0.00	0.20
Crandallite	0.02	0.65	3.30	3.68	0.00	0.00	7.65
Aluminosilicate/Gypsum	0.09	0.37	0.20	0.00	0.00	0.00	0.66
Ankerite	0.00	0.12	0.09	0.00	0.00	0.00	0.21
Unknown	0.59	4.09	4.33	0.75	0.00	0.00	9.75
Total (and PSD)	1.70	15.90	27.72	25.50	4.48	24.69	100.00

TABLE 26 (CONTINUED)

Mineral/Phase	53-74 μm Coal Particle Size Categories (microns)						Total Area %
	<1.2	1.2-2.1	2.1-4.4	4.4-8.0	8.0-11	>11	
Quartz	0.53	3.68	9.75	9.52	7.81	14.64	45.95
Aluminosilicate	0.23	2.31	5.82	3.77	4.18	9.44	25.75
Fe-aluminosilicate	0.00	0.16	0.27	0.00	0.00	0.00	0.43
K-aluminosilicate	0.03	0.34	0.89	0.57	0.00	0.00	1.84
Ca-aluminosilicate	0.20	0.93	0.82	0.17	0.00	0.00	2.12
Iron Oxide	0.00	0.23	0.08	0.00	2.09	0.00	2.40
Alumina	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Pyrite	0.00	0.09	0.88	0.86	1.09	0.00	2.92
Gypsum/Barite	0.06	0.35	0.60	0.00	0.00	0.00	1.00
Calcite	0.08	0.53	0.87	0.00	0.00	0.00	1.48
Rutile	0.04	0.15	0.34	0.00	0.00	0.00	0.53
Barite	0.09	0.41	1.02	0.59	0.00	0.00	2.11
Gypsum	0.02	0.24	0.22	0.20	1.57	1.02	3.26
Apatite	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Crandallite	0.10	0.74	1.73	0.61	0.00	0.00	3.19
Aluminosilicate/Gypsum	0.04	0.18	0.15	0.00	0.00	0.00	0.37
Ankerite	0.00	0.03	0.00	0.00	0.00	0.00	0.03
Unknown	0.39	2.05	1.55	0.66	0.00	1.98	6.64
Total (and PSD)	1.80	12.42	25.00	16.95	16.74	27.09	100.00

Mineral/Phase	74-106 μm Coal Particle Size Categories (microns)						Total Area %
	<1.2	1.2-2.1	2.1-4.4	4.4-8.0	8.0-11	>11	
Quartz	0.21	2.46	7.21	8.07	2.38	22.69	43.01
Aluminosilicate	0.13	1.35	6.00	6.14	1.48	4.31	19.41
Fe-aluminosilicate	0.00	0.01	0.00	0.00	0.00	0.00	0.01
K-aluminosilicate	0.02	0.08	0.61	0.33	0.00	0.00	1.04
Ca-aluminosilicate	0.08	0.58	0.26	0.00	0.00	1.69	2.61
Iron Oxide	0.04	0.15	0.09	0.00	2.62	1.65	4.55
Alumina	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Pyrite	0.02	0.26	0.95	0.98	0.84	4.85	7.90
Gypsum/Barite	0.03	0.42	0.52	0.00	0.00	0.00	0.97
Calcite	0.03	0.37	0.32	0.00	0.00	0.00	0.71
Rutile	0.03	0.00	1.97	0.44	0.00	0.00	2.44
Barite	0.01	0.17	0.76	0.00	0.99	0.00	1.94
Gypsum	0.00	0.06	0.41	0.14	0.00	0.00	0.61
Apatite	0.02	0.18	0.09	0.00	0.00	0.00	0.30
Crandallite	0.12	1.46	4.95	1.89	0.00	0.00	8.42
Aluminosilicate/Gypsum	0.01	0.06	0.14	0.00	0.00	0.00	0.20
Ankerite	0.00	0.00	0.00	0.00	0.00	2.10	2.10
Unknown	0.10	1.50	1.50	0.69	0.00	0.00	3.79
Total (and PSD)	0.85	9.12	25.78	18.66	8.31	37.29	100.00

* PSD = particle size distribution.

In the 53-74- μm fraction, quartz and kaolinite were again fairly evenly distributed in all the size fractions except for the two lower ones (<1.2 μm and 1.2-2.1 μm). The overall total mineral size distribution was slightly bimodal, and the total mineral content was 1.36 wt% of the coal.

The largest size fraction of 74-106 μm had a large percentage (53%) of the quartz grains in the >11- μm size range. Kaolinite was mostly distributed in the 2.1-8.0- μm size range and the >11- μm size range. The total particle size distribution was bimodal and the total mineral content was 1.93 wt%.

Figures 46 and 47 summarize the particle size distributions of quartz and kaolinite, respectively, for the three size fractions and the bulk coal. The size distributions for quartz and kaolinite are very similar for all size fractions of coal except for the >11- μm category, where there is a 10%-15% variance in content. The distributions are bimodal, showing a peak between 2 and 8 microns and >11 microns. The size distribution for all minerals in the bulk and sized fractions, as shown in Figure 48, was bimodal, showing approximately 10% variance between quantities at different size ranges.

X-ray diffraction analysis of LTA samples from each of the four coal size fractions were exactly identical and confirmed the presence of the quartz and calcite, which were observed in the CCSEM analysis. The mineral crandallite was not found in any of the XRD analyses. The only other mineral observed was bassanite ($\text{CaSO}_4 \cdot 5\text{H}_2\text{O}$), which is notorious for forming in LTA environments where there is abundant Ca and S in the coal (3).

Additional microprobe analysis of the Eagle Butte bulk coal was performed to discern the morphology of the calcium-aluminum-phosphorus mineral. It is assumed that this mineral is crandallite ($\text{CaAlPO}_4 \cdot 5\text{H}_2\text{O}$) or a mixture of various Ca-Al-P-rich minerals, although XRD did not confirm their presence. Backscatter electron imaging and microprobe analysis revealed 2-3- μm rounded particles and fine coal structure infillings of crandallite in certain Eagle Butte coal grains. Microprobe analyses of selected crandallite particles are given in Table 27. An average composition of crandallite minerals detected by CCSEM is also given in the last column of Table 27. Basically, the aluminum and phosphorous components of this mineral remain fairly consistent but the calcium and iron levels vary drastically.

4.1.2 Eagle Butte Char Characterization

Five chars were produced in the drop-tube furnace at 0.05, 0.1, 0.2, 0.5, and 0.8-second residence times. Changes in the inorganics were noted from the initial coal to the 0.8-second char using CCSEM analysis.

Figure 49 compares the particle size distribution of discernable phases in the chars and original coal. During the first 0.5 seconds of combustion there are more 2.1-8.0- μm sized particles in the chars than in the coals. At 0.8 seconds a dramatic change occurs where the finer sized particles decrease drastically and particles in the >11- μm size range increase. The 0.8-second char shows more larger sized phases than the original coal. A possible explanation for these particle size distributions is that at the onset of combustion the large organically bound and finely disseminated calcium component

Figure 46. Distribution of quartz in Eagle Butte bulk coal and sized coal fractions.

Figure 47. Distribution of kaolinite in Eagle Butte bulk coal and sized coal fractions.

Figure 48. Particle size distribution for all minerals in the Eagle Butte bulk coal and sized coal fractions.

TABLE 27

COMPOSITION OF CRANDALLITE MINERALS IN EAGLE BUTTE BULK COAL (WT%)

Oxide	Composition of Selected Grains			Average Analysis From CCSEM
Na ₂ O	1.49	0.00	5.65	0.57
MgO	0.00	0.00	1.70	0.57
Al ₂ O ₃	41.91	44.58	39.35	38.45
SiO ₂	0.00	0.00	0.00	0.58
P ₂ O ₅	25.93	23.12	21.22	21.73
SO ₃	1.76	1.87	2.99	1.66
ClO	1.39	0.00	0.58	1.73
K ₂ O	0.87	1.68	0.68	1.37
CaO	19.60	19.45	16.28	31.43
Fe ₂ O ₃	5.40	6.93	9.91	1.30

Figure 49. Particle size distribution of inorganic phases detected by CCSEM in Eagle Butte chars and original coal.

forms tiny 1-5-micron particles, which coalesce further as combustion proceeds. By 0.8 seconds of combustion, coalescence of the finer sized and more reactive particles has occurred, as evidenced by greater quantities of larger inorganic particles.

The major phases identified in the chars and coal are compared in Figure 50. Some very pronounced changes that occurred during combustion include: 1) quartz and kaolinite were drastically reduced, 2) calcium oxide and calcium aluminosilicate increased dramatically, with calcium oxide being the dominant phase in all of the chars, and 3) calcium silicate and calcium aluminate (not shown in Figure 51) were produced during combustion.

Particle size distributions for individual inorganic phases are presented for each Eagle Butte char in Table 28. Direct comparisons of the particle size distributions of certain phases in the different chars were performed. Quartz, for example, showed a sharp reduction in content, especially in the >11- μ m size category, where it was most abundant in the coal (Figure 51). Kaolinite showed a similar sharp decrease in content in all size ranges from the onset of combustion, as depicted in Figure 52.

CaO appears to be dominating the overall particle size distribution of the chars. Figure 53, which shows the CaO distribution curves in the coal and chars, is very similar in appearance to the total char and coal inorganic phase distribution curves in Figure 49. The initial chars show large

a. Eagle Butte 0.05 Second Char

74

TABLE 28 (CONTINUED)

b. Eagle Butte 0.1 Second Char							
Mineral/Phase	Particle Size Categories (μm)						Total Area %
	<1.2	1.2-2.1	2.1-4.4	4.4-8.0	8.0-11	>11	
Quartz	0.0	0.0	0.5	0.4	0.0	0.0	0.9
Aluminosilicate	0.0	0.0	0.0	0.0	0.0	0.0	6.1
Fe-aluminosilicate	0.0	0.0	0.0	0.0	0.0	0.0	0.0
K-aluminosilicate	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Ca-aluminosilicate	0.1	0.9	3.4	2.4	1.0	2.4	10.3
Iron Oxide	0.0	0.0	0.1	0.0	0.0	0.0	0.1
Alumina	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Pyrite	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Gypsum/Barite	0.0	0.0	0.0	0.4	0.0	0.0	0.4
CaO-Rich	1.6	14.2	29.1	9.2	3.4	0.0	57.5
Rutile	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Barite	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Anhydrite	0.1	0.7	1.1	0.4	0.0	0.0	2.3
Apatite	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Dolomite	0.1	0.3	0.2	0.0	0.0	0.0	0.6
Aluminosilicate/Gypsum	0.0	0.1	0.0	0.0	0.0	0.0	0.1
Ankerite	0.0	0.0	0.2	0.3	0.0	2.4	3.0
Calcium Aluminate	0.0	0.3	0.6	0.0	0.0	0.0	0.9
Calcium Silicate	0.1	0.9	3.0	3.5	0.0	0.0	7.5
Unknown	0.4	2.6	6.3	0.3	0.8	0.0	10.3
Total	2.4	19.9	44.7	16.9	5.2	10.9	100.0

c. Eagle Butte 0.2 Second Char							
Mineral/Phase	Particle Size Categories (μm)						Total Area %
	<1.2	1.2-2.1	2.1-4.4	4.4-8.0	8.0-11	>11	
Quartz	0.0	0.0	0.6	1.9	0.0	0.0	2.6
Aluminosilicate	0.0	0.0	0.0	0.3	0.0	0.0	0.3
Fe-aluminosilicate	0.0	0.0	0.0	0.0	0.0	0.0	0.0
K-aluminosilicate	0.0	0.0	0.1	0.0	0.0	0.0	0.1
Ca-aluminosilicate	0.1	0.6	3.5	2.1	0.0	0.0	6.3
Iron Oxide	0.0	0.0	0.1	0.0	0.0	0.0	0.1
Alumina	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Pyrite	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Gypsum/Barite	0.0	0.0	0.1	0.0	0.0	0.0	0.1
CaO-Rich	0.8	8.2	27.5	17.3	0.7	0.0	54.4
Rutile	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Barite	0.0	0.0	0.1	0.0	0.0	0.0	0.1
Anhydrite	0.1	1.0	2.6	2.1	0.0	0.0	5.8
Apatite	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Dolomite	0.0	0.0	0.1	0.0	0.0	0.0	0.1
Aluminosilicate/Gypsum	0.0	0.1	0.6	0.5	0.0	0.0	1.2
Ankerite	0.0	0.1	0.1	0.0	0.8	0.0	0.9
Calcium Aluminate	0.1	0.1	0.7	1.0	0.0	0.0	2.0
Calcium Silicate	0.1	0.3	3.8	2.7	0.7	0.0	7.5
Unknown	0.3	1.9	8.0	6.4	2.1	0.0	18.7
Total	1.4	12.3	47.8	34.3	4.2	0.0	100.0

TABLE 28 (CONTINUED)

d. Eagle Butte 0.5 Second Char							
Mineral/Phase	Particle Size Categories (μm)						Total Area %
	<1.2	1.2-2.1	2.1-4.4	4.4-8.0	8.0-11	>11	
Quartz	0.1	0.3	3.0	6.9	1.7	0.0	12.0
Aluminosilicate	0.0	0.3	0.6	0.4	0.0	0.0	1.2
Fe-aluminosilicate	0.0	0.0	0.0	0.0	0.0	0.0	0.0
K-aluminosilicate	0.0	0.1	1.2	0.5	0.0	0.0	1.8
Ca-aluminosilicate	0.5	2.8	10.0	6.7	0.0	0.0	20.0
Iron Oxide	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Alumina	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Pyrite	0.0	0.1	0.0	0.4	0.0	0.0	0.5
Gypsum/Barite	0.0	0.2	0.2	0.0	0.0	0.0	0.5
CaO-Rich	1.0	9.7	13.1	11.4	1.5	0.0	36.7
Rutile	0.0	0.0	0.3	0.0	0.0	0.0	0.3
Barite	0.1	0.0	0.0	0.0	0.0	0.0	0.1
Anhydrite	0.1	0.6	1.1	0.0	0.0	0.0	1.8
Apatite	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Dolomite	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Aluminosilicate/Gypsum	0.2	0.6	1.0	0.9	0.0	0.0	2.6
Ankerite	0.0	0.0	0.3	0.0	0.0	0.0	0.3
Calcium Aluminate	0.0	0.1	1.0	0.0	0.0	0.0	1.1
Calcium Silicate	0.3	2.6	5.0	2.6	0.0	0.0	10.5
Unknown	0.7	2.9	5.7	1.2	0.0	0.0	10.5
Total	3.0	20.3	42.5	30.9	3.2	0.0	100.0

e. Eagle Butte 0.8 Second Char							
Mineral/Phase	Particle Size Categories (μm)						Total Area %
	<1.2	1.2-2.1	2.1-4.4	4.4-8.0	8.0-11	>11	
Quartz	0.0	0.0	0.0	0.7	0.8	4.8	6.4
Aluminosilicate	0.0	0.0	0.0	0.2	0.2	1.1	1.6
Fe-aluminosilicate	0.0	0.0	0.0	0.0	0.0	0.0	0.0
K-aluminosilicate	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Ca-aluminosilicate	0.0	0.2	0.7	3.4	2.7	4.3	11.3
Iron Oxide	0.0	0.0	0.0	0.0	0.0	0.3	0.3
Alumina	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Pyrite	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Gypsum/Barite	0.0	0.0	0.0	0.0	0.0	0.0	0.0
CaO-Rich	0.0	0.4	4.2	12.6	15.0	21.7	53.8
Rutile	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Barite	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Anhydrite	0.0	0.0	0.1	0.0	0.0	0.0	0.1
Apatite	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Dolomite	0.0	0.0	0.0	0.1	0.1	2.5	2.8
Aluminosilicate/Gypsum	0.0	0.0	0.1	0.0	0.1	0.0	0.2
Ankerite	0.0	0.0	0.1	0.2	0.4	0.8	1.4
Calcium Aluminate	0.0	0.0	0.2	0.4	0.3	0.6	1.5
Calcium Silicate	0.0	0.1	0.9	3.4	3.9	8.0	16.3
Unknown	0.0	0.2	0.5	1.1	1.4	1.2	4.4
Total	0.0	0.8	6.7	22.2	24.9	45.3	100.0

Figure 51. Transformation of quartz particle size distribution in Eagle Butte coal and chars.

Figure 52. Transformation of kaolinite particle size distribution in Eagle Butte coal and chars.

Figure 53. Transformation of CaO particle size distribution in Eagle Butte coal and chars.

quantities of CaO in the 2.1-8.0- μm range; however, by 0.8 seconds, the majority of the phases are greater than 8 μm in diameter. This may be an indication that the abundant small sized CaO particles that are initially produced, coalesce with time to form large particles. The Ca-rich particles were probably in a molten liquid form.

Calcium silicate formed initially as smaller sized particles; however, by 0.8 seconds, most of the calcium silicate was >8.0 μm in diameter, as shown in Figure 54. The calcium silicate material that formed in the first 0.5 seconds of combustion may have been the result of reaction between the abundant CaO derived from the organic fractions and the abundant 2.1-8.0- μm quartz component.

4.1.3 Eagle Butte Char and Ash Droplet Morphology

Eagle Butte 53-74- μm coal char morphologies were examined using the scanning electron microscope (SEM) and microprobe system. Qualitative analyses of phases in the char and the char matrix were acquired using the energy-dispersive spectroscopy capabilities of the SEM microprobe system. TGA was performed on the chars to note the degree of carbon burnout.

Figure 54. Production and transformation of Ca-silicate particle size distribution in Eagle Butte chars (no Ca-silicate was detected in the coal).

After 0.05 seconds of combustion, the Eagle Butte char showed extensive formation of pore structures in the organic matrix and extensive development of inorganic ash droplets as coatings on the surface of the char particles. Figure 55 shows the heterogeneity of the char particle chemistry with calcium-aluminium-rich, sulfate-rich, calcium-iron-rich, and calcium-aluminium-silicate-rich areas on the same 110- μm char particle. The matrix of the char particles was typically high in Mg, S, and CaO. The smallest recognizable particles on the surface of the char were usually CaO-rich with minor amounts of Fe_2O_3 and MgO. Carbon burnout at this residence time was about 51% and the ash content about 39%, as shown in Figure 56.

The 0.1-second char was very similar to the 0.05-second char in appearances and chemistry. Tiny 0.1-5- μm CaO-rich inorganic ash droplets were observed coating the "honey comb" porous structure of partially burned char particles. The carbon burnout for the 0.1-second char was approximately 55% and the ash content was 41%, as depicted in Figure 56.

Char formed at 0.2-second residence times shows similar phases as the lower residence-time chars. Calcium-rich particles were very abundant as were calcium aluminates, calcium aluminosilicates, and calcium silicates. Examples

EDS Qualitative Analysis From Selected Areas
In SEM Photograph

Elemental Oxide	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>
Na ₂ O	0.0	9.0	3.3	0.0
MgO	6.8	0.0	5.7	13.7
Al ₂ O ₃	18.7	0.0	8.0	25.7
SiO ₂	7.9	0.0	3.6	4.3
P ₂ O ₅	0.5	0.0	1.7	0.0
SO ₃	1.4	83.0	3.6	0.9
ClO	0.4	0.0	1.4	0.5
K ₂ O	1.3	0.0	2.3	1.4
CaO	49.3	8.0	54.4	47.2
TiO ₂	1.5	0.0	1.9	0.8
Fe ₂ O ₃	11.7	0.0	14.1	5.5

Figure 55. SEM micrograph of 0.05-second Eagle Butte char particle with compositions of selected areas.

Figure 56. Thermal gravimetric analysis of Eagle Butte chars. The 0.5-second residence time char did not burn out properly; therefore it does not appear to fit the trend.

of particles with these chemistries are shown in Figure 57, along with their compositions. The calcium-bearing particles were most abundant in the 1-6- μm size range. Most of the Ca-bearing phases show a significant Fe_2O_3 component ranging from 3%-15%. Carbon burnout and ash content at this residence time were 66% and 50%, respectively (Figure 56).

The 0.5-second char was not formed properly in the drop-tube furnace due to an unknown problem. The result was that the carbon burnout, given in Figure 56, was only 38%, which is less than the 0.1-second char and is obviously not consistent with the trend of increasing carbon burnout with combustion residence time. This test will be repeated. Nonetheless, the results are reported here for the value of observing inorganic transformations. An interesting SEM micrograph of char produced at this residence time shows the reaction between CaO and quartz. In Figure 58 a calcium silicate bridge has been formed between high CaO and high SiO_2 particles. As further proof of the heterogeneity of these Ca-rich systems, the SiO_2 -rich particle also has a molten interface with a calcium aluminosilicate-rich particle (Figure 58).

The longest residence time char was generated at 0.8 seconds. This char showed 95% carbon burnout as shown in Figure 56. Morphological analysis revealed mostly spherical fly ash particles, which were larger in size relative to the previous chars. Calcium-bearing particles still dominated the ash.

EDS Qualitative Analysis of Inorganic Ash Particles

Elemental <u>Oxide</u>	1 Calcium Aluminate	2 CaO-rich	3 Ca-Alumino- Silicate-rich
Na ₂ O	0.0	0.0	0.0
MgO	8.6	10.8	6.4
Al ₂ O ₃	34.4	14.5	10.7
SiO ₂	0.0	3.3	23.3
P ₂ O ₅	0.0	0.9	0.0
SO ₃	0.0	2.2	0.7
ClO	0.4	0.3	0.4
K ₂ O	1.7	1.8	1.6
CaO	43.4	58.4	44.3
TiO ₂	0.0	0.0	5.5
Fe ₂ O ₃	9.8	6.9	7.0

Figure 57. SEM micrograph of 0.2-second Eagle Butte char particle with composition of selected areas.

EDS Qualitative Analysis of Areas Indicated

Elemental Oxide	1 CaO	2 Ca- Silicate	3 Quartz or Silica	4 Ca-Al- Silicate
Na ₂ O	0.0	0.0	0.0	0.0
MgO	0.5	0.0	0.5	0.8
Al ₂ O ₃	0.6	0.0	0.0	13.8
SiO ₂	7.3	78.0	89.0	20.9
P ₂ O ₅	0.0	0.0	0.0	0.0
SO ₃	0.6	1.8	0.8	1.8
ClO	1.0	1.6	0.0	0.6
K ₂ O	2.5	1.1	1.2	3.1
CaO	73.0	15.5	6.3	53.8
TiO ₂	1.1	0.0	0.0	0.0
Fe ₂ O ₃	9.5	2.1	0.0	5.1

Figure 58. SEM micrograph of 0.5-second Eagle Butte char particle showing reaction between CaO and quartz (silica).

4.1.4 Eagle Butte Fly Ash Characterization

The Eagle Butte fly ash produced in the drop-tube furnace was analyzed for its inorganic constituents using SEMPC. Table 29 gives the phases and elemental compositions for each of the multicyclone size cuts of the Eagle Butte fly ash. The majority of the fly ash mass was contained in the $>11\text{-}\mu\text{m}$ size fraction (86%). Major phases identified by SEMPC were gehlenite ($\text{Ca}_2\text{AlSi}_2\text{O}_7$), anorthite, pyroxene ($(\text{Ca,Mg,Fe})\text{Si}_2\text{O}_6$), quartz, calcium oxide, dolomite, and kaolinite derived. Minor amounts of akermanite ($\text{Ca}_2\text{MgSi}_2\text{O}_7$), calcium aluminate, and amorphous illite were also observed. The most abundant phase was calcium oxide followed by quartz and gehlenite. The size fractions that were less than $4.4\text{ }\mu\text{m}$ showed very low amounts of crystalline or chemically ordered phases. The amount of unclassifiable amorphous species seems to decrease with decreasing size of fly ash.

The chemical compositions of the fly ash multicyclone samples, given in Table 29, were scrutinized for trends in distribution. Except for Fe_2O_3 , MgO, and K_2O , the composition of the $>11\text{-}\mu\text{m}$ fraction agrees with the ASTM ash analysis of the 53-74- μm coal on a sulfur free basis, as shown in Table 30. The lower amount of iron in the $>11\text{-}\mu\text{m}$ fraction of the fly ash is probably the result of: 1) iron being associated in the coal as finely dispersed carbonate or organically bound cations which causes it to concentrate in the finer fraction of the fly ash or 2) iron particles being coated with calcium aluminosilicates or other materials that mask the identity of an iron-bearing core material. There is more MgO and K_2O in the fly ash than in the ASTM ash probably due to these species being part of surface or coating materials, and especially if these components are part of a vapor phase oxide. Other trends noticed were that Fe_2O_3 and SO_3 contents increased with decreasing particle size, and SiO_2 increased with increasing particle size.

The SiO_2 component is derived from the abundant quartz and clay minerals in the coal. Quartz and kaolinite comprised nearly 73 wt% of the total mineral matter in the coal. The particle size distribution of the quartz and kaolinite showed greater amounts of material in the $>8.0\text{-}\mu\text{m}$ size range, which explains the higher level of Si and Al in the $>11\text{-}\mu\text{m}$ size range of the multicyclone.

The multicyclone stages show fairly constant quantities of Al_2O_3 which compares well with the aluminosilicate distribution observed in the coal relative to the size category. The coal, however, had more aluminosilicate in the $>11\text{-}\mu\text{m}$ size range, which agrees with the char data presented earlier which showed that kaolinite content was drastically reduced after 0.8 seconds combustion by reacting with other inorganic constituents.

The reason for the SO_3 content being low in the fly ash when compared to the ASTM ash is because it is in a vapor state and is not trapped by the filter in the multicyclone. On the other hand, the ASTM ash retains the sulfur during the ashing procedure.

TABLE 29
PHASES DETECTED BY SEMPC FOR EAGLE BUTTE FLY ASH
(53-74 μm Coal)

	<u>Filter</u>	<u>Stage 5</u>	<u>Stage 4</u>	<u>Stage 3</u>	<u>Stage 2</u>	<u>Stage 1</u>
Particle Size Cutpoints, μm	<1.2	1.2-2.1	2.1-4.4	4.4-6.0	6.0-11.0	>11.0
Percent Mass	1.54	5.39	12.45	3.43	0.77	86.4
<u>Phases (Number %)</u>						
Akermanite	0.0	0.0	0.0	0.8	0.5	0.8
Gehlenite	0.7	8.3	0.0	12.8	15.5	6.6
Anorthite	0.0	0.0	0.0	1.2	3.4	2.9
Pyroxene	0.0	0.4	0.0	1.6	1.0	4.1
Calcium Silicate	0.0	0.0	0.0	0.4	0.0	0.4
Dicalcium Silicate	0.0	0.0	0.0	0.4	0.0	0.0
Calcium Aluminate	0.7	0.8	0.0	3.3	6.8	1.6
Quartz	0.0	0.0	0.0	0.0	1.0	7.8
Iron Oxide	0.0	0.0	0.0	0.0	0.0	0.0
Calcium Oxide	0.0	0.4	0.0	2.9	5.3	8.2
Magnesium Oxide	0.0	0.0	0.0	0.0	0.5	0.0
Ankerite (Ca,Mg,Fe)CO ₃	0.0	3.3	0.0	3.3	1.5	0.0
Dolomite	1.5	0.0	0.0	0.0	1.0	4.5
Pure Kaolinite (Amorp)	0.0	0.0	0.0	0.0	0.0	3.7
Kaolinite Derived	0.0	0.0	0.0	0.0	2.9	2.5
Illite (Amorp)	0.0	0.0	0.0	0.0	0.0	0.4
Unclassified	97.8	87.6	100.0	76.5	68.0	58.0
<u>Oxide Composition</u>						
SiO ₂	8.6	11.6	15.1	19.2	22.9	31.5
Al ₂ O ₃	8.8	19.4	19.5	17.7	20.6	16.0
Fe ₂ O ₃	8.5	10.9	8.9	7.6	6.4	1.0
TiO ₂	0.7	1.4	1.4	1.1	1.2	1.0
P ₂ O ₅	1.9	1.5	0.7	0.3	0.5	0.2
CaO	28.4	43.4	42.9	43.3	36.6	33.4
MgO	33.0	8.0	7.7	8.0	7.7	13.6
Na ₂ O	0.7	0.2	0.1	0.4	1.3	1.4
K ₂ O	1.7	1.6	1.8	1.3	1.4	1.2
SO ₃	7.5	1.7	1.6	0.9	1.0	0.6
ClO	0.2	0.3	0.3	0.2	0.4	0.1

TABLE 30

COMPARISON OF EAGLE BUTTE ASTM ASH AND >11- μ m MULTICYCLONE FLY ASH

	ASTM Ash	ASTM Ash (SO ₃ -Free)	>11- μ m Fly Ash
SiO ₂	24.8	31.5	31.5
Al ₂ O ₃	13.5	17.6	16.0
Fe ₂ O ₃	5.8	7.5	1.0
TiO ₂	1.2	1.5	1.0
P ₂ O ₅	1.3	1.6	0.2
CaO	24.9	31.5	33.4
MgO	5.6	7.1	13.6
Na ₂ O	1.2	1.5	1.4
K ₂ O	0.1	0.1	1.2
SO ₃	21.7	0.0	0.6

4.2 Characterization of Upper Freeport Coal, Char, and Fly Ash

4.2.1 Upper Freeport Coal Characterization

The results of the ash analysis of three sized fractions of Upper Freeport coal are summarized in Table 31. The XRF analysis was taken from an ASTM ash and the XRD was performed on a low temperature ash of the coal. The ashes were very similar in chemical composition and crystalline phases in all three size fractions. The 38-53- μ m fraction, however, had nearly triple the ash content of the 74-106- μ m fraction. Quartz, pyrite, and kaolinite dominated the mineral content, and traces of calcite and anhydrite were also observed.

Table 32 summarizes the mineral data obtained from CCSEM analysis of the three size fractions of Upper Freeport coal. The mixed aluminosilicates for all the coal size fractions were mostly illite, as determined from the molar ratios of the elements analyzed by the microprobe.

Illite was most dominant in the 38-53- μ m size fraction, totaling 61% of the total mineral content. Quartz, kaolinite, and pyrite were also significant contributors to the mineral content. Most of the minerals had average diameters of >11 μ m. Mixed aluminosilicates, pyrite, and kaolinite were more common in the highest size category, while quartz grains had sizes most commonly in the 4.4-8.0- μ m size range. The total mineral content in this coal size fraction was 14.43 wt%.

The 53-74- μ m size fraction again showed the mixed aluminosilicates (mostly illite) as the dominant mineral phase. Pyrite drastically increased from 0.8 wt% in the 38-53 μ m fraction to 5.1 wt% in this size fraction. Together, the illite and pyrite comprised 72% of the mineral content. Calcite and quartz were present in significant quantities as well. The >11- μ m size category gave the highest concentration of minerals (71.37%). The total mineral content for this coal was 16.8 wt%.

TABLE 31

COMPOSITION OF ASTM ASHES AND DISTRIBUTION OF CRYSTALLINE SPECIES
IN THE LTA ASHES PRODUCED FROM UPPER FREEPORT COAL

<u>Oxide</u>	(Normalized Oxide Wt%) Coal particle size fraction, μm		
	<u>38-53</u>	<u>53-74</u>	<u>74-106</u>
SiO ₂	50.30	50.50	51.20
Al ₂ O ₃	23.70	24.20	23.90
Fe ₂ O ₃	11.90	12.80	12.80
TiO ₂	1.20	1.30	1.30
P ₂ O ₅	0.20	0.10	0.10
CaO	4.50	3.10	3.20
MgO	1.60	1.50	1.60
Na ₂ O	0.00	0.00	0.00
K ₂ O	3.70	3.70	3.80
SO ₃	3.00	2.70	2.10
% Ash	30.90	19.60	11.80

<u>Crystalline Species</u>			
Major	Quartz	Quartz	Quartz
Minor	Pyrite Kaolinite	Pyrite Kaolinite	Pyrite Kaolinite
Trace	Calcite Anhydrite	Calcite Anhydrite	

TABLE 32
MINERAL DISTRIBUTION DATA FOR UPPER FREEPORT SIZE FRACTIONS
(WEIGHT %)

<u>38-53 μm Sized Fraction</u>								
Mineral/Coal	Particle Size Distribution (μ m)						Total % Min	Wt% Coal
	<u><1.2</u>	<u>1.2-2.1</u>	<u>2.1-4.4</u>	<u>4.4-8.0</u>	<u>8.0-11.0</u>	<u>>11.0</u>		
Quartz	0.12	0.89	3.59	6.62	3.10	1.34	14.66	2.11
Kaolinite	0.07	0.60	1.52	3.11	0.00	4.48	9.16	1.32
Ca-Clay	0.01	0.02	0.00	0.00	0.00	0.00	0.04	0.01
Mixed Aluminosilicate	0.50	0.52	9.95	11.71	3.56	37.29	61.32	7.23
Pyrite	0.09	0.63	0.85	0.62	0.00	3.93	5.72	0.83
Calcite	0.06	0.14	0.16	0.50	0.00	0.00	0.82	0.12
Barite	0.00	0.00	0.06	0.00	0.00	0.00	0.05	0.01
Gypsum	0.01	0.00	0.38	0.00	0.00	0.00	0.36	0.05
Coal								85.57
Total	0.91	5.17	17.65	22.57	6.66	47.03	100.00	100.00
<u>53-74 μm Sized Fraction</u>								
Mineral/Coal	Particle Size Distribution (μ m)						Total % Min	Wt% Coal
	<u><1.2</u>	<u>1.2-2.1</u>	<u>2.1-4.4</u>	<u>4.4-8.0</u>	<u>8.0-11.0</u>	<u>>11.0</u>		
Quartz	0.04	0.16	1.64	1.55	2.19	1.16	6.70	1.13
Kaolinite	0.01	0.18	0.95	0.68	0.30	0.00	2.12	0.36
Ca-Clay	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mixed Aluminosilicate	0.10	0.64	3.48	6.50	3.15	28.42	42.13	7.11
Pyrite	0.07	0.40	1.38	1.61	0.65	26.30	30.28	5.11
Calcite	0.01	0.01	0.16	0.11	0.56	12.42	13.21	2.23
Barite	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Gypsum	0.00	0.01	0.03	0.00	0.00	0.00	0.03	0.01
Coal								83.12
Total	0.23	1.51	7.87	10.84	8.18	71.37	100.00	100.00
<u>74-106 μm Sized Fraction</u>								
Mineral/Coal	Particle Size Distribution (μ m)						Total % Min	Wt% Coal
	<u><1.2</u>	<u>1.2-2.1</u>	<u>2.1-4.4</u>	<u>4.4-8.0</u>	<u>8.0-11.0</u>	<u>>11.0</u>		
Quartz	0.02	0.33	1.43	2.16	1.17	4.3	9.41	1.87
Kaolinite	0.01	0.19	0.65	0.93	0.00	2.22	4.00	0.79
Ca-Clay	0.01	0.01	0.04	0.11	0.00	0.82	0.97	0.19
Mixed Aluminosilicate	0.14	1.24	6.37	7.14	3.53	22.07	40.49	7.30
Pyrite	0.07	0.44	1.72	3.12	3.04	8.09	16.49	3.27
Calcite	0.00	0.11	0.3	0.85	0.27	16.92	18.45	3.66
Barite	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Gypsum	0.00	0.01	0.07	0.19	0.00	0.00	0.26	0.05
Coal								80.14
Total	0.32	2.86	11.84	14.93	9.06	61.00	100.00	100.00

Illite dominated the mineral components of the 74-106- μm fraction, totaling 40% of the minerals present. Most of this illite was in the $>11\text{-}\mu\text{m}$ size category. Kaolinite, quartz, pyrite, and calcite were also present in appreciable amounts. Kaolinite and illite were mostly distributed in the $>11.0\text{-}\mu\text{m}$ range. The total concentration of mineral matter in this size fraction was 19.86 wt%.

4.2.2 Upper Freeport Char Characterization

Five Upper Freeport coal (53-74- μm sieve fraction) chars were generated in the EMRC drop-tube furnace using a combustion temperature of 1500°C . The residence times used for producing the chars were 0.05, 0.1, 0.2, 0.5, and 0.8 seconds. Each char was analyzed for inorganic phases using CCSEM. Table 33 shows the size distribution of the inorganic phases that were determined as area percents. The original mineral distribution for the Upper Freeport 53-74- μm coal is given in Table 34 for the purpose of making comparisons with the inorganic contents of the chars.

The general form of the mineral/phase particle size distribution remained the same through 0.8 seconds of combustion. It is shown in Figure 59 that coal mineral and the char inorganic phases are bimodally distributed. Particles are most abundant in the size fractions of 2.1-8.0 μm and $>11\text{ }\mu\text{m}$. The 0.8-second residence time char showed the largest concentration of phases $>11\text{ }\mu\text{m}$, at 73% (Table 33). This was expected due to coalescence of particles with time.

Figure 60 displays the relative concentration of major inorganic phases in the original coal and successive chars. The most abundant phase observed in the coal and chars was K-aluminosilicate, probably derived from illite. Most likely, the illite lost its crystalline character after exposure to the high temperature environment; therefore, it became a derived illite component or simply an amorphous K-aluminosilicate. Figure 60 shows the relative stability of the K-aluminosilicate phase throughout the combustion process. Kaolinite-derived also had a fairly stable distribution in the char (15-27%), but showed only 3% in the coal.

Pyrite content was observed to decrease with time through 0.2 seconds of combustion, then it disappeared altogether. Pyrite, when exposed to high temperatures, will decompose first to pyrrhotite and then to iron oxide. The only other mineral content that decreased significantly with time was calcite. The original coal showed 14% calcite (Table 34) but no calcite or CaO was observed in the early stage chars (Table 33).

New amorphous or crystalline phases that were produced were Fe-aluminosilicate and iron oxide, which were derived from Fe in pyrite and Al-Si in the clays.

4.2.3 Upper Freeport Char and Ash Droplet Morphology

Upper Freeport char and ash droplet morphologies were examined using the scanning electron microscope (SEM). Qualitative analyses were performed on selected particles to determine their relative elemental compositions. Thermal gravimetric analysis (TGA) was performed on the chars to monitor carbon burnout. Figure 61 shows how the fixed carbon content (% C) decreased

TABLE 33
DISTRIBUTION OF INORGANIC PHASES IN UPPER FREEPORT CHARs

a. Upper Freeport 0.05 Second Char

Mineral/Phase (Area %)	Particle Size Categories (µm)						Total Area %	Wt %
	<1.2	1.2-2.1	2.1-4.4	4.4-8.0	8.0-11.0	>11		
Quartz	0.0	0.2	1.0	0.9	0.8	15.0	18.0	15.9
Aluminosilicate	0.1	1.2	3.7	3.0	0.6	9.0	17.7	14.7
Fe-Aluminosilicate	0.1	0.6	1.5	2.4	0.3	2.6	7.5	7.0
Potassium Aluminosilicate	0.2	1.9	6.1	4.2	4.2	12.0	28.5	26.1
Calcium Aluminosilicate	0.0	0.1	0.2	0.1	0.0	0.0	0.4	0.4
Iron Oxide	0.0	0.1	0.4	0.2	0.0	3.9	4.6	8.1
Pyrite	0.0	0.2	0.5	1.2	2.1	15.5	19.5	24.4
CaO-Rich	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Rutile	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.1
Aluminosilicate/Gypsum	0.0	0.1	0.0	0.0	0.0	0.0	0.1	0.1
Ankerite	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Calcium Silicate	0.0	0.1	0.2	0.3	0.5	0.0	1.1	1.1
Unknown	0.1	0.3	0.7	0.8	0.4	0.0	2.3	2.1
Total	0.6	4.9	14.3	13.2	9.0	58.0	100.0	100.0

b. Upper Freeport 0.1 Second Char

Mineral/Phase (Area %)	Particle Size Categories (µm)						Total Area %	Wt %
	<1.2	1.2-2.1	2.1-4.4	4.4-8.0	8.0-11.0	>11		
Quartz	0.0	1.1	3.3	0.2	0.0	0.0	4.6	3.9
Aluminosilicate	0.7	3.9	5.2	2.6	0.0	5.3	17.7	14.1
Fe-Aluminosilicate	0.3	1.2	1.6	0.3	0.0	9.6	13.1	11.7
Potassium Aluminosilicate	0.8	5.7	10.3	3.9	5.5	12.1	38.3	33.7
Calcium Aluminosilicate	0.1	0.4	0.5	0.0	0.0	0.0	0.9	0.8
Iron Oxide	0.0	0.2	0.3	1.6	0.0	10.5	12.6	21.1
Pyrite	0.1	0.4	0.3	0.0	0.8	2.8	4.3	5.2
CaO-Rich	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Rutile	0.0	0.2	0.0	0.0	0.0	3.1	3.3	5.1
Anhydrite	0.1	0.1	0.8	1.2	0.0	0.0	2.2	1.7
Aluminosilicate/Gypsum	0.1	0.0	1.2	0.0	0.0	0.0	0.1	0.1
Ankerite	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Calcium Silicate	0.0	0.1	0.1	0.0	0.0	0.0	0.3	0.3
Unknown	0.2	0.9	1.5	0.0	0.0	0.0	2.6	2.3
Total	2.4	14.2	23.9	10.0	6.3	43.2	100.0	100.0

TABLE 33 (CONTINUED)

c. Upper Freeport 0.2 Second Char

Mineral/Phase (Area %)	Particle Size Categories (µm)						Total Area %	Wt %
	<1.2	1.2-2.1	2.1-4.4	4.4-8.0	8.0-11.0	>11		
Quartz	0.0	0.1	1.1	2.2	0.2	14.5	18.2	17.7
Aluminosilicate	0.2	1.0	4.0	5.2	1.9	3.1	15.4	14.1
Fe-Aluminosilicate	0.1	0.4	1.0	0.7	0.0	5.1	7.2	7.4
Potassium Aluminosilicate	0.1	1.0	3.6	4.1	3.3	31.9	44.0	44.4
Calcium Aluminosilicate	0.1	0.3	0.5	0.7	0.0	0.0	1.5	1.5
Iron Oxide	0.0	0.0	0.2	0.4	0.0	0.0	0.7	1.3
Pyrite	0.0	0.0	0.2	0.3	0.0	0.0	0.5	0.7
CaO-Rich	0.0	0.0	0.3	1.3	0.3	7.2	9.1	9.4
Rutile	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.1
Aluminosilicate/Gypsum	0.0	0.1	0.3	0.0	0.3	0.0	0.8	0.7
Ankerite	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.1
Calcium Silicate	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.1
Unknown	0.0	0.2	0.5	0.8	0.4	0.4	2.3	2.4
Total	0.5	3.4	11.9	15.7	6.5	62.1	100.0	100.0

d. Upper Freeport 0.5 Second Char

Mineral/Phase (Area %)	Particle Size Categories (µm)						Total Area %	Wt %
	<1.2	1.2-2.1	2.1-4.4	4.4-8.0	8.0-11.0	>11		
Quartz	0.0	0.3	2.2	1.6	0.8	2.7	7.7	7.4
Aluminosilicate	0.2	2.0	8.0	8.1	0.6	0.0	18.8	17.0
Fe-Aluminosilicate	0.1	1.0	4.2	4.1	0.0	1.2	10.6	10.7
Potassium Aluminosilicate	0.4	2.8	11.2	8.0	2.3	24.5	49.2	49.0
Calcium Aluminosilicate	0.2	0.7	1.1	2.5	0.0	0.0	4.5	4.4
Iron Oxide	0.0	0.0	0.5	0.7	0.0	1.1	2.3	4.5
Pyrite	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
CaO-Rich	0.0	0.1	0.1	1.8	0.0	1.0	2.9	3.0
Rutile	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.1
Apatite	0.0	0.0	0.2	0.0	0.0	0.0	0.2	0.2
Aluminosilicate/Gypsum	0.0	0.0	0.1	0.0	0.0	0.0	0.2	0.1
Calcium Silicate	0.0	0.0	0.2	0.0	0.0	0.0	0.2	0.2
Unknown	0.1	0.6	1.6	1.1	0.0	0.0	3.3	3.3
Total	1.1	7.5	29.4	27.8	3.7	30.5	100.0	100.0

TABLE 33 (CONTINUED)

e. Upper Freeport 0.8 Second Char

Mineral/Phase (Area %)	Particle Size Categories (µm)						Total Area %	Wt %
	<1.2	1.2-2.1	2.1-4.4	4.4-8.0	8.0-11.0	>11		
Quartz	0.0	0.0	0.4	1.0	0.6	5.8	7.8	7.4
Aluminosilicate	0.0	0.3	2.2	3.1	3.0	18.0	26.7	23.8
Fe-Aluminosilicate	0.0	0.2	0.9	1.8	0.8	8.1	11.8	11.8
Potassium Aluminosilicate	0.0	0.2	1.8	3.0	2.2	33.3	40.6	39.9
Calcium Aluminosilicate	0.0	0.2	0.6	0.6	0.3	0.0	1.7	1.6
Iron Oxide	0.0	0.0	0.2	0.3	0.2	3.9	4.6	8.6
Pyrite	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
CaO-Rich	0.0	0.0	0.0	0.1	0.1	0.0	0.3	0.3
Rutile	0.0	0.0	0.0	0.1	0.0	0.0	0.1	0.2
Aluminosilicate/Gypsum	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.1
Calcium Silicate	0.0	0.0	0.1	0.1	0.0	0.0	0.2	0.2
Unknown	0.0	0.1	0.5	0.5	0.9	4.1	6.2	6.2
Total	0.1	1.1	6.8	10.7	8.1	73.2	100.0	100.0

TABLE 34

MINERAL DISTRIBUTION FOR UPPER FREEPORT 53-74 µm COAL

Mineral/Phase (Area %)	Particle Size Categories (µm)						Total Area %	Wt %
	<1.2	1.2-2.1	2.1-4.4	4.4-8.0	8.0-11.0	>11		
Quartz	0.04	0.18	1.89	1.79	2.53	1.34	7.77	6.08
Aluminosilicate	0.01	0.22	1.17	0.84	0.37	0.00	2.61	1.92
Fe-Aluminosilicate	0.00	0.19	0.82	0.56	0.31	7.50	9.38	7.76
K-Aluminosilicate	0.11	0.53	3.04	6.68	3.19	24.02	37.56	30.51
Ca-Aluminosilicate	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Iron Oxide	0.00	0.02	0.09	0.23	0.77	1.22	2.34	3.63
Pyrite	0.06	0.32	1.13	1.31	0.53	21.39	24.73	36.67
Gypsum/Barite	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Calcite	0.01	0.02	0.17	0.11	0.61	13.44	14.36	12.00
Rutile	0.00	0.04	0.05	0.00	0.00	0.61	0.71	1.02
Barite	0.00	0.01	0.00	0.00	0.00	0.00	0.01	0.01
Gypsum	0.00	0.01	0.03	0.00	0.00	0.00	0.04	0.03
Ankerite	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Unknown	0.00	0.04	0.18	0.27	0.00	0.00	0.50	0.37
Total (and PSD)	0.23	1.54	8.39	11.51	8.31	69.53	100.00	100.00

Figure 59. Upper Freeport coal and char mineral/phase particle size distributions.

Figure 60. Upper Freeport coal and char mineral/phase contents as a function of residence time.

Figure 61. TGA analysis of Upper Freeport 53-74- μ m coal.

with residence time. The carbon conversion (% CC) was used to calculate carbon burnout. A steady decrease in carbon content was noted between combustion residence times of 0.1 and 0.8 seconds; at 0.8 seconds, 100% carbon burnout was attained.

The 0.05-second char revealed beginning stages of coalescence and fly ash formation. Partially molten clusters of small spherical particles 1-5 μ m in diameter were observed. Carbon loss at this stage was about 14% as shown in Figure 61. Compositions of single coalesced particles were extremely variable depending on the location of the electron beam, which corresponded to a heterogeneous composition. For example, in Figure 62, a 65- μ m particle is shown that has already undergone extensive melting and is beginning to take on a spherical shape. The more granular-appearing material toward the bottom of the particle is mostly aluminosilicate, probably derived from illite. In the middle of the particle a more molten-appearing Fe-rich material was observed (41% Fe_2O_3). The iron and sulfur in this material were derived from molten pyrite or pyrrhotite and comprised the bulk of the middle region material in Figure 62. Note the interaction that has taken place between the Fe-S liquid (80%) phase and molten Al-Si (17%). Compositions of selected phases in the 0.05-second char are given in Table 35.

The 0.1-second char showed a greater degree of fly ash formation and many particles retained a heterogeneous chemical composition. Figure 63 shows a spherical grain that had molten Fe-Si phases surrounded by a Mg-Fe-Si matrix. Selected phase compositions for the 0.1-second char are given in Table 35.

Figure 62. Upper Freeport .05-second char (scanning electron micrograph and EDS data).

TABLE 35

COMPOSITION OF SELECTED INORGANIC PARTICLES IN UPPER FREEPORT CHARs
(NORMALIZED OXIDE WEIGHT PERCENT)

Oxide	Char Particles at Specific Residence Times (Seconds)									
	0.05				0.1		0.5		0.8	
Na ₂ O	0	0	0	0	0	0	0	0	0	0
MgO	0	0	0	0	5	10	0	0	0	0
Al ₂ O ₃	27	5	37	7	1	3	28	25	2	28
SiO ₂	40	10	43	10	36	44	40	28	2	48
P ₂ O ₅	0	0	0	2	0	0	0	0	0	0
SO ₃	11	2	14	39	1	0	2	1	0	1
ClO	1	1	1	0	0	0	0	1	0	0
K ₂ O	6	3	1	1	1	1	12	16	0	5
CaO	0	3	0	1	3	3	1	0	0	1
TiO ₂	2	0	0	0	1	1	4	4	0	4
Fe ₂ O ₃	12	76	4	41	49	35	13	22	94	12
Si/Al Ratio	1.4	2.0	1.1	1.4	36.0	14.7	1.4	1.1	1.0	1.7

Figure 63. Upper Freeport 0.1-second char (scanning electron micrograph and EDS data).

At 0.5 seconds of combustion, more spherical fly ash grains were beginning to develop in the smaller size ranges as displayed in Figure 64. Carbon burnout at this stage was 57% as displayed in Figure 61. Figure 64 is a backscattered electron image; therefore, particles having higher average concentrations of heavier elements appear brighter. The brighter particles have undergone nearly 100% carbon loss while the darker particles still retain carbon in their matrix. Many of the very brightest particles are Fe-rich. The brightly shaded homogeneous sphere near the bottom of Figure 64 was composed of K-Fe-aluminosilicate, most likely derived from abundant illite clays in the Upper Freeport.

Char formed at 0.8 seconds revealed 100% carbon burnout (Figure 61) with most of the particles being spherical or subspherical in form. Figure 65 shows that coalescence was still occurring, as evidenced by larger fly ash particles, 60-80 μm in diameter, having numerous smaller particles sticking to their surfaces and being assimilated. The backscattered electron image in Figure 65 shows numerous bright Fe-rich particles that are 10-40 μm in diameter. Many of the Fe-rich particles show significant quantities of aluminosilicate in their composition and illite-derived particles commonly show high Fe₂O₃ contents (Figure 65).

A comparison was made between normalized oxide weight percents of elements in illite in the initial Upper Freeport coal and illite-derived or K-aluminosilicate phases observed in the chars (Table 36). Illite in the coal had higher Si/Al ratios than the illite-derived in the char. The average Si/Al ratio for the illite in the coal was 2.4, and for the illite-derived in the char was 1.4. The data in Table 36 suggests that a depletion of Si has occurred during the combustion process, possibly due to the incorporation of kaolinite particles.

Figure 64. Upper Freeport 0.5-second char (scanning electron micrograph obtained using backscattered electron imaging).

Figure 65. Upper Freeport 0.8-second char (scanning electron micrograph obtained using backscattered electron imaging).

TABLE 36
COMPOSITION OF ILLITE AND K-ALUMINOSILICATE
IN UPPER FREEPORT COAL AND CHAR

Oxide	(Normalized Oxide Weight Percent)							
	Coal				Char			
Na ₂ O	0	0	0	0	0	0	0	0
MgO	0	0	0	0	0	0	0	0
Al ₂ O ₃	29	21	15	36	27	28	25	28
SiO ₂	56	48	51	59	40	40	28	48
P ₂ O ₅	0	0	0	0	0	0	0	0
SO ₃	1	1	3	0	11	2	1	1
ClO	1	0	0	0	1	0	1	0
K ₂ O	7	18	13	1	6	12	16	5
CaO	0	0	0	0	0	1	0	1
TiO ₂	1	3	2	0	2	4	4	4
Fe ₂ O ₂	4	9	13	2	12	13	22	12
Si/Al Ratio	0.5	0.4	0.3	0.6	0.7	0.7	0.9	0.6

The Upper Freeport 0.05-second char was analyzed in more detail using SEMPC analysis. The major phases present in the Upper Freeport 0.05-second char were montmorillonite, illite, kaolinite, calcite or calcium oxide, anhydrite, plagioclase (anorthite-albite), quartz, and unclassified material (Table 37). Some of these phases may lack a true crystalline structure because of thermal alteration. The large unclassified component (42-96%) in all of the stages reveals that substantial melting and transformation of mineral matter occurred even at a short residence time. The SEMPC chemical composition of the fly ash in the >11- μ m size fraction (Table 37) was similar to that observed by x-ray fluorescence ash analysis of the bulk coal as shown in Table 38.

Table 34 displays the original Upper Freeport 53-74 μ m coal mineral content as determined by CCSEM. About 71% by weight of the coal minerals were greater than 11 μ m in average diameter. The 0.05-second char also had most of its inorganic mass (~90%) in the >11- μ m multicyclone stage (Table 37). Comparisons were made between the >11- μ m fractions of the coal minerals and 0.05 second char phases on an area percent basis, as shown in Table 39. There was a depletion of calcite, mixed aluminosilicate, illite, and pyrite; most likely because of melting and interaction with other liquid- or gas-phase inorganic components. Pyrite content was reduced substantially (only 0.4% remained in the char). The limited number of points analyzed by SEMPC may account for the low pyrite content. The 0.05-second char showed 24% pyrite when analyzed using CCSEM, which analyzes 6 times as many particles as SEMPC. Some phases were enriched, according to these results, including quartz and kaolinite. Some of the illite or mixed silicates may have lost alkali or alkaline earth elements during combustion to produce the kaolinite phase detected in the char. Quartz may have been enriched by the melting of clays to produce Si-rich glass, which would be categorized by SEMPC as quartz.

TABLE 37
PHASES DETECTED BY SEMPC FOR UPPER FREEPORT 0.05-SECOND CHAR
(FROM 53-74- μ m COAL)

	<u>Stage 1</u>	<u>Stage 2</u>	<u>Stage 3</u>	<u>Stage 4</u>	<u>Stage 5</u>	<u>Filter</u>
Particle Size Cutpoint (μ m)	>11.0	6.0	4.4	2.1	1.2	<1.2
Percent Mass	89.5	2.3	3.4	1.1	1.9	1.8
<u>Phase (Number %)</u>						
Calcium Oxide/Calcite	1.5	0.4	0.0	0.0	0.0	0.0
Montmorillonite	5.7	1.1	10.2	0.0	8.2	0.0
Illite	25.7	14.3	16.1	50.0	3.6	3.7
Iron Oxide/Siderite	1.9	0.4	0.0	0.4	0.0	0.0
Kaolinite-derived	12.8	33.2	3.6	4.4	26.3	0.0
Anhydrite	1.5	0.8	7.2	0.4	0.0	0.0
Anorthite	1.1	1.9	0.6	1.2	1.8	0.0
Albite	2.3	0.0	4.8	0.0	0.9	0.0
Quartz	3.0	6.0	7.2	0.8	0.0	0.0
Pyrrhotite	0.0	0.0	1.2	0.0	0.0	0.0
Pyrite	0.4	0.0	0.0	0.0	0.0	0.0
Spinel	0.0	0.0	0.0	0.0	0.0	0.0
Dolomite	1.5	0.0	1.2	0.0	0.0	0.0
Unclassified	42.7	42.3	48.4	42.8	59.9	96.3
<u>Average Composition, wt%</u>						
Na ₂ O	0.3	0.3	0.6	0.2	0.6	1.2
MgO	0.5	1.4	0.6	0.6	0.9	0.7
Al ₂ O ₃	25.1	31.6	18.5	27.4	32.3	17.5
SiO ₂	48.4	54.6	50.5	47.7	52.0	28.0
P ₂ O ₅	0.1	0.0	0.5	0.4	0.0	0.4
SO ₃	6.5	3.6	13.3	7.1	6.2	39.9
ClO	0.0	0.0	0.0	0.0	0.0	0.0
K ₂ O	4.9	3.9	3.8	5.6	3.9	6.5
CaO	3.8	1.3	3.7	2.1	0.9	1.7
TiO ₂	1.2	0.6	0.8	1.2	0.6	0.6
Fe ₂ O ₃	9.2	2.7	7.7	7.6	2.6	3.5
<u>Average Si/Al Molar Ratio</u>						
	1.9	1.7	2.7	1.7	1.6	1.6

TABLE 38
COMPARISON OF SEMPC AND XRF CHEMICAL COMPOSITION FOR UPPER FREEPORT
(WT %)

	<u>XRF of Coal Ash*</u>	<u>SEMPC Char Composition</u>
SiO ₂	50.5	48.4
Al ₂ O ₃	24.2	25.0
Fe ₂ O ₃	12.8	9.2
TiO ₂	1.3	1.2
P ₂ O ₅	0.1	0.1
CaO	3.1	3.8
MgO	1.5	0.5
Na ₂ O	0.0	0.3
K ₂ O	3.7	4.9
SO ₃	2.7	6.5

* CIT Ninth Quarterly Technical Progress Report, 1988.

TABLE 39
COMPARISON OF SELECTED UPPER FREEPORT 0.05-SECOND CHAR PHASES AND
COAL MINERALS FOR >11-μm SIZE RANGE*
(AREA PERCENT)

<u>Mineral</u>	<u>Char</u>	<u>Coal</u>
Calcium Oxide/Calcite	1.5	19.3
** Mixed Aluminosilicates	9.1	10.8
Illite	25.7	34.6
Iron Oxide/Siderite	1.9	1.8
Kaolinite/Aluminosil.	12.8	0.0
Pyrite	0.4	30.8
Quartz	3.0	1.9
Unknown/Unclassified	42.7	0.0

* Char phase percents from the >11-μm multicyclone size cut and mineral percents from the >11-μm size category.

** Includes Fe-aluminosilicate for the coal; and montmorillonite, anorthite, and albite for the char.

4.2.4 Upper Freeport Fly Ash Characterization

Fly ash was generated from Upper Freeport coal in the EMRC drop-tube furnace and analyzed for inorganic phases using SEMPC. SEMPC data for each multicyclone size fraction is presented in Table 40. The first multicyclone stage ($>11\ \mu\text{m}$) contained nearly 94% of the fly ash. The major phases identified by SEMPC included illite-derived, iron oxide, kaolinite-derived, anorthite, and an unclassified phase. Minor occurrences of quartz, albite, montmorillonite-derived, calcium oxide, spinel, and calcium titanate were also observed.

Illite-derived was the most abundant phase that was recognized by SEMPC. Illite-derived is an amorphous K-aluminosilicate derived from the clay mineral, illite. The original Upper Freeport coal showed 37.6% illite on a mineral matter basis (Table 34). The illite-derived had a steady decline in quantity with decreasing fly ash size (Table 40). The distribution of kaolinite-derived was similar to that of illite-derived; Stage 1 showing the largest quantity with successively decreasing quantities in the smaller size fractions. Kaolinite was not very abundant in the coal; therefore, the derived kaolinite is coming from some of the other aluminosilicate clays by volatilization of their loosely bound cations. This conclusion is supported by the enrichment of K_2 in the final filter ($<1.2\ \mu\text{m}$). Quartz and iron oxide have fairly even distributions in all of the stages except Stage 5 and the filter.

The SEMPC chemical compositions of the multicyclone stages showed fairly uniform Si/Al ratios except for the filter fraction, which had an excessively high ratio of 18.9. The filter fraction had 57% SiO_2 and only 3% Al_2O_3 . Concentrations of SiO_2 decreased with decreasing fly ash size, and TiO_2 increased, generally, with decreasing size.

4.3 Characterization of Robinson Coal, Char, and Fly Ash

4.3.1 Robinson Coal Characterization

The results of the chemical fractionation, ash, and proximate/ultimate analyses of the Robinson 53-74- μm coal are given in Tables 41 and 42, respectively. The majority of the sodium, magnesium, and calcium are organically bound as shown by their removal by ammonium acetate. The ASTM ash showed a moderate amount of Na_2O at 3.5% and a very high CaO content of 19.7%. The sodium present was most likely in an organic salt form and calcium was probably in the form of a salt of an organic acid group and carbonate minerals.

The mineral distributions for Robinson size fractions are summarized in Table 43. The 38-53- μm size fraction of Robinson coal had generally even amounts of quartz, kaolinite, and pyrite, which made up 82% of the mineral content. Additional minerals observed were Ca-clay (montmorillonite) and gypsum. The $>11\text{-}\mu\text{m}$ size category contained most of the minerals. Quartz, kaolinite and pyrite had higher concentrations in the $>11\text{-}\mu\text{m}$ size range, while Ca-clays were most abundant in the 2.1-8.0- μm size range. The total mineral content was 8.4 wt%.

TABLE 40
PHASES DETECTED BY SEMPC FOR UPPER FREEPORT FLY ASH
(FROM 53-74- μ m COAL)

	<u>Stage 1</u>	<u>Stage 2</u>	<u>Stage 3</u>	<u>Stage 4</u>	<u>Stage 5</u>	<u>Filter*</u>
Particle Size Cutpoints (μ m)	>11.0	6.0	4.4	2.1	1.2	<1.2
Percent Mass	93.9	1.0	1.9	0.7	1.3	1.2
<u>Phase (Number %)</u>						
Calcium Oxide	1.1	.4	0.0	0.0	0.0	0.0
Montmorillonite	0.0	.4	0.0	1.9	0.8	0.0
Illite-derived	63.1	46.5	35.5	29.9	27.6	0.0
Iron Oxide	2.5	2.3	2.5	1.2	0.4	0.0
Kaolinite-derived	18.1	9.5	3.7	1.2	0.0	0.0
Anhydrite	0.0	0.0	0.0	0.0	0.0	0.0
Anorthite	0.0	2.3	8.7	3.7	6.6	0.0
Albite	0.4	0.0	0.0	0.0	0.0	0.0
Quartz	1.1	1.5	1.2	1.2	0.8	0.0
Pyrrhotite	0.0	0.0	0.0	0.0	0.0	0.0
Pyrite	0.0	0.0	0.0	0.0	0.0	0.0
Spinel	0.0	0.4	0.0	1.2	0.0	0.0
Dolomite	0.0	0.0	0.0	0.0	0.0	0.0
Calcium Titanate	0.0	1.1	1.2	1.2	3.7	0.0
Meli'ite	0.0	0.0	0.0	0.0	0.0	1.6
Unclassified	14.5	36.2	47.3	58.5	60.5	98.4
<u>Average Composition, wt%</u>						
Na ₂ O	0.14	0.35	0.20	0.24	0.28	0.0
MgO	0.46	0.44	0.50	0.59	0.60	0.1
Al ₂ O ₃	30.70	28.00	29.70	29.60	29.20	3.0
SiO ₂	51.50	47.80	44.30	43.70	41.80	56.8
P ₂ O ₅	0.00	0.19	0.28	0.19	0.28	0.1
SO ₃	0.21	0.34	0.32	0.31	0.62	12.4
ClO	0.00	0.00	0.00	0.00	0.00	0.1
K ₂ O	5.96	4.69	4.08	4.07	3.97	8.2
CaO	1.81	3.29	4.36	3.67	4.83	5.8
TiO ₂	1.25	1.87	2.35	3.26	3.96	3.1
Fe ₂ O ₃	7.85	12.90	13.80	14.20	14.20	10.4
Average Si/Al Molar Ratio	1.7	1.7	1.5	1.5	1.4	18.9

* Previous SEMPC results reported in the 11th Quarterly Technical Progress Report were incorrect due to analytical error.

TABLE 41
CHEMICAL FRACTIONATION RESULTS FOR ROBINSON COAL

	Initial ($\mu\text{g/g}$ dry coal)	% Removed by H_2O	% Removed by NH_4OAc	% Removed by HCl	% Remaining
Na	1440	48	60	0	-8
Mg	730	1	72	7	20
Al	4420	0	0	13	87
Si	7030	1	0	1	98
Ca	4940	0	75	21	4
Ti	110	0	0	7	93
Fe	3220	0	0	21	79
Sr	170	0	71	19	10

TABLE 42
RESULTS OF ROBINSON COAL AND ASH ANALYSIS^a

	Robinson (Montana Subbituminous)
<u>Proximate, Wt %</u>	
Moisture	22.0
Volatile Matter	35.1
Fixed Carbon	54.3
Ash	10.6
<u>Ultimate, Wt %</u>	
Carbon	66.6
Hydrogen	5.0
Nitrogen	0.9
Oxygen (diff)	16.4
Sulfur	1.1
<u>Ash Analysis, Wt %^b</u>	
SiO_2	38.0
Al_2O_3	18.7
Fe_2O_3	13.0
TiO_2	1.3
P_2O_5	1.4
CaO	19.7
MgO	3.5
Na_2O	4.3
K_2O	0.1

- ^a Results reported on a dry basis except for the moisture determination.
^b SO_2 -free basis.

TABLE 43

MINERAL DISTRIBUTION DATA FOR ROBINSON SIZE FRACTIONS (WEIGHT %)

<u>38-53 μm Sized Fraction</u>								
<u>Particle Size Distribution (μm)</u>								
<u>Mineral/Coal</u>	<u><1.2</u>	<u>1.2-2.1</u>	<u>2.1-4.4</u>	<u>4.4-8.0</u>	<u>8.0-11.0</u>	<u>>11.0</u>	<u>Total % Min</u>	<u>Wt % Coal</u>
Quartz	0.04	0.05	1.52	3.27	5.81	20.21	28.09	2.37
Kaolinite	0.04	0.34	2.33	4.13	0.97	25.79	32.67	2.76
Ca-Clay	0.07	0.45	2.45	2.83	0.00	1.74	7.32	0.62
Mixed Aluminosilicate	0.02	0.09	0.43	0.50	0.00	0.00	1.00	0.09
Pyrite	0.00	0.19	0.92	0.97	0.85	19.60	21.80	1.85
Calcite	0.00	0.01	0.00	0.38	0.00	0.00	0.38	0.03
Barite	0.01	0.00	0.24	1.05	0.49	0.00	1.74	0.15
Gypsum	0.00	0.04	0.30	0.43	1.17	0.00	1.88	0.16
Coal								91.54
Total	0.20	1.35	9.49	7.28	67.34	100.00	100.00	100.00

<u>53-74 μm Sized Fraction</u>								
<u>Particle Size Distribution (μm)</u>								
<u>Mineral/Coal</u>	<u><1.2</u>	<u>1.2-2.1</u>	<u>2.1-4.4</u>	<u>4.4-8.0</u>	<u>8.0-11.0</u>	<u>>11.0</u>	<u>Total % Min</u>	<u>Wt % Coal</u>
Quartz	0.08	0.69	4.18	9.59	6.67	21.66	42.73	1.20
Kaolinite	0.01	0.66	6.18	6.29	2.06	2.85	18.00	0.51
Ca-Clay	0.08	0.69	2.51	2.25	0.97	0.00	6.47	0.18
Mixed Aluminosilicate	0.00	0.03	0.46	0.74	0.00	0.00	1.22	0.21
Pyrite	0.03	0.44	3.21	4.69	1.49	3.50	13.32	0.37
Calcite	0.00	0.07	0.32	0.00	0.00	0.00	0.38	0.01
Barite	0.00	0.00	0.21	0.44	0.00	4.27	4.90	0.14
Gypsum	0.07	0.18	1.68	3.52	0.00	0.00	5.44	0.15
Coal								97.19
Total	0.28	3.18	20.23	28.50	13.59	34.21	100.00	100.00

<u>74-106 μm Sized Fraction</u>								
<u>Particle Size Distribution (μm)</u>								
<u>Mineral/Coal</u>	<u><1.2</u>	<u>1.2-2.1</u>	<u>2.1-4.4</u>	<u>4.4-8.0</u>	<u>8.0-11.0</u>	<u>>11.0</u>	<u>Total % Min</u>	<u>Wt % Coal</u>
Quartz	0.06	1.01	4.39	4.27	3.74	32.73	44.80	2.03
Kaolinite	0.07	0.72	2.88	3.94	2.18	20.12	29.00	1.32
Ca-Clay	0.02	0.22	0.93	0.00	0.00	0.00	1.13	0.05
Mixed Aluminosilicate	0.02	0.07	0.60	0.21	0.00	0.00	0.87	0.04
Pyrite	0.05	0.57	2.86	3.35	0.78	6.33	13.52	0.51
Calcite	0.00	0.05	0.14	0.00	0.00	0.00	0.18	0.01
Barite	0.00	0.05	0.14	1.38	0.00	0.00	1.53	0.07
Gypsum	0.01	0.15	0.36	0.69	0.96	2.67	4.69	0.21
Coal								95.46
Total	0.25	3.07	12.86	14.32	7.66	61.84	100.00	100.00

The major minerals present in the 53-74- μm size fraction consisted of quartz, kaolinite, and pyrite. Minor species included Ca-clay, gypsum, and barite. Quartz grains were most commonly $>11\ \mu\text{m}$ in size, while kaolinite, pyrite, gypsum, and Ca-clay were most commonly 2.1-8.0 μm in size. The $>11\ \mu\text{m}$ size range contained the majority of the minerals; however, it did not dominate as in the 38-53- μm coal size fraction. The total mineral content, which was only 2.81 wt%, was much lower than the 8.46 wt% observed in the 38-53- μm fraction.

Within the highest coal size fraction of 74-106 μm , quartz was most frequently observed, followed by kaolinite, pyrite, and gypsum. All three of the above minerals had grain sizes that mostly fell in the $>11\text{-}\mu\text{m}$ range. The small amount of Ca-clays present were observed in the <1.2 to 4.4- μm size range. A greater percentage of the minerals observed were in the $>11\ \mu\text{m}$ size category. Overall, this coal size fraction had a mineral distribution that was very near to the 53-74- μm size fraction, except that its total mineral content of 4.54 wt% was approximately 2 wt% higher.

4.3.2 Robinson Coal Char Characterization

The distribution of inorganic phases for Robinson chars produced at four residence times are listed in Table 44. The quantities are expressed as area percents, except for a column that converts bulk area percent to weight percent by weighting the inorganic phases according to their specific gravities.

The major phases shown in Table 44 included quartz, aluminosilicate, and calcium aluminosilicate, with quartz being the most abundant. Minor components were pyrite, calcium oxide or calcium carbonate (CaO-rich), anhydrite, aluminosilicate/gypsum and unknown phases. Quartz and pyrite were mostly concentrated in the $>11\text{-}\mu\text{m}$ size category while aluminosilicate, calcium aluminosilicate, pyrite, CaO-rich, anhydrite, and aluminosilicate/gypsum were more distributed in the lower size categories (i.e., 2.1-11.0 μm). The 2.1-4.4- μm and $>11\text{-}\mu\text{m}$ size ranges comprised 64.1% of the phases in nearly equal proportions.

In this char, calcium aluminosilicate was the dominant phase (Table 44). Other major phases included calcium silicate and CaO-rich. Minor quantities of aluminosilicate, iron oxide, aluminosilicate/gypsum, alumina, and calcium aluminate were present. Quartz and calcium silicate were concentrated in the $>11\ \mu\text{m}$ size category. Calcium aluminosilicate, as in the 0.1-second char, showed its highest concentration in the 2.1-4.4- μm range along with calcium aluminate and the CaO-rich phase. The highest concentrations of CCSEM phases were observed in the 2.1-4.4- μm and $>11\text{-}\mu\text{m}$ size ranges.

After 0.5 seconds of combustion, quartz, aluminosilicate, calcium aluminosilicate and iron oxide were the major constituents (Table 44). Minor amounts of CaO-rich and calcium silicate and pyrite were also observed. The pyrite may actually have been a form of pyrrhotite or Fe-sulphate. A dramatic change occurred with respect to the size distribution. All of the major inorganic phases show larger concentrations in the $>11\text{-}\mu\text{m}$ size range. The $>11\text{-}\mu\text{m}$ size range totaled nearly 90% of the phase content.

TABLE 44
DISTRIBUTION OF INORGANIC PHASES IN THE ROBINSON CHARs
a. Robinson 0.1 Second Char

Mineral/Phase (Area %)	Particle Size Categories (μm)						Total Area %	Wt %
	<1.2	1.2-2.1	2.1-4.4	4.4-8.0	8.0-11	>11		
Quartz	0.1	0.4	3.1	2.3	2.1	24.3	32.3	31.2
Aluminosilicate	0.0	0.8	3.6	0.7	2.8	5.0	13.0	11.8
Fe-Aluminosilicate	0.0	0.0	1.4	0.0	0.0	0.0	1.5	1.5
Potassium aluminosilicate	0.0	0.2	0.6	0.3	0.0	0.0	1.1	1.1
Calcium Aluminosilicate	0.7	4.9	7.8	0.7	1.0	1.5	16.5	16.2
Iron Oxide	0.0	0.1	0.7	0.4	0.0	0.0	1.2	2.3
Pyrite	0.0	0.0	0.8	1.2	0.0	1.9	4.0	5.5
CaO-Rich	0.2	1.4	2.5	2.0	0.0	0.0	6.2	6.3
Rutile	0.0	0.0	0.1	0.0	0.0	0.0	0.1	0.2
Anhydrite	0.1	0.9	1.6	1.1	1.0	0.0	4.7	4.2
Apatite	0.1	0.0	0.3	0.0	0.0	0.0	0.4	0.4
Dolomite	0.0	0.1	0.4	0.0	0.0	0.0	0.5	0.5
Aluminosilicate/Gypsum	0.4	3.2	3.1	0.0	0.0	0.0	6.8	6.3
Ankerite	0.0	0.3	0.6	0.7	0.0	0.0	1.6	1.7
Calcium Aluminate	0.1	0.6	0.6	0.3	0.0	0.0	1.6	1.7
Calcium Silicate	0.1	0.6	0.6	0.5	0.0	0.0	1.8	2.0
Unknown	0.3	3.0	3.5	0.0	0.0	0.0	6.8	7.0
Total	2.2	16.6	31.4	10.2	6.8	32.7	100.0	110.0

b. Robinson 0.2 Second Char

Mineral/Phase (Area %)	Particle Size Categories (μm)						Total Area %	Wt %
	<1.2	1.2-2.1	2.1-4.4	4.4-8.0	8.0-11	>11		
Quartz	0.0	0.1	0.7	2.7	1.5	16.2	21.2	19.9
Aluminosilicate	0.0	0.0	0.2	1.8	1.8	2.2	4.4	3.9
Fe-Aluminosilicate	0.0	0.0	0.0	0.0	0.0	1.3	1.3	1.3
Calcium Aluminosilicate	0.2	3.1	10.8	5.7	4.4	2.9	27.2	25.9
Iron Oxide	0.0	0.0	0.1	0.6	0.0	1.3	1.9	3.6
Alumina	0.0	0.0	0.0	0.3	0.5	0.7	1.5	2.1
Pyrite	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
CaO-Rich	0.1	1.3	6.2	5.2	0.7	3.8	17.4	17.4
Rutile	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Barite	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Anhydrite	0.0	0.1	0.2	0.0	0.0	0.0	0.3	0.3
Dolomite	0.0	0.0	0.1	0.2	0.0	0.0	0.4	0.4
Aluminosilicate/Gypsum	0.1	0.5	1.3	0.0	0.6	0.0	2.5	2.2
Ankerite	0.0	0.1	0.0	0.5	0.0	0.0	0.6	0.7
Calcium Aluminate	0.1	1.4	4.1	1.4	0.0	0.0	7.0	7.4
Calcium Silicate	0.0	0.6	2.1	2.4	0.4	6.3	11.8	12.5
Unknown	0.1	0.4	1.1	0.3	0.4	0.0	2.4	2.3
Total	0.7	7.6	26.9	19.5	10.5	34.8	100.0	100.0

TABLE 44 (CONTINUED)

c. Robinson 0.5 Second Char

Mineral/Phase (Area %)	Particle Size Categories (µm)						Total Area %	Wt %
	<1.2	1.2-2.1	2.1-4.4	4.4-8.0	8.0-11	>11		
Quartz	0.0	0.0	0.1	0.3	0.4	14.0	14.8	12.9
Aluminosilicate	0.0	0.0	0.0	0.1	0.4	33.9	34.4	28.2
Fe-Aluminosilicate	0.0	0.0	0.0	0.0	0.0	0.2	0.2	0.2
Calcium Aluminosilicate	0.0	0.1	1.4	2.1	1.5	17.5	22.8	20.2
Iron Oxide	0.0	0.0	0.0	0.0	0.0	13.9	14.0	24.1
Alumina	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Pyrite	0.0	0.0	0.0	0.0	0.0	3.8	3.8	4.6
CaO-Rich	0.0	0.1	0.4	0.5	0.5	2.1	3.6	3.4
Dolomite	0.0	0.0	0.0	0.0	0.0	0.1	0.2	0.2
Aluminosilicate/Gypsum	0.0	0.0	0.2	0.2	0.0	0.0	0.4	0.4
Calcium Aluminate	0.0	0.1	0.3	0.5	0.0	0.4	1.3	1.3
Calcium Silicate	0.0	0.0	0.3	0.6	0.5	2.4	3.8	3.8
Unknown	0.0	0.0	0.2	0.2	0.0	0.3	0.7	0.6
Total	0.0	0.4	3.0	4.6	3.3	88.6	100.0	100.0

d. Robinson 0.8 Second Char

Mineral/Phase (Area %)	Particle Size Categories (µm)						Total Area %	Wt %
	<1.2	1.2-2.1	2.1-4.4	4.4-8.0	8.0-11	>11		
Quartz	0.0	0.0	0.2	0.4	1.0	7.3	8.9	8.1
Aluminosilicate	0.0	0.1	0.3	0.4	1.6	6.3	8.6	7.4
Fe-Aluminosilicate	0.0	0.0	0.0	0.0	0.0	1.6	1.6	1.6
Potassium Aluminosilicate	0.0	0.0	0.0	0.0	0.2	0.5	0.8	0.8
Calcium Aluminosilicate	0.2	0.6	2.0	4.4	2.9	21.7	31.7	29.4
Iron Oxide	0.0	0.0	0.0	0.1	0.9	4.6	5.6	10.2
CaO-Rich	0.0	0.1	0.7	1.8	1.7	8.8	13.1	12.7
Anhydrite	0.0	0.0	0.0	0.0	0.3	0.0	0.4	0.3
Apatite	0.0	0.0	0.0	0.0	0.0	0.3	0.3	0.3
Dolomite	0.0	0.0	0.0	0.0	0.4	3.0	3.4	3.4
Aluminosilicate/Gypsum	0.0	0.1	0.2	0.0	0.0	0.0	0.3	0.3
Ankerite	0.0	0.0	0.0	0.1	0.2	0.5	0.9	0.9
Calcium Aluminate	0.0	0.1	0.4	0.3	1.2	5.4	6.4	6.5
Calcium Silicate	0.0	0.1	0.5	0.7	1.2	10.2	12.7	13.1
Unknown	0.0	0.2	0.2	0.3	0.9	3.6	5.2	5.1
Total	0.2	1.3	4.6	8.5	11.5	73.9	100.0	100.0

The 0.8-second char showed high levels of quartz, aluminosilicate, calcium aluminosilicate, iron oxide, calcium aluminate, CaO-rich and calcium silicate (Table 44). Calcium aluminosilicate was the most abundant phase. There were minor occurrences of Fe-aluminosilicate and dolomite phases. All of the above constituents had greater concentrations in the size range of >11 μm . The bulk CCSEM particle size distribution revealed that 74% of the inorganic phases were in the >11- μm range.

4.3.3 Discussion of Inorganic Transformation

Since the Robinson chars were produced using differing residence times, the transformations of specific inorganic phases were studied with respect to time in the hot zone of the drop-tube furnace. In order to directly compare the initial coal content to the inorganic content of successive chars, the quantities of the inorganic constituents were reported as area percents. Table 45 reports the initial mineralogical content of the 74-106- μm sieve fraction of Robinson coal. The major phases observed were quartz, kaolinite, and pyrite. Also present were minor gypsum and ankerite $\{(\text{CaFe})_2\text{CO}_3\}$ phases. These were discrete mineral phases and did not include elements that were organically bound in the coal matrix. Table 41 reported the chemical fractionation results for the bulk Robinson coal. The results showed the distribution of major elements in the coal, and were particularly useful for identifying the distribution of organically bound elements. For example, calcium, which comprised approximately 20% of the bulk ash, was mostly distributed as salt of an organic acid group (Table 41).

Figure 66 compares the original Robinson mineral content with the inorganic phase content of the chars produced at the four combustion times. It appears that after 0.2 seconds of combustion, extensive fragmentation of larger size mineral grains occurred. Evidence for this conclusion is seen in Figure 66, where the total mineral content in the >11- μm category was less for the 0.1- and 0.2-second chars than for the initial coal. In comparison, the total mineral content in the smaller size ranges, particularly between 1.2 and 8.0 microns, was greater for the 0.1- and 0.2-second chars than for the coal.

At longer residence times of 0.5 and 0.8 seconds, there was successive coalescence of finer sized inorganic phases (Figure 66). Total inorganic phase content was less for the 0.5- and 0.8-second chars than for the coal in the 1.2-8.0- μm size range, and the chars in the >11- μm size range had successively greater inorganic contents than the coal.

4.3.4 Kaolinite Transformation

The mechanism for the fragmentation phenomenon in the first 0.2 seconds of combustion was based on the break-up of aggregates of aluminosilicate clays, which comprised 31.5% of the discrete mineral matter.

In Figure 67, the distribution of kaolinite (aluminosilicate in the char) is seen for the initial coal and successive chars. After the first 0.2 seconds of combustion, there was a significant decrease in kaolinite content in the >11- μm range and an increase in the 1.2-8.0- μm range. This corresponded to larger kaolinite grains undergoing fragmentation during early stages of combustion. In the later stages of combustion (0.5 and 0.8 seconds) the kaolinite content was nearly 100% contained in the >11- μm size category. The shift to larger sizes during late combustion was due to coalescence of the finer kaolinite-derived aluminosilicate particles, which were more molten at this stage and more easily coalesced.

TABLE 45

MINERAL DISTRIBUTION DATA FOR ROBINSON 74-106- μm COAL SIZE FRACTION

Mineral/Phase (Area %)	Particle Size Categories (μm)						Total Area %
	<1.2	1.2-2.1	2.1-4.4	4.4-8.0	8.0-11	>11	
Quartz	0.06	1.00	4.37	4.25	3.72	32.55	45.95
Aluminosilicate	0.07	0.76	3.04	4.15	2.30	21.21	31.53
Fe-Aluminosilicate	0.01	0.05	0.42	0.00	0.00	0.00	0.48
K-Aluminosilicate	0.01	0.01	0.15	0.20	0.00	0.00	0.37
Ca-Aluminosilicate	0.02	0.22	0.90	0.00	0.00	0.00	1.14
Iron Oxide	0.00	0.02	0.06	0.00	0.00	0.00	0.09
Pyrite	0.03	0.40	2.00	2.35	0.54	4.43	9.76
Calcite	0.00	0.04	0.13	0.00	0.00	0.00	0.18
Rutile	0.01	0.03	0.00	0.18	0.00	0.00	0.21
Barite	0.00	0.04	0.11	1.08	0.00	0.00	1.23
Gypsum	0.01	0.16	0.39	0.74	1.04	2.87	5.21
Apatite	0.02	0.11	0.36	0.12	0.00	0.00	0.60
Aluminosilicate/Gypsum	0.00	0.02	0.13	0.11	0.00	0.00	0.27
Ankerite	0.01	0.01	0.00	0.00	0.78	2.20	3.00
Unknown	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total (and PSD)	0.23	2.88	12.06	13.18	8.38	63.27	100.00

Figure 66. Particle size distribution of Robinson coal minerals and char inorganic phases as determined by CCSEM.

Figure 67. Distribution of kaolinite or aluminosilicate in the Robinson coal and chars.

Figures 68 and 69 show the form of in situ aluminosilicate clay in a cross section of Robinson coal. The aluminosilicate material occurred as aggregates of 2- μ m circular-shaped particles. This morphology is more characteristic of halloysite, which is a hydrated form of kaolinite. Halloysite commonly occurs as agglomerations of spheroidal or elongate tubular grains (4, 5). The halloysite-kaolinite aggregates were deposited authigenically in the coal during coal deposition; thus, they were intimately associated with the organic matrix (6, 7). Upon combustion, the loosely bound aggregates easily fragmented to form separate small particles.

4.3.5 Quartz Transformations

Quartz underwent a uniform decrease in its content with time. Figure 70 reveals that quartz content, at successively longer residence times, had the same general particle size distribution, but different quantities at each size range. This was evidence for gradual interaction of the quartz particle surface with alkali-earth elements and aluminosilicates during combustion. Quartz probably interacted directly with CaO released from organic sites in the coal matrix. Approximately 71% of the quartz in the original coal was >11 μ m in size. After 0.2 seconds of combustion, there was a calcium silicate component in the char that totaled about 12% of the inorganic phases. Over half of the calcium silicate was >11 μ m in size. The obvious conclusion is that some of the CaO was reacting with the large quartz grains after about 0.2 seconds in the heat zone. The calcium silicate content gradually increased with time as quartz decreased, as shown in Figure 71.

Figure 68. Individual kaolinite or halloysite spherules separated by organic coal matrix.

Figure 69. Aggregates of kaolinite or halloysite spherules in a coal particle.

Figure 70. Distribution of quartz in the Robinson coal and chars.

Figure 71. Distribution of quartz and calcium silicate as a function of residence time in the drop-tube furnace.

4.3.6 Gypsum Transformation

The gypsum content in the coal was initially about 5% on a mineral basis and the majority was $>11\text{ }\mu\text{m}$ in size. Figure 72 shows that after 0.1 seconds of combustion, the large gypsum grains disappeared and a more prominent gypsum/anhydrite component was formed in the 2.1-4.4- μm ranges. With increased time the gypsum/anhydrite component disappeared altogether. The possible explanation for the transformation of gypsum is that initially the larger gypsum minerals underwent fragmentation or reaction with other inorganic phases, much the same as did kaolinite. Gypsum is also an authigenic mineral and is intimately associated with the coal organic minerals as larger crystalline laths, platelets, or infillings of cavities and micropores in the coal. The authigenic origin of gypsum causes it to be more susceptible to fragmentation when the adjacent organic matrix is burned away and water was released from hydrated gypsum crystals. The smaller sized gypsum fragments would then account for the sudden increase in gypsum/anhydrite material at the 2.1-4.4- μm size range. Another explanation for the increase in gypsum/anhydrite at 0.1 seconds is that sulfation and coalescence of fine CaO particles may have occurred as they were released from the organic structure of the coal.

4.3.7 Formation of New Inorganic Phases

As mentioned earlier, several new inorganic phases were formed during the combustion process. These phases were more amorphous in nature, but their chemical composition was consistent enough for CCSEM to identify them as distinct phases.

Calcium was a major reacting element in most of the new phases that were being developed. Table 46 shows EDS compositions of selected inorganic phases that formed during combustion. The aluminosilicate compositions in Table 46 were fairly pure, but still revealed interaction with Na and Ca. Typically, kaolinite in the Robinson coal will show only trace amounts of extraneous elements in addition to Al and Si. Aluminosilicate material in these particles provided a framework for interaction of alkali and alkaline earth elements such as Na and Ca, as shown in Table 46.

The chemical compositions for the calcium aluminosilicates, calcium silicate, and calcium oxides were fairly well defined as depicted in Table 46. Phase diagrams reveal that the melilite-group mineral, gehlenite, may result from the calcium aluminosilicate compositions observed in the Robinson chars, given the correct temperature environment. The eutectic for crystallization of gehlenite ($\sim 1500\text{--}1600^\circ\text{C}$) may have been attained on the char particle surface even though the gas temperature was only 1300°C . Manual search for calcium aluminosilicate crystals using the SEM microprobe in a backscattered electron imaging mode did not prove a success. However, fly ash generated from Robinson coal at approximately 1500°C did reveal significant quantities of melilite (25). The general conclusion is that most of the calcium aluminosilicate phase is amorphous during the early combustion stage. A similar explanation holds for the calcium silicate and calcium oxide at their compositions shown in Table 46. In summary, the calcium-bearing phases that were produced during Robinson char formation were mostly amorphous, but had fairly consistent chemical compositions.

Figure 72. Distribution of gypsum and anhydrite in Robinson coal and chars.

TABLE 46
SELECTED INORGANIC PHASE COMPOSITIONS FOR ROBINSON CHAR*

Composition	Calcium Aluminosilicate			Calcium Silicate		Calcium Oxide		Aluminosilicate			
Na ₂ O	0	4	0	0	0	0	3	3	1	9	6
MgO	1	3	4	3	2	0	0	0	0	0	0
Al ₂ O ₃	18	25	24	1	4	8	5	41	37	32	44
SiO ₂	31	30	33	32	37	3	4	50	57	51	45
P ₂ O ₅	0	0	0	0	0	0	0	0	0	0	0
SO ₃	1	0	1	2	1	1	1	2	0	0	0
ClO	0	1	1	0	1	0	1	0	0	0	0
K ₂ O	0	0	0	0	0	0	0	0	0	0	0
CaO	42	37	32	59	51	82	78	3	3	7	4
TiO ₂	2	0	1	2	0	4	0	0	1	0	0
Fe ₂ O ₃	5	0	4	1	4	1	8	1	1	1	1

* EDS Normalized Oxide Weight Percents.

Figure 73 shows the concentration of five phases that developed in the chars at different residence times including: calcium aluminosilicate, iron oxide, calcium oxide, calcium silicate, and calcium aluminate. None of these constituents were observed in the original mineral analysis in significant amounts (Table 45). Calcium aluminosilicate, calcium silicate, and calcium aluminate showed increasing contents with residence time. The iron oxide and calcium oxide contents were only generally increasing with time. The availability of calcium was a major factor in the production of the calcium phases. It is proposed here that CaO, which was very abundant in the organic fraction of the coal, reacted with aluminosilicate clays that were abundant as discrete minerals. It appears that aluminosilicate content decreased and calcium aluminosilicate increased with residence time. This may have been the result of melt phase CaO and aluminosilicate clay reacting at the char surface as the organic matrix receded. Calcium aluminosilicate may have resulted from CaO reacting with alumina or mullite derived from the collapse and melting of kaolinite at 950°F or 1050°C. Some of the alumina may also be coming from the 13% of the total Al that was organically associated.

Calcium silicate formed as a result of the assimilation of vapor- or liquid-phase CaO into the partially molten surface of quartz grains. The iron oxide component was most likely a derivative of the breakdown of the 4.4% pyrite in the original coal. At the 0.1- and 0.5-second residence times there was still about 4% pyrite (Table 44) in the char, but at 0.8 seconds, pyrite was not detected (Table 44). Previous studies have established that at high temperatures, pyrite (FeS_2) decomposes to pyrrhotite (FeS) (8). With further heating, the pyrrhotite melts (950-1100°C) and iron oxide will crystallize first as magnetite (Fe_3O_4) and then as hematite (Fe_2O_3).

Finally, calcium oxide particles detected in the char were either directly derived from organically bound Ca or crystallized out from Ca-rich melts.

4.3.8 Robinson Char and Ash Droplet Morphology

The SEM/microprobe system was used to examine the morphology and composition of inorganic ash particles and char matrix in the Robinson chars. The 0.8-second Robinson char showed nearly complete char burnout upon visual examination, since very few char particles remained. Char particles that still had organic matrix at this residence time showed CaO-rich and calcium silicate-rich inorganic ash particles (1-10 microns) in intimate association with the char matrix, similar to the char particle shown in Figure 74. The char matrix was fairly rich in calcium and sulfur. Selected EDS analyses of the inorganic ash droplets and char matrix are given in Table 47.

More partially burned char particles were found with the 0.5-second residence time relative to the 0.8 second run; however, most of the combustion products consisted of fly ash. A char particle shown in Figure 75 reveals that combustion has been extremely thorough on the coal grains, leaving a heavy coating of fly ash over most of the surface area of the char particles. Not all of the fly ash that is seen coating this particle has been derived from the char. Some of the particles have been deposited onto the surface of the char particle after collection. Typical of this run were particles rich in Ca-aluminosilicate that had significant amounts of Na and Mg. Small 3-5- μm particles had compositions that were high in CaO; up to 80% CaO in some cases. Table 47 summarizes the compositions of random fly ash particles that were embedded in or were observed coating the surface of char particles.

Figure 73. Concentrations of major phases produced during combustion as a function of residence time.

Figure 74. SEM micrograph of a 0.8-second char particle showing association of inorganic ash particles and char matrix.

TABLE 47

COMPOSITION OF REPRESENTATIVE INORGANIC ASH PARTICLES
AND CHAR MATRIX IN ROBINSON CHARs
(QUALITATIVE EDS NORMALIZED OXIDE WEIGHT PERCENTS)

Elemental Oxide	Inorganic Ash Particles										Char Matrix			
	0.1 sec			0.2 sec		0.5 sec			0.8 sec			0.8 sec	0.5 sec	0.1 sec
Na ₂ O	0	19	0	0	0	2	0	3	0	0	9	0	8	0
MgO	0	0	4	0	1	7	0	1	3	3	0	2	4	2
Al ₂ O ₃	5	36	24	8	46	16	6	30	9	1	31	14	25	4
SiO ₂	9	39	35	3	23	24	5	38	6	32	50	9	19	37
SO ₃	1	1	1	1	0	4	0	0	2	2	0	24	7	1
ClO	0	0	1	0	0	0	0	0	0	0	0	2	0	1
K ₂ O	0	0	0	0	0	0	0	0	0	0	0	0	0	0
CaO	79	5	33	83	30	42	78	27	74	59	7	47	30	50
TiO ₂	4	0	1	4	1	1	0	0	2	2	0	0	3	0
Fe ₂ O ₃	1	0	4	1	0	3	8	2	4	1	1	1	0	4

Figure 75. SEM micrograph showing char burnout of particle and the formation of fly ash on surface (0.5 sec RT).

There was a dramatic increase in the amount of uncombusted char particles in the 0.2-second char relative to the 0.5- and 0.8-second chars, as revealed in Figure 76. Still present, however, was a heavy coating of inorganic ash droplets over the char particles. Figure 77 reveals small, 1-3- μm fly ash particles lining coal char structures. The intimate association of the inorganic ash particles with the char reflect the derivation of the fly ash from original inorganic constituents in the char. These particles are rich in CaO. Similar trends of small CaO-rich ash particles on char grains were noted in the longer-residence-time chars. Table 47 lists the compositions of randomly selected ash particles that were observed on the surface of char grains.

Char particles with very high levels of unburned organic matrix were very abundant in the 0.1-second run, as illustrated in Figure 78. Figure 79 reveals the early stage of inorganic ash droplet formation on the surface of a char particle. The ash droplets are 0.1 to 1 μm in diameter. Some of these particles are high in Na, as shown in Table 47, and are intimately associated with the char matrix. As the char combusts, it leaves behind the inorganic matter in the form of the spherical particles that sometimes are aligned along previous char ridges or structures. The inorganic ash particles had concentrations of CaO that were as high as 79%. Table 47 gives normalized oxide values of randomly selected fly ash particles that were observed on the surface of char particles.

4.3.9 Characterization of Robinson Fly Ash

Results from the SEMPC analysis of Robinson fly ash are summarized in Table 48. The major phases observed include quartz, an amorphous form of kaolinite, iron oxide, anhydrite, melilite and plagioclase, (both are calcium aluminosilicates) and hauyne. Hauyne (complex aluminosilicate containing sulfur) melilite, and anhydrite were found only in the smaller sized fraction of the fly ash. Iron oxide and quartz were concentrated in the larger size fractions. Kaolinite-derived phases were distributed evenly in all size fractions.

Average elemental compositions of the fly ash size fractions showed greater CaO, Na₂O, and SO₃ in the smaller sized fractions.

4.4 Characterization of Beulah Coal, Char, and Fly Ash

4.4.1 Beulah Coal Characterization

Three size fractions of Beulah lignite were ashed using ASTM and LTA procedures and the ashes were analyzed using XRF and XRD, respectively. Table 49 shows that the Beulah ash is moderately high in sodium and calcium. The total ash content was nearly the same for all of the size fractions. XRD analysis of the LTA ash revealed quartz as a major mineral and calcite, pyrite, kaolinite, and calcium sulfate (gypsum or bassanite) as minor constituents.

Chemical fractionation analysis was performed on a Beulah bulk coal sample and a 53-74 μm sieve fraction. Table 50 summarizes the results of the Beulah bulk analysis. The sodium and magnesium appear to be found primarily as water-soluble and cation-exchangeable ions. The calcium is in the form of

Figure 76. SEM micrograph of Robinson 0.2-second char showing abundant uncombusted char particles.

Figure 77. SEM micrograph of small 1-3-μm inorganic ash particles lining coal char structures in the Robinson 0.2-second char.

Figure 78. SEM micrograph of Robinson 0.1-second char particles.

Figure 79. SEM micrograph of minute ($<1\ \mu\text{m}$) inorganic ash droplets that formed on the surface of a char particle. Spherical particles in center of photo are high in Na.

TABLE 48
PHASES DETECTED BY SEMPC FOR ROBINSON FLY ASH

	<u>Bulk</u>	<u>Stage 1</u>	<u>Stage 2</u>	<u>Stage 3</u>	<u>Stage 4</u>	<u>Stage 5</u>	<u>Filter</u>
Particle Size							
Cutpoints							
D50 (μm)	--	11.0	6.0	4.4	2.1	1.5	1.2
Percent Mass	--	74.3	5.3	2.1	3.5	10.5	3.9
<u>Phase (Number %)</u>							
Hauyne	0.0	1.9	2.0	9.8	5.0	4.9	8.8
Calcium Oxides	0.0	1.9	0.0	0.0	0.0	0.7	0.0
Calcium Silicate	0.6	1.9	0.0	0.0	0.0	0.0	0.0
Iron Oxides*	5.5	15.5	0.0	0.9	0.0	0.0	0.0
Kaolinite ⁺	18.4	19.2	12.6	23.2	14.4	12.6	20.8
Anhydrite	2.5	0.0	4.0	5.4	1.7	0.0	1.8
Plagioclase ⁻	1.8	1.9	2.0	3.6	2.8	2.1	0.0
Quartz	17.2	26.9	26.0	2.7	7.2	5.6	0.0
Melilite**	4.9	0.0	0.0	9.8	2.8	12.6	1.3
Unidentified	49.1	34.6	54.0	44.6	66.3	61.5	67.3
<u>Average Composition, wt% (SO₃-Free)</u>							
SiO ₂	48.8	54.0	45.7	33.0	42.3	27.9	35.0
Al ₂ O ₃	19.6	17.6	19.7	20.3	21.8	22.5	14.2
Fe ₂ O ₃	7.3	12.8	3.6	2.5	2.1	2.3	5.0
TiO ₂	1.2	0.3	1.1	1.5	0.6	1.2	0.8
P ₂ O ₅	0.3	0.1	0.9	0.4	0.1	1.0	1.3
CaO	18.6	11.0	22.0	35.3	22.7	35.5	24.8
MgO	2.3	1.8	4.3	4.2	6.8	6.3	16.8
Na ₂ O	2.2	2.1	2.6	2.6	3.4	2.9	2.2
K ₂ O	0.2	0.2	0.2	0.2	0.1	0.1	0.0
(SO ₃)***	5.9	1.6	6.2	10.5	5.9	11.5	12.2
<u>Average Si/Al Molar Ratio</u>	2.2	2.6	2.0	1.4	1.7	1.1	2.1

* Technique does not distinguish between polymorphs.

+ Points with Si/Al molar ratios equal to 1.

- Plagioclase solid solution between albite and anorthite.

** Melilite solid solution between akermanite and gehlenite.

*** SO₃ is included for comparison purposes.

TABLE 49
COMPOSITION OF ASTM AND LTA ASHES FROM BEULAH COAL
USING XRF AND XRD

	(Normalized Oxide wt%) Coal size fraction, μm		
	38-53	53-74	74-106
SiO ₂	23.30	21.50	20.90
Al ₂ O ₃	14.10	13.50	13.20
Fe ₂ O ₃	10.10	10.80	11.40
TiO ₂	1.30	1.00	1.00
P ₂ O ₅	0.90	0.90	0.90
CaO	15.50	16.10	16.60
MgO	4.50	4.00	4.10
Na ₂ O	6.30	6.20	6.80
K ₂ O	0.30	0.20	0.10
SO ₃	23.70	25.70	25.00
% Ash	6.8	6.9	6.6

<u>XRD Results</u>			
Major	Quartz	Quartz	Quartz
Minor	Calcite Pyrite Kaolinite Gypsum	Calcite Pyrite Bassanite Kaolinite	Calcite Pyrite Bassanite Kaolinite

TABLE 50
CHEMICAL FRACTIONATION RESULTS FOR BEULAH COAL

	Initial ($\mu\text{g/g}$ dry coal)	% Removed by H ₂ O	% Removed by NH ₄ OAc	% Removed by HCl	% Remaining
Na	5700	42	57	1	0
Mg	2600	1	97	2	0
Al	5180	0	1	22	77
Si	7230	1	4	2	93
Ca	11500	0	74	26	0
Fe	10650	0	1	27	72

an ion-exchangeable cation and a carbonate mineral. The iron and aluminum may be associated with the organic structure or as acid-soluble oxides or hydroxides, but for the most part are insoluble. The insoluble portion of the iron is likely to be in the form of pyrite and the insoluble portion of the aluminum is associated with the clay minerals. The silicon in the insoluble portion is in the form of clay minerals and quartz.

The Beulah 53-74- μ m coal fraction had more calcium in a mixed association than the bulk coal (Table 51). Sodium and magnesium were both removed mostly by ammonium acetate, revealing their organic association. Sodium was also removed by water extraction, implying a possible association. Mg and Ca showed a significant association with carbonates (22%). The HCl extraction removed 22% of the Fe, which was probably in a carbonate form because the remaining 78% of Fe was associated with pyrite.

Table 52 describes the mineralogic content of the three Beulah size fractions. For the 38-53- μ m fraction, pyrite, quartz and clay comprised 60% of the mineral content in nearly equal quantities. Other significant additions to the mineral content were Ca-clays, mixed aluminosilicates, and gypsum. The Ca-clays are probably a form of montmorillonite and the mixed aluminosilicates in this case are probably illite and Fe-montmorillonite. The bulk of the mineral matter was observed in the >11- μ m size range. The most abundant minerals, quartz, pyrite, and kaolinite, were observed in the >11- μ m range. The total mineral content for this size fraction was 4.76 weight percent (dry coal basis).

For the 53-74- μ m Beulah size fraction, quartz and kaolinite were the most commonly observed minerals, making up 71% of the minerals present (Table 52). Kaolinite by far dominated all other mineral species, comprising 50% of the mineral content. One considerable difference noted in this coal size fraction was that the quantity of mixed aluminosilicates was much lower than in the 38-53- μ m size fraction. There was a definite shift of the occurrence of most of the mineral types to the lower size categories. Quartz, kaolinite, and gypsum

TABLE 51
CHEMICAL FRACTIONATION RESULTS FOR BEULAH 53-74- μ m COAL

	Initial μ g/g	Wt% Extracted by Each Solvent			Wt% Remaining
		H ₂ O	NH ₄ OAc	HCl	
Na	6900	26	66	1	7
Mg	3870	1	73	22	4
Al	9460	1	0	10	89
Si	15,400	1	2	1	96
K	168	16	53	3	28
Ca	14,200	1	45	22	32
Fe	11,500	0	0	22	78

TABLE 52
MINERAL DISTRIBUTION DATA FOR BEULAH SIZE FRACTIONS (WT%)

<u>38-53 μm Sized Fraction</u>								
<u>Mineral/Coal</u>	<u>Particle Size Distribution (μm)</u>						<u>Total % Min</u>	<u>Wt% Coal</u>
	<u><1.2</u>	<u>1.2-2.1</u>	<u>2.1-4.4</u>	<u>4.4-8.0</u>	<u>8.0-11.0</u>	<u>>11.0</u>		
Quartz	0.00	0.04	1.46	5.02	2.21	10.08	20.40	0.97
Kaolinite	0.00	0.01	0.39	3.22	2.16	16.13	16.13	0.77
Ca-Clay	0.01	0.08	0.89	2.20	2.54	2.18	8.55	0.41
Mixed Aluminosilicate	0.00	0.01	0.12	0.82	0.00	6.53	8.11	0.38
Pyrite	0.01	0.05	0.32	8.08	5.42	18.37	23.82	1.25
Barite	0.00	0.00	0.11	0.68	1.60	2.34	3.50	0.18
Gypsum	0.00	0.08	0.40	1.84	0.22	3.12	6.13	0.29
Coal								95.24
Total	0.03	0.26	3.81	24.84	16.99	54.07	100.00	100.00

<u>53-74 μm Sized Fraction</u>								
<u>Mineral/Coal</u>	<u>Particle Size Distribution (μm)</u>						<u>Total % Min</u>	<u>Wt% Coal</u>
	<u><1.2</u>	<u>1.2-2.1</u>	<u>2.1-4.4</u>	<u>4.4-8.0</u>	<u>8.0-11.0</u>	<u>>11.0</u>		
Quartz	0.06	0.55	3.16	7.29	4.27	4.16	19.48	0.93
Kaolinite	0.44	2.80	9.18	17.97	5.62	15.63	51.64	2.48
Ca-Clay	0.22	1.75	3.57	0.73	0.00	0.00	6.27	0.30
Mixed Aluminosilicate	0.03	0.09	0.58	0.24	0.00	0.00	0.94	0.04
Pyrite	0.05	0.15	1.58	0.36	2.25	0.00	4.38	0.21
Barite	0.02	0.50	1.33	2.47	0.00	2.01	6.34	0.30
Gypsum	0.00	0.03	0.60	2.23	1.82	0.00	4.68	0.22
Coal								95.20
Total	1.06	7.10	21.77	33.54	14.73	21.80	100.00	100.00

<u>74-106 μm Sized Fraction</u>								
<u>Mineral/Coal</u>	<u>Particle Size Distribution (μm)</u>						<u>Total % Min</u>	<u>Wt% Coal</u>
	<u><1.2</u>	<u>1.2-2.1</u>	<u>2.1-4.4</u>	<u>4.4-8.0</u>	<u>8.0-11.0</u>	<u>>11.0</u>		
Quartz	0.00	0.34	4.39	5.17	6.88	4.76	20.12	1.24
Kaolinite	0.02	0.40	4.04	8.62	4.43	10.19	25.88	1.60
Ca-Clay	0.05	0.54	4.73	5.80	0.92	2.02	13.13	0.81
Mixed Aluminosilicate	0.00	0.02	0.48	0.57	0.00	0.00	1.00	0.06
Pyrite	0.00	0.23	2.81	2.48	0.00	2.33	7.33	0.45
Barite	0.00	0.00	0.42	4.41	1.00	0.00	5.45	0.34
Gypsum	0.00	0.08	0.98	0.21	0.70	0.00	1.34	0.11
Coal								93.84
Total	0.08	1.66	22.79	30.43	13.93	31.12	100.00	100.00

were most abundant in the 4.4-8.0- μm size range, Ca-Clay, was more concentrated in the 2.1-4.4- μm range, and pyrite was most abundant in the 8.0-11.0- μm range. The 4.4-8.0- μm size category had the highest amount of mineral matter. Total concentration of minerals for this size fraction was 4.8 wt%.

In the 74-106- μm coal size fraction, quartz, kaolinite, Ca-clay, and pyrite dominated the mineral distribution. The most abundant minerals were kaolinite and quartz, with kaolinite being slightly more abundant than quartz. Quartz, pyrite, and kaolinite did not concentrate in any particular size category but were fairly evenly distributed throughout the last four size categories. Ca-clay was definitely more abundant in the 2.1-8.0- μm size range. This coal size fraction showed a mineral content of 6.16 wt%, which was greater by only approximately 1% than the two smaller size fractions.

The distribution and association of mineral grains in the Beulah coal are summarized in Table 53. The mineral grains are listed as extraneous, inherent, and associated with other minerals. For example, the mineral type kaolinite/gypsum indicates that kaolinite and gypsum are associated together; the table shows that 20% of these associated particles were within coal particles and 80% were extraneous.

4.4.2 Beulah Char Characterization

The phase compositions of the four Beulah chars, expressed as area percents, are shown in Table 54. The phases represent thermally unaltered discrete mineral phases, thermally altered derived phases, and amorphous phases. The phases are classified by size, with the size ranges corresponding to the six stages of the multicyclone.

The major phases present in the 0.1-second char, as depicted in Table 54, were Ca-aluminosilicate, pyrite, quartz, aluminosilicate or kaolinite, iron oxide, and Ca-oxide. Calcium-aluminosilicate and pyrite comprised 66% of the char inorganic components. The pyrite content indicates that it has not been thermally decomposed or assimilated with other inorganic components to a great degree at this stage of combustion. The quartz, aluminosilicate, Ca-aluminosilicate, and Ca-oxide particles were mostly 4.4-8.0 μm in size, while the iron oxide and pyrite were mostly >11.0 μm in size.

The 0.2-second char, as shown in Table 54, revealed quartz, aluminosilicate, Ca-aluminosilicate, iron oxide, pyrite, Ca-oxide, and aluminosilicate gypsum as primary phases. Minor phases of gypsum and a gypsum-aluminosilicate mixture were also present. The Ca-aluminosilicate, Ca-oxide, gypsum, and aluminosilicate/gypsum particles were most abundant in the 2.1-8.0- μm size range, whereas quartz, aluminosilicate, iron oxide, and pyrite were most abundant in the >11- μm range.

In the 0.5-second Beulah char, the dominant phases were quartz, aluminosilicate, K-aluminosilicate, Ca-aluminosilicate, Ca-oxide, and gypsum. Only a trace of pyrite was observed (0.13%). Quartz and kaolinite were found primarily in the >11- μm size range. A large portion of the Ca-aluminosilicate and Ca-oxide particles were either 4.4-8.0 μm or >11 μm in size. The K-aluminosilicate was mostly 8.0-11.0 μm in size and gypsum was mostly 2.1-4.4 μm in size.

TABLE 53

MINERAL GRAINS PRESENT AS EXTRANEEOUS, INHERENT,
AND ASSOCIATED WITH OTHER MINERALS IN THE 53-74-MICROMETER
SIZE FRACTION OF BEULAH LIGNITE

<u>Mineral Types</u>	<u>Extraneous, %</u>	<u>Inherent, %</u>
Kaolinite	31	69
Kaolinite/gypsum	20	80
Barite	50	50
Barite/kaolinite	0	100
Calcite	0	100
Calcite/kaolinite	0	100
Ca-clay/gypsum	0	100
Ca-clay	33	67
Ca-clay/gypsum/barite	100	0
Fe-clay	44	56
Gypsum	33	67
Gypsum/quartz	50	50
Gypsum/barite	25	75
Gypsum/barite/K-clay	100	0
Gypsum/barite/kaolinite	0	100
Iron oxide	0	100
K-clay	0	100
Pyrite	36	64
Pyrite/kaolinite	0	100
Pyrite/barite	0	100
Pyrite/quartz	0	100
Quartz	51	49
Quartz/barite	67	33
Quartz/gypsum/barite	33	67
Quartz/calcite	0	100
Quartz/pyrite/gypsum	100	0
Rutile	67	33
Rutile/quartz	0	100

TABLE 54
DISTRIBUTION OF INORGANIC PHASES IN THE BEULAH CHARs

<u>Beulah 0.1 Second Char</u>								
<u>Mineral (Area Percent)</u>	<u>Particle Size Distribution (μm)</u>						<u>Total</u>	
	<u><1.2</u>	<u>1.2-2.1</u>	<u>2.1-4.4</u>	<u>4.4-8.0</u>	<u>8.0-11.0</u>	<u>>11.0</u>	<u>Area %</u>	<u>Wt %</u>
Quartz	0.01	0.13	0.18	3.42	1.63	2.45	7.82	6.35
Aluminosilicate	0.01	0.16	0.15	2.34	1.48	0.00	4.14	3.17
Iron Aluminosilicate	0.00	0.00	0.13	0.00	0.00	0.00	0.13	0.11
Potassium Aluminosilicate	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Calcium Aluminosilicate	0.07	0.98	8.13	14.84	6.93	2.95	33.90	28.03
Iron Oxide	0.00	0.00	0.00	0.47	0.97	3.43	4.87	7.84
Alumina	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Pyrite	0.00	0.00	0.12	0.37	0.86	23.33	24.69	37.94
Gypsum/Barite	0.01	0.03	0.29	0.92	0.00	0.00	1.25	1.34
Calcium-Rich	0.07	0.38	1.36	3.05	0.67	1.59	7.13	6.18
Rutile	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Barite	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Gypsum	0.04	0.45	0.83	0.23	0.73	0.00	2.28	1.71
Apatite	0.00	0.14	0.41	0.18	0.00	0.00	0.74	0.68
Dolomite	0.00	0.00	0.10	0.00	0.00	0.00	0.10	0.09
Aluminosilicate/Gypsum	0.11	0.59	1.73	0.47	0.00	0.00	2.90	2.26
Unknown	0.05	0.57	2.97	3.29	2.21	0.97	10.05	4.31
Total	0.37	3.44	16.39	29.59	15.48	34.72	100.00	100.00

<u>Beulah 0.2 Second Char</u>								
<u>Mineral (Area Percent)</u>	<u>Particle Size Distribution (μm)</u>						<u>Total</u>	
	<u><1.2</u>	<u>1.2-2.1</u>	<u>2.1-4.4</u>	<u>4.4-8.0</u>	<u>8.0-11.0</u>	<u>>11.0</u>	<u>Area %</u>	<u>Wt %</u>
Quartz	0.01	0.07	0.45	2.01	1.61	7.53	11.67	9.89
Aluminosilicate	0.00	0.12	0.79	1.97	0.44	10.37	13.69	10.95
Iron Aluminosilicate	0.00	0.02	0.00	0.00	0.55	0.00	0.57	0.51
Potassium Aluminosilicate	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Calcium Aluminosilicate	0.08	1.03	8.18	11.69	3.60	2.58	27.14	23.45
Iron Oxide	0.00	0.00	0.12	0.54	0.00	5.12	5.77	9.72
Alumina	0.00	0.00	0.03	0.00	0.00	0.00	0.03	0.04
Pyrite	0.00	0.01	0.11	0.13	0.00	16.74	16.99	27.29
Gypsum/Barite	0.00	0.02	0.11	0.15	0.00	0.00	0.28	0.31
Calcium-Rich	0.01	0.08	0.95	4.70	3.49	0.84	10.07	9.11
Rutile	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Barite	0.00	0.00	0.03	0.31	0.00	0.00	0.33	0.48
Gypsum	0.03	0.13	0.59	1.10	0.00	0.00	1.84	1.44
Calcium Silicate	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Dolomite	0.00	0.00	0.03	0.00	0.00	0.00	0.03	0.03
Aluminosilicate/Gypsum	0.09	0.82	1.86	1.03	0.49	0.00	4.30	3.51
Unknown	0.09	0.36	1.19	2.91	1.37	1.36	7.28	3.26
Total	0.30	2.66	14.43	26.53	11.55	44.54	100.00	100.00

TABLE 54 (CONTINUED)

<u>Beulah 0.5 Second Char</u>								
<u>Mineral (Area Percent)</u>	<u>Particle Size Distribution (μm)</u>						<u>Total</u>	
	<u><1.2</u>	<u>1.2-2.1</u>	<u>2.1-4.4</u>	<u>4.4-8.0</u>	<u>8.0-11.0</u>	<u>>11.0</u>	<u>Area %</u>	<u>Wt %</u>
Quartz	0.00	0.00	0.10	0.88	0.66	12.33	13.98	14.02
Aluminosilicate	0.01	0.05	0.10	0.82	0.40	5.37	6.77	6.40
Iron Aluminosilicate	0.00	0.02	0.03	0.00	0.00	0.00	0.05	0.05
Potassium Aluminosilicate	0.00	0.03	0.31	1.10	2.39	0.88	4.71	4.90
Calcium Aluminosilicate	0.07	0.47	4.87	16.08	8.27	16.38	46.14	47.15
Iron Oxide	0.00	0.00	0.11	0.86	0.00	0.00	0.98	1.95
Alumina	0.00	0.01	0.00	0.21	1.16	0.57	1.95	2.97
Pyrite	0.00	0.01	0.00	0.12	0.00	0.00	0.13	0.25
Gypsum/Barite	0.00	0.00	0.07	0.00	0.00	0.00	0.07	0.09
Calcium-Rich	0.00	0.03	0.75	3.04	2.88	3.17	9.87	10.57
Rutile	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Barite	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Gypsum	0.00	0.55	2.42	1.71	0.35	1.00	6.11	5.67
Calcium Silicate	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Dolomite	0.00	0.01	0.00	0.26	0.00	0.00	0.27	0.29
Aluminosilicate/Gypsum	0.04	0.32	0.86	0.95	0.00	0.00	2.17	2.09
Unknown	0.02	0.12	1.14	2.37	1.03	2.14	6.81	3.61
Total	0.22	1.62	10.77	28.40	17.14	41.85	100.00	100.00

<u>Beulah 0.8 Second Char</u>								
<u>Mineral (Area Percent)</u>	<u>Particle Size Distribution (μm)</u>						<u>Total</u>	
	<u><1.2</u>	<u>1.2-2.1</u>	<u>2.1-4.4</u>	<u>4.4-8.0</u>	<u>8.0-11.0</u>	<u>>11.0</u>	<u>Area %</u>	<u>Wt %</u>
Quartz	0.01	0.03	0.23	0.38	2.01	16.71	19.38	18.10
Aluminosilicate	0.00	0.03	0.27	0.51	0.00	8.01	8.82	7.78
Iron Aluminosilicate	0.00	0.02	0.08	0.13	0.00	0.00	0.22	0.22
Potassium Aluminosilicate	0.00	0.02	0.00	0.00	0.00	0.00	0.02	0.02
Calcium Aluminosilicate	0.07	0.48	3.00	10.48	6.66	19.12	39.81	37.89
Iron Oxide	0.00	0.02	0.12	0.47	0.00	4.19	4.80	8.90
Alumina	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Pyrite	0.00	0.01	0.50	0.10	0.00	1.01	1.63	2.88
Gypsum/Barite	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Calcium-Rich	0.01	0.03	0.35	2.17	0.50	1.49	4.55	4.54
Rutile	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Barite	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Gypsum	0.10	0.56	2.36	2.34	0.86	0.00	6.22	5.37
Calcium Silicate	0.00	0.19	0.36	0.52	1.55	7.01	9.64	10.19
Dolomite	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Aluminosilicate/Gypsum	0.07	0.59	1.18	1.10	0.48	0.72	4.15	3.73
Unknown	0.02	0.17	0.19	0.39	0.00	0.00	0.77	0.38
Total	0.28	2.14	8.66	18.60	12.05	58.27	100.00	100.00

The 0.8-second char showed two dominant phases: quartz and Ca-aluminosilicate (Table 54). Other less abundant phases observed were aluminosilicate, iron oxide, Ca-oxide, gypsum, calcium silicate, and an aluminosilicate/gypsum mixture. Quartz, aluminosilicate, Ca-aluminosilicate, iron oxide, and calcium silicate were all most abundant in the $>11\text{-}\mu\text{m}$ size category. Calcium-oxide and gypsum were most common in the $2.1\text{-}8.0\text{-}\mu\text{m}$ size range.

4.4.3 Discussion of Inorganic Transformations

The four Beulah chars were examined for trends and changes in phase composition with respect to residence time. Several trends were noted that provide information pertaining to the transformation of inorganic constituents during combustion. All of the chars in Table 54 share three aspects in common: they reveal Ca-aluminosilicate as the most abundant phase; they show the greatest area percent of their inorganic constituents in the $>11\text{-}\mu\text{m}$ range; and they suggest a coalescing of finer-sized inorganic constituents.

Figure 80 shows the relative changes in abundance of inorganic phases with respect to time. Aluminosilicate, or kaolinite, which was the dominant mineral phase in the coal, decreased drastically in the first 100 milliseconds of combustion and then remained stable through 800 milliseconds of combustion residence time. In contrast, Ca-aluminosilicate started out as a minor constituent of the coal, probably in the form of montmorillonite, and then dramatically increased and stabilized after 100 milliseconds in the hot zone of the drop-tube furnace. Quartz content dropped from 19% to 8% during the first 100 milliseconds of combustion and then steadily increased through 800 milliseconds of residence time. Pyrite virtually disappeared after 200 milliseconds of combustion. The gypsum content remained fairly constant after decreasing significantly during the initial 200 milliseconds of combustion.

Some of the changes in the distribution of phases with residence time can be explained. The large amount of Ca-aluminosilicate may have resulted from an incorporation of calcium (organically associated) into the aluminosilicate material during combustion. The resulting Ca-aluminosilicate was most likely a derived phase composed of aluminosilicate from kaolinite and calcium from the abundant source of organically bound calcium in the coal. The increase of quartz or silica with residence time may be attributed to a concentration effect, whereby quartz is simply being concentrated as the organic char matrix is burned away. The concentration of quartz may also be decreasing with time due to interaction at its surface with alkali-alkaline earth metals and molten aluminosilicate material.

Comparing the particle size distribution of the inorganic phases contained in the coal and the four char phases gave strong evidence for the concept of coalescence of inorganic constituents. Figure 81 reveals that the concentration of inorganic phases in the $<8.0\text{-}\mu\text{m}$ size ranges decreased with residence time, while the concentration of phases greater than $8.0\text{ }\mu\text{m}$ increased with time. This implies that the finer-grained inorganic constituents -- such as clays, quartz, and organically bound cations -- coalesced with time to form larger particles.

Figure 80. Mineral and other inorganic phases present in original Beulah coal and chars at set residence times.

Figure 81. Particle size distribution of total minerals in original Beulah lignite and in successive chars produced at set residence times.

A closer look at what minerals are being assimilated revealed that quartz and kaolinite are being incorporated into larger fly ash grains during combustion. Figures 82 and 83 clearly reveal a significant initial drop in quantity of quartz and kaolinite upon introduction to the hot zone, followed by a successive depletion in quantity with time. This is true for all the quartz particles except the $>11\text{-}\mu\text{m}$ size range. It was shown earlier that both quartz and kaolinite had most of their mass in the 4.4 to $8.0\text{-}\mu\text{m}$ range. The small sizes of these particles probably allowed them to be more readily assimilated with other inorganic components. The pronounced decrease in kaolinite after the first 100 milliseconds of combustion was an indication of destruction of the kaolinite compositional structure by addition of other elements. The CCSEM analytical program will not identify kaolinite if the Si/Al ratio deviates from that characteristic of kaolinite or if significant amounts of other elements are incorporated into its structure or melt phase. The phenomenon most likely responsible for the decrease of kaolinite was the addition of organically-bound calcium or other calcium-bearing minerals. By comparing Figures 83 and 84, it was observed that the rapid decrease in fine particulate kaolinite with time corresponds to the rapid increase of Ca-aluminosilicate materials. The great increase in Ca-aluminosilicate is mainly in the particle size range between 4.4 and $8.0\text{ }\mu\text{m}$ (Figure 84), which is a size range that showed abundant aluminosilicate or kaolinite in the coal.

4.4.4 Beulah Fly Ash Characterization

A sized fraction of Beulah ($53\text{--}74\text{ }\mu\text{m}$) was combusted at approximately 1500°C and the fly ash produced was collected in a six-stage multicyclone. The SEMPC results for the Beulah multicyclone samples are summarized in Table 55 and Figure 85. The iron oxides and quartz derived particles are concentrated in the larger size fractions. Kaolinite-derived particles are evenly distributed in Stages 2 through 5 but are lower in Stage 1 and Stage 6. The Stage 6 ash consisted mainly of sodium sulfate and calcium sulfate. The small size of the particles in this stage makes it difficult to discern various types of ash particles due to limitations of the SEM/microprobe. The excitation depth under the conditions used in this study is approximately 1 to 2 μm . As a result, the x-rays generated may originate from material adjacent to the beam spot.

The results of the SEMPC analysis were compared with the particle size distribution of various mineral components found in the coal. Figures 86-88 illustrate the comparisons made between the content of selected coal minerals using CCSEM and the content of corresponding phases using SEMPC. Figure 86 shows that the quartz in the fly ash (SEMPC) follows the same general trend of decreasing abundance with decreasing particle size as the quartz in the coal (CCSEM). One of the reasons for the difference between the two plots is that the SEM technique ignores the organically associated inorganic components. The chemical fractionation data infers that a significant level of the inorganic constituents are associated organically. The quantity of organically associated elements is approximately 40 to 50% of the total ash-forming constituents in the coal. A second reason why the quartz content in the ash is lower than that found in the coal is due to the interaction of quartz with other ash forming species to produce some other material that is not identified as quartz by the SEMPC technique (e.g., calcium silicate). Figure 87 illustrates the distribution of kaolinite particles found in the coal and kaolinite-derived particles found in the ash. The level of kaolinite-derived

Figure 82. Distribution of quartz in Beulah coal and chars.

Figure 83. Distribution of aluminosilicate in Beulah coal and chars.

Figure 84. Distribution of Ca-aluminosilicate in Beulah coal and chars.

TABLE 55

SEMPG RESULTS FOR BEULAH FLY ASH MULTICYCLONE SIZE FRACTIONS
(WT % VALUES)

STAGE # SIZE, μm	1 >11	2 8.0-11	3 4.4-8.0	4 2.1-4.4	5 1.2-2.1	6 <1.2
CaO	3	0	0	0	0	0
Fe-oxides	7.2	2.3	0	0.6	0	0
Kaolinite*	36.2	50.4	63.5	60.2	60.1	10
Anhydrite	0.4	0	0	0	0	5
Anorthite	5.1	3.1	2.9	6.4	1.2	0
Quartz	4.7	2.3	0.7	1.2	0.4	0.
Melilite	1.7	2.3	5.8	1.2	1.2	0
Na-Ca-Sulfate	0	0	0	0	0	76
Unclassified	41.7	35.7	34.3	33.9	36.6	8

* kaolinite-derived

Figure 85. Distribution of inorganic phases in each stage of the multicyclone for Beulah fly ash.

Figure 86. Comparison of quartz content as a function of particle size for Beulah coal using CCSEM, and for Beulah fly ash using SEMPC.

Figure 87. Comparison of kaolinite content as a function of particle size for Beulah coal using CCSEM, and for Beulah fly ash using SEMPC.

Figure 88. Comparison of iron oxide and pyrite content as a function of particle size for Beulah coal using CCSEM, and for Beulah fly ash using SEMPC.

particles found in the ash is higher than what was found in the coal. Kaolinite readily reacts with other components such as organically associated calcium and iron components. The result of this interaction is most likely the cause of the increase in the level of kaolinite-derived particles. The distribution of iron in the coal as pyrite and iron oxide particles is compared to the distribution of iron oxide particles in the ash, as shown in Figure 88. The level of iron decreases with decreasing particle size for both the coal and the ash. The differences in the size distributions between the coal and the ash may be a result of the aerodynamic classification method used to collect the fly ash. This effect will cause the smaller sized iron oxide particles to end up in the larger sized fractions. In addition, the iron particles have been found to readily react with other ash components and become transformed into another type of fly ash particle not classified by the SEMPC technique to be iron oxide.

X-ray photoelectron spectroscopy (XPS) was used to determine the composition of the surfaces of particles collected in the various stages of the multicyclone. The XPS technique determines the binding energy of an electron removed from the outer 50 angstroms of the surface of a material due to the impingement of a beam of X-rays. The binding energy of the electrons is a function of the elements present and their electronic environment. Thus, the use of XPS provides both chemical composition and chemical species data.

The composition of the surfaces of the ashes collected in the multicyclone for Beulah lignite was determined using the XPS technique. The analysis obtained with XPS is an average for many particles in each stage because the area in which the x-ray beam excites is approximately 5 mm². A plot of the major inorganic constituents present at the surfaces of the particles as a function of ash particle size is illustrated in Figure 89. The elements are expressed as their equivalent oxide normalized to 100%. The results show that sodium is enriched on the surface of the particles relative to the level of sodium found in the ASTM ash. The sodium oxide content in the ASTM ash is 6.2%. The most significant increase in the level of sodium was shown in the <1.2- μ m sized fraction. In addition to the chemical composition of the surface, the chemical species were also identified. These results are summarized in Table 56. The chemical species were determined based on shifts of the binding energies of the electrons associated with each element. Sodium was found to be associated mostly with silicates in Stages 1 through 5, but in the final stage it is present as a sulfate. Calcium is present as a sulfate on the surfaces of the particles in most of the stages, but in Stage 1 was present with a silicate. The sulfur peaks showed that it was predominantly associated as a sulfate, most likely calcium sulfate.

4.4.5 Surface Analysis of Beulah Multicyclone Fly Ash

Beulah coal, sized to 53-74 μ m, was combusted in the drop-tube furnace at an average residence time of 2.3 seconds. The resulting multicyclone ash samples were analyzed to determine surface chemistry of the fly ash particles and element distribution with depth. The five cyclone size-fraction splits and the final filter sample were analyzed by XPS to determine chemical species present on the particle surfaces and by secondary ion mass spectroscopy (SIMS) to determine a chemical depth profile of selected elements. These two surface analysis techniques give an indication of the interaction between the fly ash particle and surrounding combustion gases.

Figure 89. Surface composition determined by XPS of Beulah fly ash collected in each stage of the multicyclone.

TABLE 56

CHEMICAL SPECIES IDENTIFIED IN BEULAH FLY ASH USING XPS ANALYSIS

MULTICYCLONE STAGE CUTPOINT, MICRONS						
Stage #	1	2	3	4	5	6
Size	>11	8.0-11	4.4-8.0	2.1-4.4	1.2-2.1	<1.2
Na	Silicate	Silicate	Silicate	Silicate	Silicate	Sulfate
S			CaSO ₄	CaSO ₄	CaSO ₄	CaSO ₄
Ca	Silicate		CaSO ₄	CaSO ₄	CaSO ₄	CaSO ₄

A summary of the XPS results is given in Tables 57 and 58 and portrayed graphically in Figures 90 and 91. The results are an average of two ESCA survey scans from each stage. Carbon content on the surface of the particles ranges between 35.8-43.9% through the first five cyclone stages and indicates that complete burnout has not been achieved at this residence time. Particles collected on the final filter, those less than 1.2 μm , show 6.1% carbon and have reached complete burnout. The results calculated on a carbon-free basis show that oxygen remains fairly constant over the size ranges at about 66%. Sodium, sulfur, calcium, and barium show slight increases as the size of the ash particle decreases. Aluminum and iron decrease slightly. The increases in sodium, sulfur, and calcium in the Stage 5 and final filter samples may indicate a volatilization-condensation process.

Table 59 is a summary of binding energies determined from XPS analysis and can indicate chemical states of the elements of interest. The sodium binding energy shift to a slightly higher value and the sodium auger parameter value, suggests that sodium exists as an oxide and possibly as an undefined silicate. Sulfur is found to exist as CaSO_4 . Silicon and aluminum appear to be present as oxides.

The results of SIMS chemical depth profiling are shown graphically in Figures 92A through 92F. Sodium decreases with depth in all of the size fractions, as would be expected in a volatilization-condensation situation. Other SIMS data on the remaining elements is inconclusive except that fluctuations in concentration from the surface downward have generally reached some constant value by ten minutes sputtering time. In most cases the decrease in sodium to a constant value seems to occur at a greater depth than other elements.

4.5 Characterization of Monticello Coal, Char, and Fly Ash

4.5.1 Monticello Coal Characterization

The chemical fractionation results for the Monticello coal are found in Table 60. The large percentage of aluminum, silicon, potassium, and titanium remaining after the extraction implies that these elements were mostly associated with insoluble minerals as clays, quartz, and possibly rutile (titanium oxide). The results suggest that significant amounts of the alkali and alkaline earth elements are associated in the coal as salts of organic acid groups. For example, most of the magnesium, calcium, and strontium were removed by the ammonium acetate extraction. Potassium appears to be associated with a clay mineral. The iron was distributed as roughly half acid-insoluble sulfides (probably pyrite) and half organically coordinated or acid-soluble minerals.

Coal and ash analysis results for the Monticello bulk coal are given in Table 61. The Monticello coal had a relatively high ash content of 22%. The 53-74- μm fraction, however, had an ash content of only 15%. The ASTM ash had fairly high silica and calcium contents and a very low sodium content (Table 61).

The mineral distributions for Monticello are summarized in Table 62. The 38-53- μm size fraction displayed quartz as the dominant mineral species by far, with kaolinite, Ca-clay, mixed aluminosilicate, and calcite also present

TABLE 57
XPS RESULTS ON BEULAH ASH FROM MULTICYCLONE STAGES
(WT %)

	<u>Stage 1</u>	<u>Stage 2</u>	<u>Stage 3</u>	<u>Stage 4</u>	<u>Stage 5</u>	<u>Filter</u>
Carbon	35.8	38.3	37.0	43.9	42.8	6.1
Oxygen	41.2	41.0	41.6	36.9	38.0	62.7
Sodium	2.1	2.4	2.3	1.4	2.7	4.7
Aluminum	5.6	4.2	4.3	4.1	3.5	4.4
Silicon	8.8	4.6	5.4	5.9	3.9	6.1
Sulfur	2.9	4.7	4.9	4.1	4.5	7.6
Calcium	2.7	3.9	3.8	3.2	3.8	7.1
Iron	0.4	0.3	0.1	0.0	0.2	0.2
Barium	0.2	0.4	0.3	0.2	0.4	0.9
Total	99.7	99.8	99.7	99.7	99.8	99.8

TABLE 58
XPS RESULTS ON BEULAH ASH FROM MULTICYCLONE STAGES,
CARBON-FREE CALCULATION (WT %)

	<u>Stage 1</u>	<u>Stage 2</u>	<u>Stage 3</u>	<u>Stage 4</u>	<u>Stage 5</u>	<u>Filter</u>
Carbon	0.0	0.0	0.0	0.0	0.0	0.0
Oxygen	64.5	66.7	66.3	66.1	66.7	66.9
Sodium	3.3	3.9	3.7	2.5	4.7	5.0
Aluminum	8.8	6.8	6.9	7.3	6.1	4.7
Silicon	13.8	7.5	8.6	10.6	6.8	6.5
Sulfur	4.5	7.6	7.8	7.3	7.9	8.1
Calcium	4.2	6.3	6.1	5.7	6.7	7.6
Iron	0.6	0.5	0.2	0.0	0.4	0.2
Barium	0.3	0.7	0.5	0.4	0.7	1.0
Total	100.0	100.0	100.0	100.0	100.0	100.0

Figure 90. XPS analysis of Beulah fly ash multicyclone stages: A) analysis for C, O, Al, and Si, and B) analysis for Na, S, Ca, Fe, and Ba.

Figure 91. XPS analysis of Beulah fly ash multicyclone stages (carbon free):
 A) analysis for C, O, Al, and Si, and B) analysis for Na, S, Ca, Fe, and Ba.

TABLE 59
XPS BINDING ENERGIES FROM DETAILED SCANS OF BEULAH FLY ASH
(eV)

	<u>Stage 1</u>	<u>Stage 2</u>	<u>Stage 3</u>	<u>Stage 4</u>	<u>Stage 5</u>	<u>Filter</u>
	<1.2	1.2-2.1	2.1-4.4	4.4-6.0	6.0-11.0	>11.0
Carbon, uncorr.	288.66	288.44	289.00	288.70	288.80	288.30
Carbon, corr.	284.60	284.60	284.60	284.60	284.60	284.60
Charge c.f.*	4.06	3.84	4.40	4.10	4.20	3.70
Oxygen 1S	531.09	531.51	531.55	531.85	532.00	531.75
Oxygen 2S	23.99	24.21	24.60	24.80	24.95	25.10
Oxygen Auger	745.44	745.16	745.30	745.70	745.85	745.60
Sodium 1S	1072.04	1072.46	1072.25	1072.70	1072.60	1072.85
Sodium Auger	263.89	264.01	264.00	264.40	264.25	264.40
Na Auger Param.	808.15	808.45	808.25	808.30	808.35	808.45
Na Auger & PE**	2061.75	2062.05	2061.85	2061.90	2061.95	2062.05
Aluminum 2S	117.84	118.11	118.00	118.50	118.55	119.15
Aluminum 2P	72.89	73.01	73.40	73.95	73.65	73.80
Silicon 2S	152.39	152.31	152.55	153.30	153.00	153.05
Silicon 2P	101.29	101.36	101.65	103.50	101.95	102.20
Sulfur 2P	168.19	168.56	169.20	0.00	169.65	169.40
Calcium 2P 1/2	350.54	350.66	350.45	351.00	351.10	351.05
Calcium 2P 3/2	346.84	347.11	374.15	347.60	347.60	347.65
Calcium diff.	3.70	3.55	3.30	3.40	3.50	3.40

* Charging correction factor.

** Photon Energy = 1253.6 eV for Mg anode.

A. Beulah ash, Multicyclone 1.

D. Beulah ash, Multicyclone 4.

B. Beulah ash, Multicyclone 2E.

E. Beulah ash, Multicyclone 5.

C. Beulah ash, Multicyclone 3F.

F. Beulah ash, Multicyclone Final Filter.

Figure 92. SIMS profiles of six elements in Beulah multicyclone fly ash samples.

TABLE 60
CHEMICAL FRACTIONATION RESULTS FOR MONTICELLO COAL

	Initial ($\mu\text{g/g}$ dry coal)	% Removed by H_2O	% Removed by NH_4OAc	% Removed by HCl	% Remaining
Na	315	31	51	0	18
Mg	1180	0	70	4	26
Al	9110	0	0	5	95
Si	23600	0	0	1	99
K	335	21	5	0	74
Ca	7320	0	77	13	10
Ti	395	0	0	15	85
Fe	2200	0	0	53	47
Sr	130	0	72	11	17
Ba	100	0	52	26	22

TABLE 61
RESULTS OF MONTICELLO COAL AND ASH ANALYSIS^a

Monticello (Texas Lignite)	
<u>Proximate, Wt%</u>	
Moisture	34.1
Volatile Matter	41.2
Fixed Carbon	37.8
Ash	22.0
<u>Ultimate, Wt%</u>	
Carbon	56.5
Hydrogen	4.5
Nitrogen	1.0
Oxygen (by diff)	16.4
Sulfur	0.8
<u>Ash Analysis, Wt%^b</u>	
SiO_2	56.1
Al_2O_3	17.2
Fe_2O_3	4.1
TiO_2	1.9
P_2O_5	0.1
CaO	16.8
MgO	2.5
Na_2O	0.5
K_2O	0.5

- ^a Results reported on a dry basis except for the moisture determination.
^b SO_3 -free basis.

TABLE 62
MINERAL DISTRIBUTION DATA FOR MONTICELLO SIZE FRACTIONS (WT%)

38-53 μ m Sized Fraction								
Particle Size Distribution (μ m)							Total	Wt%
Mineral/Coal	<1.2	1.2-2.1	2.1-4.4	4.4-8.0	8.0-11.0	>11.0	% Min	Coal
Quartz	0.06	0.93	7.10	10.30	5.54	37.94	61.65	2.37
Kaolinite	0.03	0.28	2.69	3.31	3.68	5.89	15.82	0.61
Ca-Clay	0.01	0.17	0.81	0.26	0.51	1.10	2.85	0.11
Mixed Aluminosilicate	0.00	0.08	0.75	0.55	0.80	5.03	7.19	0.27
Pyrite	0.00	0.03	0.00	0.00	0.00	0.00	0.03	0.00
Calcite	0.00	0.00	0.00	0.00	0.00	9.54	9.51	0.37
Barite	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
Gypsum	0.00	0.00	0.05	0.00	0.00	0.00	0.05	0.00
Coal								96.16
Total	0.11	1.52	11.90	15.62	11.36	59.50	100.00	100.00

53-74 μ m Sized Fraction								
Particle Size Distribution (μ m)							Total	Wt%
Mineral/Coal	<1.2	1.2-2.1	2.1-4.4	4.4-8.0	8.0-11.0	>11.0	% Min	Coal
Quartz	0.39	2.82	10.47	8.16	2.09	55.41	79.35	4.34
Kaolinite	0.11	0.61	2.13	1.6	2.65	0.0	7.09	0.39
Fe-Aluminosilicate	0.02	0.14	0.25	0.0	0.0	0.0	1.40	0.02
K-Aluminosilicate	0.03	0.27	1.26	1.05	0.0	0.0	3.04	0.17
Ca-Aluminosilicate	0.14	0.58	0.68	0.0	0.0	3.42	4.82	0.26
Iron Oxide/Carbonate	0.0	0.10	0.10	0.0	0.0	0.0	0.9	0.01
Rutile	0.03	0.12	0.32	0.0	0.0	0.0	0.48	0.03
Aluminosilicate/Gypsum	0.03	0.13	0.07	0.37	0.0	2.73	3.34	0.18
Pyrite	0.0	0.06	0.07	0.0	0.0	0.0	0.13	0.01
Unknown	0.0	0.02	0.35	0.21	0.47	0.0	1.05	0.06
Coal								94.53
Total	2.75	4.89	15.77	11.40	5.63	61.56	100.0	100.00

74-106 μ m Sized Fraction								
Particle Size Distribution (μ m)							Total	Wt%
Mineral/Coal	<1.2	1.2-2.1	2.1-4.4	4.4-8.0	8.0-11.0	>11.0	% Min	Coal
Quartz	0.05	0.55	6.86	10.85	6.09	37.53	61.46	4.12
Kaolinite	0.03	0.19	1.62	2.81	0.33	7.63	12.51	0.84
Ca-Clay	0.01	0.16	1.54	0.89	0.25	13.74	16.74	1.10
Mixed Aluminosilicate	0.00	0.08	0.70	2.00	0.00	1.20	3.95	0.27
Pyrite	0.00	0.00	0.00	0.42	0.00	2.07	2.47	0.17
Calcite	0.00	0.00	0.00	0.21	0.32	0.00	0.53	0.04
Barite	0.00	0.00	0.09	0.42	0.00	0.00	0.51	0.03
Gypsum	0.00	0.01	0.13	0.00	0.00	0.00	0.14	0.01
Coal								93.29
Total	0.10	1.01	11.44	18.28	6.99	62.17	100.00	100.00

in significant quantities. The above minerals, which comprised 60% of the minerals observed, were concentrated in the $>11\text{ }\mu\text{m}$ size category. The overall mineral concentration within this coal size fraction was 3.85 wt%.

The major minerals observed in the $53\text{--}74\text{ }\mu\text{m}$ fraction included: quartz, kaolinite, Fe-aluminosilicate, K-aluminosilicate, Ca-aluminosilicate, and an aluminosilicate/gypsum mixture. The Fe and Ca-aluminosilicates were probably a type of montmorillonite and the K-aluminosilicate was most likely illite. Quartz was the most abundant mineral and was the dominant phase in all of the size ranges except for the $8.0\text{--}11.0\text{ }\mu\text{m}$ range, where kaolinite was the major phase. Quartz and Ca-aluminosilicate (montmorillonite) show approximately 70% of their mass in the $>11\text{ }\mu\text{m}$ size range. Kaolinite was evenly distributed in a $1.2\text{--}11.0\text{ }\mu\text{m}$ size range. The mineral content was calculated to be 5.5 wt% of the coal.

The $74\text{--}106\text{ }\mu\text{m}$ coal size fraction revealed quartz as the major mineral species with relatively minor amounts of kaolinite, Ca-clay, pyrite, and mixed aluminosilicates. Pyrite was observed here, which was not seen in the previous smaller coal fractions. All of the aforementioned minerals had a higher frequency of mineral grain sizes that were $>11\text{ }\mu\text{m}$. The total mineral content for this coal fraction was 6.71 wt%.

4.5.2 Characterization of Monticello Char

Monticello chars were produced at residence times of 0.1, 0.2, 0.5, and 0.8, seconds and were examined using SEM/microprobe analysis to determine the morphology and qualitative elemental composition of early-stage inorganic ash particles.

The 0.8-second residence time char contained more fly ash than any of the others; however, significant amounts of organic-rich char particles were still observed. Table 63 lists compositions of selected inorganic ash particles and char matrix.

Some of the ash particles in the 0.8-second char have kaolinite-derived compositions and aluminum-to-silicon ratios of approximately 1. Abundant submicron particles were observed in contact with the receding char surface. These spheres contained relatively high levels of calcium, similar to analyses shown in Table 63. Larger fly ash particles (15-30 micrometers) also showed high levels of Ca. There is usually some Fe associated with the higher-Ca particles.

Partially combusted char matrix was more pronounced with the 0.5-second residence time. Figure 93 illustrates a char particle with very small submicron ash particles exuding from the surface along with loosely attached 2-5-micron inorganic ash particles. Qualitative microprobe analyses of several inorganic droplets are tabulated in Table 63. The inorganic ash droplets are usually high in CaO , have a pervasive Si-Al content and a ratio that is nearly 1:1, and commonly show Fe_2O_3 quantities that are between 10-20%. Figure 94 shows that the initial inorganic ash droplets are typically $0.1\text{--}1.0\text{ }\mu\text{m}$ in diameter and form on the surface of the char as the organic matrix is burned away.

TABLE 63

COMPOSITION OF REPRESENTATIVE INORGANIC ASH PARTICLES
AND CHAR MATRIX IN MONTICELLO CHAR
(EDS NORMALIZED OXIDE WEIGHT PERCENTS)

Elemental Oxide	Inorganic Ash Particles												Char Matrix	
	0.1 Sec				0.2 Sec				0.5 Sec				0.5 Sec	0.8 Sec
Na ₂ O	0	1	1	3	0	0	0	0	0	0	0	0	0.0	0.0
MgO	5	10	1	6	2	5	2	1	1	2	0	0	3.1	3.4
Al ₂ O ₃	7	14	32	10	12	13	9	27	6	4	42	0	8.4	9.5
SiO ₂	7	11	46	18	25	11	9	37	11	23	51	0	11.3	12.5
SO ₃	15	16	1	17	6	7	13	5	5	2	0	0	19.8	20.7
ClO	1	0	0	0	0	1	0	1	0	0	0	0	0.5	0.7
K ₂ O	0	6	0	1	0	0	0	1	0	0	0	0	0.4	0.0
CaO	52	34	15	36	42	51	35	25	57	54	3	0	47.4	41.5
TiO ₂	3	0	1	1	3	0	2	0	5	3	1	0	4.3	0.0
Fe ₂ O ₃	10	8	3	9	10	14	31	5	15	13	3	0	4.9	11.7

Figure 93. Monticello char particle produced at 0.5-second residence time at 1300°C.

Figure 94. Monticello char particle produced at 0.5-second residence time, showing inorganic ash droplets on surface.

Very few large, isolated fly ash particles were generated in the 0.1 second char. However, the char particles were all nearly covered with small ash particles. Smaller submicron fly ash grains lying in direct contact with the char surfaces were rich in Ca, with moderate or low concentrations of the other major elements, as summarized in Table 63. Larger fly ash particles (5-30 micrometers) had higher Al, Si, and Ca levels. The fly ash was slightly different from that produced in the previous longer-residence-time runs in that Na was found in some of the fly ash analyses. This was the only combustion run that showed any detectable amounts of sodium. Selected particles listed in Table 63 gave sodium concentrations of 1-3%.

4.5.3 Characterization of Monticello Fly Ash

The results of the SEMPC analysis of Monticello fly ash are listed in Table 64. The major inorganic phases in the fly ash were quartz, kaolinite-derived, and the unclassified material. Quartz content varied markedly between size categories. In the >11-μm and 4.4-8.0-μm size fractions, 25.4 and 31.8% quartz were detected, respectively. Kaolinite-derived was observed in significant quantities in all size fractions with the highest level (22.4%) found in the 1.2-2.1-μm range. Melilite was present in all of the multi-cyclone stages except for the 2.1-4.4-μm size range. Anhydrite was the major component on the final filter (28%). Plagioclase in the form of solid solution phases between end members albite (NaAlSi₃O₈) and anorthite (CaAl₂Si₂O₈), was observed at low levels, in the fly ash. Hauyne, which is a sodium-calcium aluminosilicate with sulfur, was observed in all of the samples except the 2.1-4.4-μm range. The highest content (11.2%) of hauyne was observed in the 1.2-2.1-μm range.

TABLE 64
PHASES DETECTED BY SEMPC FOR MONTICELLO FLY ASH

	<u>Filter</u>	<u>Stage 5</u>	<u>Stage 4</u>	<u>Stage 3</u>	<u>Stage 2</u>	<u>Stage 1</u>
Particle Size Cutpoints (μm)	<1.2	1.2-2.1	2.1-4.4	4.4-8.0	8.0-11.0	>11.0
Percent Mass	2.0	2.4	1.1	1.6	2.0	90.9
<u>Phase (Number %)</u>						
Hauyne	1.6	11.2	1.0	0.0	2.9	0.5
Calcium Oxide	0.0	0.0	0.0	0.0	0.0	0.5
Montmorillonite ⁺	0.0	0.7	1.0	0.0	0.0	1.5
Calcium Silicate	0.0	0.7	1.0	0.0	0.0	0.0
Illite	0.0	0.0	0.0	0.0	0.6	0.0
Iron Oxide	0.0	0.0	1.0	0.0	1.7	0.0
Kaolinite ⁺	1.2	22.4	13.0	18.2	16.6	12.2
Anhydrite	28.0	1.4	0.0	2.3	6.3	0.5
Plagioclase	0.0	1.4	1.0	0.0	1.2	1.0
Quartz	0.0	2.1	16.3	31.8	6.3	25.4
Melilite	0.4	2.8	0.0	2.3	1.1	2.0
Pyroxene	0.8	0.0	0.0	0.0	0.0	0.0
Unclassified	67.9	56.6	65.4	45.5	63.5	56.3
<u>Average Composition, wt% (SO₃-Free)</u>						
SiO ₂	29.5	37.7	51.5	51.7	43.5	64.0
Al ₂ O ₃	10.2	18.2	15.2	11.6	17.5	15.1
Fe ₂ O ₃	26.0	6.7	5.7	4.6	5.8	2.6
TiO ₂	0.9	2.1	1.5	2.6	1.9	1.7
P ₂ O ₅	0.2	0.3	0.5	0.4	0.4	0.5
CaO	15.8	27.4	19.9	23.1	23.7	12.6
MgO	16.0	5.6	3.7	4.0	4.6	2.3
Na ₂ O	1.1	1.6	1.7	1.6	2.0	0.8
K ₂ O	0.1	0.3	0.3	0.3	0.4	0.4
(SO ₃)*	8.7	6.4	4.2	3.7	4.6	0.7
<u>Average Si/Al Molar Ratio</u>						
	2.5	1.8	2.9	3.8	2.1	3.6

⁺ Derived phases resemble the original mineral in the coal.

* SO₃ is included for comparison purposes.

The chemical compositions (on an SO_3 -free basis) of each sample are listed in Table 64 along with the Si/Al molar ratio. The most striking result shown in Table 64 was the high level of Mg and Fe in the ash collected on the final filter. The very high Fe and Mg contents in the final filter suggests they may have vaporized and subsequently condensed to form submicron-size particles, or that they were organically associated, which can also produce very small particles during combustion. The chemical fractionation results revealed that approximately 53% of the iron was associated as either organically bound cations or as acid-soluble minerals such as Fe-carbonate. Since the CCSEM data showed only small quantities of Fe-bearing minerals including iron oxide, Fe-carbonate (siderite), and pyrite, most of the Fe was probably organically bound.

4.5.4 Discussion of Inorganic Transformations for Monticello

Using the comprehensive inorganic data base of Monticello coal and combustion products, some hypotheses can be made regarding the processes of inorganic transformation. Three major stages will be used to explain the transformation of Monticello inorganic constituents: 1) initial distribution of inorganic constituents in the coal; 2) early-stage combustion, which encompasses the first few tenths of a second of combustion after a coal particle enters the combustion chamber; and 3) late-stage combustion, which includes processes that take place 1-1.5 seconds after a coal particle enters the combustion chamber.

The initial distribution of inorganic constituents in the Monticello coal included major discrete mineral phases of quartz and aluminosilicate and large organically bound Ca and Fe components. During early stages of combustion, Ca was released from its organic bonding sites and formed liquid CaO-rich inorganic ash droplets that often contained Al-Si-Fe constituents as well. The pervasive aluminosilicate component in these ash droplets came mostly from clays that were concentrated in the finer fraction of the coal. The Fe content in the ash droplets may have been derived from the approximately 50% Fe that was associated with the organic fraction of the coal. Finely disseminated organically bound elements are more likely to surface as small sized ash particles upon combustion. In the later stages of combustion, complete char burnout was attained, leaving only fly ash. The fly ash consisted of a complex mixture of crystalline and amorphous liquid phases, with the majority of the material being amorphous.

4.5.5 Fly Ash Particle Size Distributions as a Function of Different Combustion Temperatures and Coal Sizes

Comparisons were made of fly ash particle size distributions for five test coals. The fly ash was sized using multicyclone and impactor aerodynamic-size-classification devices.

In the first set of comparisons presented here, the combustion temperature was constant at 1500°C and three different sized fractions of each coal were used to generate fly ash. Figure 95 presents the multicyclone and impactor data for the smallest size fraction of coal used, which was 38-53 μm . The Eagle Butte, Monticello, and Upper Freeport fly ash showed larger percentages of 1-5 micron sized fly ash, for both multicyclone and impactor runs, than the Beulah and Robinson. Most of the fly ash for the coals was greater than 10 microns in average diameter.

Figure 95. Fly ash particle size distributions for multicyclone and impactor runs as a function of coal size (38-53- μ m coal).

The 53-74- μm coals produced fly ash that was again mostly greater than 10 microns in size as shown in Figure 96. Quantities of ash that was >10 microns ranged from 75-95% by mass. Of the five coals, the Robinson and Beulah showed greater than 10% of their mass in the 1-5- μm category.

The 74-106- μm coal fly ash, displayed in Figure 97, was again mostly >10 microns in diameter for all the coals, with the Beulah and Robinson fly ash having significantly more mass in the 1-5-micron range.

In summary, fly ash from the test coals followed similar size distribution trends when different size fractions of coal were combusted at the same temperature of 1500°C. The Beulah and Robinson fly ash seem to have more mass in the 1-5-micron size range than the other coals.

The 53-74- μm coal fraction from each test coal was combusted at varied temperatures and the particle distribution of the fly ash was scrutinized. Eagle Butte fly ash was generated at 1300, 1400, and 1500°C, and collected in the multicyclone. The particle size distributions of the fly ash are shown in Figure 98. The 1400°C fly ash showed the highest amount of material in the 1-6 μm range, followed by the 1500°C and 1300°C fly ashes.

The Upper Freeport fly ash particle size distributions at 1300, 1400, and 1500°C were very similar, having a mass percent variance of, at the most, 1% at each cutpoint (Figure 99).

Fly ash particle size distributions generated from the Beulah coal, shown in Figure 100, were slightly varied with the 1300°C fly ash showing greater mass in the smaller 1-6- μm fraction, followed by the 1500°C and 1400°C fly ashes.

Fly ash was generated at 1300°C and 1500°C for the 53-74- μm Robinson coal and the particle size distributions are shown in Figure 101. The smallest size fraction in the 1500°C fly ash has more material than the 1300°C fly ash.

Monticello fly ash was produced at temperatures of 1300°C and 1500°C. The 1300°C fly ash had more mass in the smaller 1-6- μm size fractions than in the 1500°C fly ash, as shown in Figure 102.

In summary, examination of coal fly ash particle size distributions as a function of initial combustion temperature, does not reveal any trends. All of the coals tested had the majority of their mass in the >11- μm size fraction of the multicyclone, regardless of temperature. Particle temperatures were probably much higher than the gas temperature in the drop-tube furnace. Therefore, even at the 1300°C combustion temperature, the particles were probably at temperatures above the melting points of organic constituents.

4.5.6 Fly Ash Classification Scheme

The fundamental mechanisms of fly ash formation are being investigated by observing the interactions of inorganic constituents during coal combustion. A scanning electron microscope/microprobe was used to determine the physical and chemical interactions taking place during the initial stages of fly ash formation. The SEM/microprobe system allows for morphological and chemical analysis of the samples. Of particular concern were the composition of the

Figure 96. Fly ash particle size distribution for multicyclone and impactor runs as a function of coal size (53-74- μ m coal).

Figure 97. Fly ash particle size distribution for multicyclone and impactor runs as a function of coal size (74-106- μm coal).

Figure 98. Eagle Butte fly ash particle distribution as a function of temperature.

Figure 99. Upper Freeport fly ash particle size distribution as a function of temperature.

Figure 100. Beulah fly ash particle size distribution as a function of temperature.

Figure 101. Robinson fly ash particle size distribution as a function of temperature.

Figure 102. Monticello fly ash particle size distribution as a function of temperature.

particles derived from organically associated Ca, K, Mg, and Na prior to interaction with discrete mineral grains such as quartz and clays. A classification scheme for fly ash particles is presently being developed. The preliminary results are discussed.

In this part of the study, partially combusted coal produced from a 53-74- μ m sized fraction of Beulah coal was collected at 0.1, 0.2, 0.5, and 0.8-second residence times at a combustion temperature of 1500°C in a drop-tube furnace.

The fly ash and particles were grouped into several types based on morphology and chemical composition. Figure 103 shows an example of the most abundant fly ash type (Type 1) found in the samples. Type 1 fly ash particles display a distinctively spherical-to-ovoid morphology, a relatively smoother surface, and are composed of Fe-, Ca-, and Na-rich aluminosilicates. A second fly ash type (Type 2) also has a spherical-to-ovoid overall morphology, but tends to display complex crystalline patterns on the surfaces of particles as shown in Figure 103b and 103c. Type 2 particles are composed primarily of iron with minor amounts of Ca and Na.

Fly ashes in the Type 3 category are aluminosilicates with Al/Si ratios similar to those of the clay mineral kaolinite. The Type 3 particles consist of irregular, partially molten or agglomerated particles as illustrated in Figure 103d. These particles are probably derived from the agglomeration of partially molten clay minerals. Type 4 fly ash particles are angular in morphology and are rich in silica. These particles are derived from the

Figure 103. Secondary electron images of fly ash particles produced from Beulah lignite.

mineral quartz and are shown in Figures 103e and 103f. Table 65 summarizes the chemical compositions of randomly selected fly ash particles at all of the residence times examined with reference to the fly ash types discussed above. The compositions were derived using energy-dispersive spectrometry (EDS) on unpolished fly ash mounts. The EDS results are at best semiquantitative, but adequately reflect chemical compositions of the materials analyzed.

The longest residence time showed nearly complete combustion of the coal as evidenced by the small amount of char present. The bulk of the 0.8-second residence time sample consisted of Type 1 fly ash particles ranging in size from 1 to 100 μm ; although all of the fly ash particles discussed earlier were present.

Analysis of fly ash particles coating the few remaining char particles in the 0.8-second residence time sample showed that these particles were rich in calcium.

Samples collected at the 0.5-second residence time consisted primarily of fly ash, indicating that combustion was nearly complete. Several analyses were obtained from the char particle illustrated in Figure 104a. This particle was covered with protuberances, which are believed to reflect inorganic materials exuding from the char as the combustion processes are occurring. Analysis of these protuberances should reflect the compositions of organically associated materials prior to their interactions with the discrete mineral phases. Table 66 summarizes the analysis of these protuberances from the residence times of 0.1, 0.2, and 0.5 seconds. Calcium is the dominant constituent of the material intimately associated with the chars. Other common elements present in the protuberances include Al, Si, S, Fe, K, and Na.

The samples generated in the 0.2-second residence time run showed many more char particles present than in either of the previous runs. Fly ash particles appeared larger in size and more incompletely formed. Angular quartz grains were more abundant showing less melting and interaction of the inorganic components present. Figure 104b illustrates the interaction and melting of aluminosilicate particles on the surface of an iron-rich particle derived from pyrite. Analysis of the particles interacting with the iron-rich particle show (in order of abundance) major amounts of Al, Si, and Ca along with minor amounts of Fe, Na, S, and Mg. Figures 104c and 104d also illustrate a char particle from the 0.2-second residence time and the calcium-rich protuberances on the particle surface.

Char particles were the dominant constituent of the 0.1-second residence time sample with only a few fly ash particles formed. Type 1 fly ash particles had chemical compositions close to that of the clay mineral kaolinite and were probably derived from the mineral kaolinite. Type 2 and Type 3 particles were also present but were far less abundant than in the longer residence time samples.

Upper Freeport fly ash was used in addition to Beulah fly ash to develop a general classification scheme for fly ash. A 53-74- μm sized fraction of Upper Freeport coal was combusted in the drop-tube furnace at three combustion temperatures (1300, 1400, and 1500°C). The resulting fly ash was collected and aerodynamically classified by a multicyclone.

TABLE 65

EDS ANALYSIS OF FLY ASH TYPES (WEIGHT PERCENT EXPRESSED
AS EQUIVALENT OXIDE)

Type	Residence Time, Sec	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	SO ₃	K ₂ O	CaO	TiO ₂	Fe ₂ O ₃
1	0.2	2	1	23	49	2	0	16	0	8
1	0.5	1	0	33	59	2	0	2	1	1
1	0.8	3	0	39	53	0	0	5	0	1
2	0.1	0	0	1	1	0	0	1	0	96
2	0.1	0	0	0	1	0	0	2	0	97
2	0.2	0	0	0.3	1	1	0	1	0	97
2	0.8	0	0	0.4	1	0	0	2	0	97
3	0.1	0	0	44	55	0	0	1	0	1
3	0.8	1	0	42	48	1	1	4	0	3

Figure 104. Secondary electron images of char and fly ash particles produced from Beulah lignite.

TABLE 66
EDS ANALYSIS OF CALCIUM-RICH PARTICLES (WEIGHT PERCENT
EXPRESSED AS EQUIVALENT OXIDE)

Residence Time, Sec	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	SO ₃	K ₂ O	CaO	TiO ₂	Fe ₂ O ₃
0.1	3	0	14	19	2	0	55	0	8
0.1	6	0	21	17	3	0	44	2	8
0.1	0	1	3	8	1	0	78	1	8
0.1	0	1	5	12	1	0	75	0	6
0.1	0	7	4	2	5	0	73	3	4
0.1	0	9	11	14	14	0	46	2	3
0.2	0	2	3	12	3	0	74	0	7
0.2	1	0	24	45	1	1	21	0	8
0.2	0	1	4	7	3	0	79	0	7
0.5	0	1	4	8	34	0	49	0	4
0.5	0	5	15	21	17	1	32	1	8

Scanning electron microscopy and electron microprobe analysis were used to determine the effects of the various combustion temperatures on the morphology and composition of the fly ash particles. The SEM system allowed for simultaneous analysis of the morphology and composition of the fly ash. A similar classification scheme was used to describe the Upper Freeport fly ash (described earlier in this report in reference to Beulah lignite fly ash).

The Upper Freeport fly ash, as a whole, displayed less marked morphological differences than the previously described Beulah fly ash. In general, the fly ash tended to be more regular in morphology and an overwhelming majority of the particles are Type 1. Type 1 fly ash particulates display a distinctively spheroid-to-ovoid morphology and a relatively smooth surface. In the Upper Freeport samples, fly ash particles with other morphologies were found only in the largest size fraction of the multicyclone. Secondary electron images of the fly ash collected in Stage 1 of the multicyclone for the samples produced at 1300, 1400, and 1500°C are illustrated in Figure 105. It is evident that the regularity and sphericity of the particles increases with increasing combustion temperatures. There was a significant quantity of partially combusted char present in the 1300°C sample and some char material is present in the 1400°C sample as well. The 1500°C sample shows complete combustion with little or no evidence of char present.

Compositional changes between the samples subjected to the various temperatures seem to parallel morphological changes. With increased temperature both the compositional and morphological homogeneity increased. This is to be expected assuming increased interaction and assimilation of the inorganic components with increasing combustion temperature.

The particles collected in Stage 1 at 1300°C are shown in Figure 106. Table 67 shows the analysis of selected points indicated by the numbers on Figure 106. Particles that are relatively iron-rich (2, 4, and 5) are smooth-surfaced and spherical (Type 1). Larger more irregular particles (points 1 and 3) are rich in Al and Si.

Figure 105. Secondary electron images of Upper Freeport fly ash particles found in Stage 1 of the multicyclone ($>11\ \mu\text{m}$), (A) 1300°C, (B) 1400°C, and (C) 1500°C.

Figure 106. Secondary electron image of Upper Freeport char and fly ash produced at 1300°C.

TABLE 67

ANALYSIS OF PARTICLES IN FIGURE 106, WEIGHT PERCENT
EXPRESSED AS EQUIVALENT OXIDE

Particle	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	SO ₃	K ₂ O	CaO	TiO ₂	Fe ₂ O ₃
1	0.0	0.0	33.7	48.5	6.2	2.6	0.0	0.0	4.5
2	0.0	0.0	22.5	43.0	0.0	3.3	0.9	1.13	29.3
3	0.0	0.0	15.0	70.5	0.4	6.4	0.0	0.0	7.6
4	0.0	0.0	20.3	27.4	0.0	0.8	13.2	0.0	38.3
5	0.0	0.0	14.4	29.9	0.6	6.2	13.5	8.6	22.7

An image of some of the particles collected in Stage 1 at 1400°C is shown in Figure 107. Table 68 summarizes the analysis of selected particles. The two iron-rich particles analyzed (1 and 4) are small spherical particles. Larger and occasionally more irregular particles (3, 4, 5, and 7) are aluminosilicate derived from clay minerals in the original coal. Samples collected in the other stages of the multicyclone were compositionally and morphologically quite homogeneous, as shown in Figure 108 and Table 69. These particles are primarily iron-rich aluminosilicates.

The particles collected in Stage 1 of the multicyclone for Upper Freeport combusted at 1500°C are illustrated in Figure 109. Table 70 shows the analysis of selected particles. Again, the iron-rich particles (5, 6, and 7) tend to be Type 1 particles (smooth and spherical). Irregularly shaped particles tend to be rich in aluminum and silicon (1 and 3). However, several Type 1 particles were aluminosilicates (2 and 4). A backscattered electron image of the same area reveals that the iron-rich particles (those that are light in color) are the smaller more irregularly shaped particles.

5.0 CONCLUSIONS

The Eagle Butte coal consists of the following major mineral constituents: quartz, kaolinite, gypsum, calcite, and a calcium aluminophosphate that might be a form of wavellelite, crandallite, or millisite. Also present in the Eagle Butte inorganic content is high amounts of organically bound calcium and magnesium. The total of discrete minerals and organically bound elements is about 6 wt% of the coal. Mineral content in three Eagle Butte sonically sieved coal fractions were very similar. Also, the mineral particle size distributions were very similar between coal fractions.

Chars produced from the Eagle Butte 53-74- μm coal exhibited surface coatings of ash particles that were very high in CaO. Other major products of the combustion process were calcium silicate, calcium aluminate, and calcium aluminosilicate. Quartz was drastically reduced in content in the chars due to reaction with calcium aluminosilicate and CaO. Submicron calcium-rich minerals or organically bound calcium is the source for ubiquitous CaO-rich inorganic ash droplets that appear on the surface of early-stage chars. By 0.8-seconds of combustion, 95% carbon burnout had been achieved.

The most abundant phases observed in the Eagle Butte fly ash multicyclone samples were calcium oxide followed by quartz and gehlenite. Fly ash that was classified as less than 6.0 microns in the multicyclone showed very low amounts of crystalline or chemically ordered phases. The amount of unclassifiable amorphous species seems to decrease with decreasing size of fly ash. Iron in the Eagle Butte fly ash was more concentrated in the smaller size fraction most likely because iron was associated in the coal as finely dispersed carbonate or organically bound cations, or because iron particles in the largest fly ash size fraction were being coated with calcium aluminosilicates or other materials that mask the identity of an iron-bearing core material. Other trends noticed were that Fe_2O_3 and SO_3 contents increased with decreasing particle size. The SiO_2 and Al_2O_3 contents in the fly ash follow trends observed with the other coals.

Figure 107. Secondary electron image of Upper Freeport fly ash produced at 1400°C.

TABLE 68

ANALYSIS OF SELECTED PARTICLES IN FIGURE 107, WEIGHT PERCENT
EXPRESSED AS EQUIVALENT OXIDE

Point	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	SO ₃	K ₂ O	CaO	TiO ₂	Fe ₂ O ₃
1	0.0	0.0	2.5	2.4	0.0	0.6	0.0	0.0	94.5
2	0.0	0.0	31.9	47.1	0.0	6.9	0.5	3.6	9.9
3	0.0	0.0	36.2	45.3	0.0	4.7	1.7	2.3	9.8
4	0.0	0.4	8.4	18.3	0.0	0.7	0.7	0.0	7.2
5	0.0	0.0	37.2	47.3	0.0	2.8	2.2	0.7	9.8
6	0.0	0.0	28.8	57.9	0.0	5.6	0.7	2.1	2.3
7	0.0	0.0	28.0	47.4	0.0	2.3	7.5	3.1	10.9

Figure 108. Secondary electron image of Upper Freeport fly ash from Stage 5 of the multicyclone produced at 1400°C.

TABLE 69

ANALYSIS OF SELECTED PARTICLES IN FIGURE 108, WEIGHT PERCENT
EXPRESSED AS EQUIVALENT OXIDE

Point	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	SO ₃	K ₂ O	CaO	TiO ₂	Fe ₂ O ₃
1	0.0	0.0	29.7	47.1	0.0	3.8	0.7	0.0	16.5
2	0.0	0.0	28.7	52.6	0.4	5.2	0.4	1.0	11.3
3	0.0	0.6	27.7	47.2	0.8	3.7	1.3	2.4	16.0
4	0.0	0.4	25.6	49.3	0.6	3.8	0.7	3.6	15.5

Figure 109. Secondary electron image of Upper Freeport fly ash from Stage 1 produced at 1500°C.

TABLE 70

ANALYSIS OF SELECTED PARTICLES IN FIGURE 109, WEIGHT PERCENT
EXPRESSED AS EQUIVALENT OXIDE

Point	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	SO ₃	K ₂ O	CaO	TiO ₂	Fe ₂ O ₃
1	0.0	0.0	14.3	27.2	36.3	0.0	8.7	0.0	13.5
2	0.0	0.0	29.9	56.1	0.6	6.4	0.0	1.4	5.6
3	0.0	0.0	39.2	51.1	0.0	3.5	1.7	0.9	3.6
4	0.0	0.0	22.1	54.4	0.0	4.4	1.7	12.5	4.9
5	1.0	0.0	16.8	25.9	0.0	6.7	3.4	6.6	39.8
6	0.0	0.0	0.3	0.3	0.0	0.0	0.0	0.0	99.1
7	0.0	0.0	11.4	27.0	0.0	0.7	0.0	1.1	59.8

The early-stage chars show greater quantities of discrete phases that are 1.2-8.0 μm in size, which is evidence for initial fragmentation of mineral grains. By 0.8 seconds, the char shows greater quantities of discrete phases or particles that are >8.0 μm in size, which is evidence for coalescence of fly ash particles.

The most common minerals observed in the Upper Freeport coal were quartz, mixed aluminosilicate (illite), kaolinite, and pyrite. Minor amounts of calcite and gypsum were also noted. The quartz grains were evenly distributed through the various size ranges except for the 74-106 μm coal fraction, where there was an unusually high amount of quartz in the >11 μm range. Illite and pyrite were found most frequently in the >11 μm size category. In all three coal size fractions there were higher quantities of minerals in the upper size ranges (>8.0 μm).

Chars were produced in the drop-tube furnace from 53-74- μm sonically sieved Upper Freeport coal. The chars were collected at five different residence times. The general form of the mineral/phase particle size distribution remained the same through 0.8 seconds of combustion. The coal mineral and the char inorganic phases were bimodally distributed. Upper Freeport char morphologies were examined using the scanning electron microscope (SEM). Qualitative analyses were performed on selected particles to determine their relative elemental compositions. Thermal gravimetric analysis (TGA) was performed on the chars to monitor carbon burnout. Many of the Fe-rich particles showed significant quantities of aluminosilicate in their composition and illite-derived particles commonly had high Fe_2O_3 contents. Illite in the coal had lower Si/Al ratios than the illite-derived in the char. The data suggests that a depletion of Si has occurred during the combustion process. The particle distribution of phases in the chars and coal reveal fragmentation of mineral grains within the first 0.5 seconds of combustion. At 0.8 seconds, the sizes of phases or particles in the char were greater than those in the coal and preceding chars, which is evidence for coalescence.

An additional DTF run was made to collect Upper Freeport 0.05-second char, where the char was quenched using the fly ash quench probe and then collected in the multicyclone. The major phases present in the Upper Freeport 0.05 second char were montmorillonite, illite, kaolinite, calcite or calcium oxide, anhydrite, plagioclase (anorthite-albite), quartz, and unclassified material. When compared to the coal, the char revealed a depletion of calcite, mixed aluminosilicate, illite, and pyrite; most likely because of melting and interaction with other liquid or gas-phase inorganic components. Some phases were enriched including quartz and kaolinite.

Upper Freeport fly ash was generated from a 53-74- μm size fraction and analyzed for inorganic phases using SEMPC. Illite-derived was the most abundant phase recognized by SEMPC. Illite-derived is an amorphous K-aluminosilicate derived from the clay mineral illite.

Analysis of the Robinson coal size fractions showed major quantities of quartz, kaolinite, Ca-clay (montmorillonite), and pyrite. Other minerals observed were mixed aluminosilicates, gypsum, and barite. Quartz was predominantly concentrated in the >11- μm range. Ca-clay had a size distribution mostly in the 1.2-8.0- μm range. The size distribution of pyrite and kaolinite were variable. Overall, the majority of the mineral matter was in the >11- μm size category.

Short residence time combustion tests were conducted to produce chars from Robinson 74-106 μm coal. It appeared that after 0.2 seconds of combustion, extensive fragmentation of larger size mineral grains occurred. The mechanism for the fragmentation phenomenon in the first 0.2 seconds of combustion was based on the break-up of aggregates of aluminosilicate clays. At longer residence times of 0.5 and 0.8 seconds there was successive coalescence of finer sized inorganic phases. It is proposed that CaO , which was very abundant in the organic fraction of the coal, reacted with aluminosilicate clays that were abundant as discrete minerals. Calcium silicate formed as a result of the assimilation of vapor- or liquid-phase CaO into the partially molten surface of quartz grains.

The distribution of phases identified in the Robinson fly ash samples collected in the stages of the multicyclone indicated some significant changes as a function of particle size. Hauyne, a complex aluminosilicate containing sulfate, and melilite, were found to be concentrated in the small size fraction of the fly ash multicyclones. Iron oxide and quartz-derived particles were found to be concentrated in the large size fractions of the Robinson sample, and kaolinite-derived particles appeared to be evenly distributed across all size fractions.

Major minerals identified in the Beulah coal were quartz, kaolinite, Ca-clay (montmorillonite), and pyrite. Minor minerals included mixed aluminosilicates (montmorillonite), barite, and gypsum. Quartz, kaolinite, and pyrite were generally more abundant in the upper size ranges (4.4 to $>11 \mu\text{m}$) for all the size fractions. Ca-clay was observed more in the middle-to-lower size categories (2.1-8.0- μm). On the whole, most of the Beulah minerals were greater than 4.4 μm in size.

The Beulah fly ash shows sharp increases in concentrations of Na and S in the finer size fraction. Sodium and sulfur may be bound together as sulfates that condense from a vapor phase as fine particulate matter. Silica content decreased with particle size. The larger size of silicate-rich particles can probably be attributed to abundant quartz minerals in the original Beulah coal that are normally more abundant in the coarser size fraction.

Chars were produced from the Beulah 53-74- μm lignite in the drop-tube furnace and analyzed using CCSEM for the inorganic phases. The most common phases identified in the chars were Ca-aluminosilicate, quartz, aluminosilicate, gypsum, and iron oxide. Pyrite virtually disappeared from the chars after 200 milliseconds of residence time.

Distribution of major inorganic components in the Beulah chars and their comparisons to similar components in the original coal revealed some interesting trends. The overall area percent distribution of the inorganic phases showed a general decrease in material with time in the lower size ranges ($<8.0 \mu\text{m}$) and an increase in material with time in the higher size ranges ($>8.0 \mu\text{m}$). Quartz and kaolinite decreased in concentration with residence time, and Ca-aluminosilicate increased dramatically with time. The above data may be indicative of coalescence of finer-grained minerals and interaction of organically bound inorganics to form larger fly ash grains. In the case of kaolinite (or aluminosilicate) particles, there is strong evidence to suggest that these particles are undergoing a chemical transformation from pure kaolinite to

amorphous Ca-aluminosilicate particles of nearly the same size. This inorganic transformation results in Ca-aluminosilicate particles having nearly the same size distribution as the kaolinite particles (4.4 to 8.0 μm). The infusion of calcium from organically bound calcium, with the mineral form of kaolinite, may have been the mechanism by which Ca-aluminosilicate was formed.

Monticello coal exhibited the following major minerals: quartz (most abundant), kaolinite, Ca-clay, and mixed aluminosilicate. Quartz, kaolinite, and Ca-clay had grain sizes that were largely in the $>11\text{-}\mu\text{m}$ range for the 38-53- μm and 74-106- μm fractions. These same minerals showed higher concentrations in the 2.1-8.0- μm category within the 53-74- μm coal fraction.

Several conclusions can be drawn after examining the Monticello coal particles burned at various short residence times in the drop-tube furnace. For all of the residence time runs, small (< 1 micrometer) fly ash particles were observed forming on or at the char surface as it receded. These initial particles are typically composed of 40% to 60% calcium oxide and 5% to 15% iron oxide. The exact composition of these particles could not be discerned with the microprobe due to the small sizes of the particles and the roughness of the surfaces being analyzed.

Sodium was observed in appreciable quantities only in the 0.1-second residence time particles. This observation is consistent with the short-residence-time studies performed on the Robinson coal. The shorter residence time may not allow the Na to vaporize from the char and disperse as readily with the other particles. Therefore, more sodium remains within the fly ash particles and is detected during electron microprobe analysis.

The distribution of phases in the Monticello fly ash samples collected in the multicyclone indicated some significant changes as a function of particle size. Quartz-derived and kaolinite-derived particles dominated the larger size fractions, while pyroxene, hauyne, akermanite, and anhydrite comprised the bulk of the smallest size fractions. Comparison of these results with a drop-tube combustion run that used 53-74- μm Monticello coal revealed some differences. The Monticello coal used in this report had a unimodal distribution of quartz and showed very small amounts of anhydrite. In contrast, the Monticello fly ash had a bimodal distribution of quartz and showed greater amounts of anhydrite in most of the size fractions, especially in the filter fraction (28% anhydrite). Over 90% of the Monticello fly ash was greater than 11 μm in diameter, as compared to only 62% for mineral grains in the original coal. This suggests that the smaller minerals coalesced during combustion.

Bulk composition of the Monticello fly ash indicated that the organically bound elements, such as Na, Ca, S, Mg, and Fe, are distributed primarily in the finer fraction multicyclone stages. Aluminum and Si, which are primarily mineralogic constituents, were more often associated with the larger size fractions.

The fly ash size distributions were determined using the multicyclone and impactor for Beulah, Upper Freeport, Robinson and Monticello ashes produced in the drop-tube furnace. Initial comparisons show no dramatic differences in size distribution of fly ash produced as a function of coal particle size and temperature of combustion.

A fly ash particle classification scheme is being developed based on particle morphology and composition. Four types of particles have been initially classified for Beulah and Upper Freeport.

XPS was used to determine the form of selected elements and the composition of the surfaces of particles in the multicyclone size cuts. The highest level of sodium was found on the surfaces of the particles in Stage 6 ($<1.2 \mu\text{m}$). Aluminum and silicon levels were relatively constant but dropped off in Stage 6. Sulfur content increased with decreasing particle size. The forms of sodium, calcium, and sulfur were determined for each stage of the multicyclone. Sodium was in a silicate form in Stages 1 to 5, and a sulfate form in Stage 6 ($<1.2 \mu\text{m}$). Calcium was found to be in a silicate form in Stage 1 and a sulfate form in Stages 3 through 6.

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U.S. DEPARTMENT OF ENERGY
FEDERAL ASSISTANCE MANAGEMENT SUMMARY REPORT

1. Program/Project Identification No.		2. Program/Project Title Combustion Inorganic Transformation		3. Reporting Period 5-01-89 through 6-30-89	
4. Name and Address University of North Dakota Energy and Mineral Research Center Box 8213, University Station, Grand Forks, ND 58202				5. Program/Project Start Date 4/1/88	
				6. Completion Date 3/31/92	
Milestone ID. No.	Description	Planned Completion Date	Actual Completion Date	Comments	
a.1	Determine sodium release as a function of temperature/flame position for pure solids	1/88	6/88		
a.2	Determine the effects of gas stream composition on the release of sodium from solid sources	7/88	9/88		
a.3	Determine sodium release as a function of temperature/flame position for solids in a carbon matrix	7/88	7/88		
a.4	Detailed study of coals	1/89	5/89		
a.5	Determine the effects of more complex matrices on sodium release	4/89	4/89		
b.1	Prepare and characterize Beulah and Upper Freeport	6/88	6/88		
c.1	Determine inorganic interactions during char formation for Beulah and Upper Freeport	10/88	10/88		
c.2	Determine the effects of temperature and residence times on the condensation of flame volatilized inorganic phases on the surfaces of ash particles	3/89	3/89		
d.1	Determine the effects of aluminosilicate matrices on gas-phase sodium atom concentrations during combustion	6/89	6/89		
e.1	Complete characterization of Eagle Butte subbituminous coal	5/89	5/89		
e.2	Complete combustion testing of Eagle Butte subbituminous coal	5/89	6/89		
e.3	Complete characterization of chars and fly ashes	6/89	6/89		

20/11

3.3 Coal/Char Reactivity

COAL/CHAR REACTIVITY

**Final Technical Progress Report for the Period April 1, 1988 - June 30, 1989
Including the Quarterly Technical Progress Report
for the Period April through June 1989**

by

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TABLE OF CONTENTS

	<u>Page</u>
LIST OF TABLES.....	ii
LIST OF FIGURES.....	iv
1.0 EXECUTIVE SUMMARY.....	1
1.1 Single-Particle Reactor.....	1
1.2 Ignition Studies.....	1
2.0 GOALS AND OBJECTIVES.....	5
3.0 EFFECTS OF CALCIUM ON COMBUSTION.....	5
3.1 Experimental Equipment.....	5
3.1.1 Laminar-Flow Reactor.....	5
3.1.2 Calcium-Selective Electrode.....	6
3.2 Test Plan.....	9
3.3 Char Preparation.....	9
3.3.1 Demineralization Procedure.....	9
3.3.2 Char Preparation Procedure.....	9
3.3.3 Calcium-Loading Procedure.....	10
3.4 Char Combustion.....	11
3.5 Data Reduction.....	11
3.6 Results and Discussion.....	15
4.0 IGNITION BEHAVIOR.....	23
4.1 Introduction.....	23
4.2 Experimental Equipment and Procedures.....	24
4.3 Data Analyses.....	33
4.4 Results and Discussion.....	37
4.4.1 General.....	37
4.4.2 Effects of Oxygen Concentration.....	52
4.4.3 Inorganic Constituents.....	59
4.4.4 Volatile Matter.....	70
4.4.5 Moisture.....	75
4.4.6 Gas Temperature.....	77
4.4.7 Lithotype.....	78
4.4.8 Material Rank.....	78
4.4.9 Modeling.....	79
4.5 Publications.....	79
4.6 Future Work.....	80
5.0 REFERENCES.....	80

LIST OF TABLES

<u>Table</u>	<u>Page</u>
1 Calcium-Selective Electrode Response Data.....	8
2 LWX Coal Fragmentation and Swelling During Charring.....	10
3 Explanation of the Abbreviations for Tables 4 and 5.....	12
4 Calcium Concentration in the Calcium-Loaded Chars (ppm).....	13
5 Char Combustion Data Summary (New and Old Data).....	14
6 Major Components of the Ignition Apparatus.....	25
7 Cation Concentrations of Coals Used in the Ignition Studies.....	28
8 Densities of the Materials used in Ignition Experiments.....	29
9 Ignition and Combustion Parameters of Dry Beulah Lignite (PSOC-1507) Vitrain: The Effects of Oxygen Concentration, Inorganic Constituents and Volatiles.....	39
10 Ignition and Combustion Parameters of Beulah Lignite (PSOC-1507) Vitrain: The Effects of Moisture, Temperature, and Lithotype.....	41
11 Ignition and Combustion of Smith Roland Subbituminous Coal (PSOC-1520) Vitrain: The Effects of Lithotype, Inorganic Constituents, and Oxygen Concentration.....	44
12 Ignition and Combustion Parameters of Lower-Wilcox Lignite (PSOC-1443) Vitrain: The Effects of Lithotype, Temperature, and Oxygen Concentration.....	46
13 Ignition and Combustion Parameters of Lower-Wilcox Lignite (PSOC-1443) Vitrain: The Effects of Inorganic Constituents and Volatile Matter.....	48
14 Ignition and Combustion Parameters of Pittsburgh #8 Bituminous Coal (PSOC-1451) Vitrain: The Effects of Temperature and Oxygen Concentration.....	50
15 Optical Microscopy Results From the Combustion of Dry 180- to 250- μ m Beulah Lignite (PSOC-1507) Particles.....	53

LIST OF TABLES (CONT.)

<u>Table</u>		<u>Page</u>
16	Optical Microscopy Results from the Combustion of Dry 180- to 250- μ m Beulah Lignite (PSOC-1507) and Char Particles.....	61
17	Optical Microscopy Results of Dry 180- to 250- μ m Lower-Wilcox Lignite (PSOC-1443) Particles.....	64
18	Optical Microscopy Results of Dry 180- to 250- μ m Pittsburgh #8 (PSOC-1451) Bituminous Coal Particles.....	65

LIST OF FIGURES

<u>Figure</u>	<u>Page</u>
1 Response curve of the calcium-selective electrode.....	7
2 Combustion of LWX calcium-loaded chars.....	16
3 Combustion of NMB calcium-loaded chars.....	16
4 Contrast of LWX and NMB chars at 6% O ₂	17
5 Contrast of LWX and NMB chars at 8% O ₂	17
6 Contrast of LWX and NMB chars at 10% O ₂	18
7 Combustion of LWX(DEM) and LWX(NH ₄ OH) chars.....	19
8 Char combustion vs. oxygen concentration.....	20
9 LWX char combustion: χ values vs. calcium concentration.....	21
10 LWX char combustion: ρ values vs. calcium concentration.....	21
11 NMB char combustion: χ values vs. calcium concentration.....	22
12 NMB char combustion: ρ values vs. calcium concentration.....	22
13 Layout of ignition apparatus.....	24
14 Detailed front view of ignition apparatus combustion zone furnace.....	26
15 Detailed side view of the ignition apparatus combustion zone furnace.....	26
16 Flow system calibrator for the ignition apparatus.....	30
17 Modified timing chart: A) software delay, B) malonic acid response time, C) total coal delay, D) coal particle ignition delay = C-B and E) decarboxylation delay.....	31
18 Schematic of optical microscopy apparatus.....	31
19 Diagram of modified heated stage.....	32
20 Response of integral detector to a pulse-type signal.....	34
21 Evaluation of sample distortion.....	34
22 Calculated particle temperature profiles for 240- μ m particles in the ignition apparatus.....	37

LIST OF FIGURES (CONT.)

<u>Figure</u>		<u>Page</u>
23	Effect of O ₂ concentration on the production of CO ₂ from Beulah lignite vitrain at 650°C (BVLC, 0% O ₂ ; BVLE, 5% O ₂ ; BVLD, 11% O ₂ ; BVLA, 20% O ₂ ; BVLJ, 50% O ₂).....	54
24	Correlations of CO:CO ₂ product ratios with particle temperature: A) Arthur (25), B) this work, C) Hardesty (26).....	55
25	Rates of CO and CO ₂ production from dry Smith Roland subbituminous coal vitrain at 650°C, 5% O ₂ (SVLB).....	57
26	Rates of CO and CO ₂ production from dry Smith Roland subbituminous coal vitrain at 650°C, 20% O ₂ (SVLA).....	57
27	Rates of CO and CO ₂ production from dry Lower-Wilcox lignite vitrain at 1000°C, 5% O ₂ (LVHB).....	58
28	Rates of CO and CO ₂ production from dry Lower-Wilcox lignite vitrain at 1000°C, 20% O ₂ (LVHB).....	58
29	Effect of O ₂ concentration on the combustion of dry Pittsburgh #8 vitrain at 650°C.....	59
30	Rates of CO and CO ₂ production from dry demineralized Beulah lignite at 650°C, 5% O ₂ (BDLA).....	60
31	Rates of CO and CO ₂ production from dry Beulah lignite vitrain at 650°C, 5% O ₂ (BVLE).....	60
32	Rates of CO and CO ₂ production from dry demineralized Smith Roland subbituminous coal vitrain at 650°C, 5% O ₂ (SDLA).....	63
33	Rates of CO and CO ₂ production from dry demineralized Lower-Wilcox lignite at 1000°C, 20% O ₂ (LDHA).....	63
34	Rates of CO and CO ₂ production from dry demineralized Pittsburgh #8 bituminous coal at 1000°C, 20% O ₂ (PDHA).....	65
35	Rates of CO and CO ₂ production from dry Pittsburgh #8 bituminous coal at 1000°C, 20% O ₂ (PVHB).....	65
36	Rates of CO and CO ₂ production from dry, calcium-reloaded Beulah lignite at 650°C, 5% O ₂ (BRLA).....	68
37	Rates of CO and CO ₂ production from dry, calcium-reloaded Smith Roland subbituminous coal at 650°C, 5% O ₂ (SRLA).....	69

LIST OF FIGURES (CONT.)

<u>Figure</u>	<u>Page</u>
38 Rates of CO and CO ₂ production from dry, calcium-reloaded Lower-Wilcox demineralized lignite at 1000°C, 20% O ₂ (LRHA).....	70
39 Rates of CO and CO ₂ production from dry, calcium-reloaded Pittsburgh #8 demineralized coal at 1000°C, 20% O ₂ (PRHA).....	71
40 Rates of CO and CO ₂ production from dry Beulah lignite vitrain at 500°C, 20% O ₂ (BV5A).....	71
41 Rates of CO and CO ₂ production from Beulah lignite char at 500°C, 20% O ₂ (BC5A).....	72
42 Rates of CO and CO ₂ production from Beulah lignite char at 650°C, 5% O ₂ (BCLB).....	73
43 Rates of CO and CO ₂ production from dry Smith Roland subbituminous coal char at 650°C, 5% O ₂ (SCLA).....	74
44 Rates of CO and CO ₂ production from dry Lower-Wilcox lignite char at 1000°C, 20% O ₂ (LCHA).....	74
45 Rates of CO and CO ₂ production from moist Beulah lignite vitrain at 650°C, 5% O ₂ (BVLF).....	76
46 Rates of CO and CO ₂ production from dry Beulah lignite vitrain at 1000°C, 20% O ₂ (BVHA).....	77

COAL/CHAR REACTIVITY

1.0 EXECUTIVE SUMMARY

1.1 Single-Particle Reactor

- Factors affecting the sensitivity of the calcium-selective electrode were examined. It was found that leaving the electrode in a saturated calcium acetate solution for more than a few days reduced the electrode's sensitivity and that extended exposure could lead to extensive loss of sensitivity. Also, the presence of ammonium hydroxide in the solutions, in addition to resulting in higher potentials, tended to minimize the amount of drift in the electrode's response.
- The technique of monitoring the calcium loading of the chars with a calcium-selective electrode was examined further. It was determined that the electrode was capable of following with reasonable accuracy the loading level of the char until the calcium concentration in the filtrate dropped below approximately 1×10^{-5} M. Limitation in the accuracy of the electrode becomes apparent when the amount of extractable humic acid from the char becomes large. This loss in accuracy was attributed to the calcium becoming complexed with the humic acid and thus undetectable to the electrode. It was predicted that if the filtrates were reacidified prior to the measurement of the calcium concentration, then the accuracy of the electrode could be improved.
- Samples of Lower-Wilcox (LWX)(PSOC-1443D) and New Mexico Blue (NMB)(PSOC-1445D) coals were demineralized, charred, loaded with calcium to concentrations ≤ 2500 ppm, and then combusted in the laminar-flow reactor at varying oxygen concentrations. The loading procedure consisted of stirring the char in a calcium acetate solution at pHs adjusted with ammonium hydroxide to >10 . A significant amount of swelling occurred for both coals during the charring process. It was found that the greatest enhancement of the rate of the reaction by calcium occurred when the calcium concentration was about 2500 ppm. The observed rates of reaction were significantly greater than those observed for noncalcium-loaded chars examined in the past.
- Portions of the demineralized chars of different particle sizes and a demineralized Lower-Wilcox char that had been stirred in ammonium hydroxide to assess the effect of the loading procedure were combusted. It was found that the larger particle sizes resulted in lower particle temperatures and, therefore, lower rates of reaction. It was also found that the effect of the loading procedure is to result in lower particle temperatures. This decrease in reactivity was attributed to greater stability of carboxylate and phenolate ions to thermal degradation.

1.2 Ignition Studies

- The operational procedure and experimental design of the ignition apparatus was optimized for 240- μ m-diameter coal particles. Ignition and combustion characteristics of four coals were examined using this procedure and design. The sensitivity of the ignition apparatus was

simulated. It was determined that the production of CO_2 could be monitored from particles as small as $50\text{ }\mu\text{m}$. Limitations in the particle handling technique and sensitivity of the optical trigger set the practical minimal particle size at $200\text{ }\mu\text{m}$. The average particle examined had a volume similar to that of a $240\text{-}\mu\text{m}$ sphere.

- An apparatus for visually monitoring combusting coal and char particles was assembled. This apparatus consists of a video camera, microscope and heated stage. An Associated Western Universities (AWU) fellow used this apparatus to examine the same suite of coals characterized in the ignition apparatus. The optical microscopy observations were complementary to those obtained in the ignition apparatus.
- The characterization of the effect of oxygen concentration on the ignition and combustion of Beulah lignite (PSOC-1507) was completed. In general, increased oxygen concentration decreased the ignition delay, increased the proportion of CO to CO_2 produced, increased the maximum combustion rate, and decreased the combustion duration. The decreased ignition delay was attributed to the more rapid onset of heterogeneous ignition at the elevated oxygen concentrations. The increased combustion rates were consistent with accepted ignition theory. The change in the product distribution with CO being favored at high oxygen concentrations was attributed to increased particle temperatures.
- A correlation of the CO_2 : CO product distribution with particle temperature was established. This correlation was based on the assumption that the measured product distribution was indicative of that produced at the particle surface; i.e., that no CO oxidation occurred in the boundary layer. It was shown that at a gas temperature of 650°C , no more than 30% of the CO_2 produced could have originated in the boundary layer.
- Based on the rate constant data, the Beulah lignite was estimated to have an activation energy of 11 kcal/mole. The apparent order of the reaction with respect to oxygen concentration was 0.25.
- The effect of oxygen concentration on the ignition and combustion of Smith Roland subbituminous coal (PSOC-1520) at 650°C was examined in the ignition apparatus. Ignition of this material at oxygen concentrations of 5% and greater was observed. The effects of increased oxygen were similar to those observed for Beulah lignite; i.e., the combustion rate increased, the ignition delay decreased and the CO_2 : CO ratios decreased with increased oxygen concentration.
- The effect of oxygen concentration on the ignition and combustion of Pittsburgh #8 bituminous coal (PSOC-1451) was examined at 650°C in the ignition apparatus. The production of CO and CO_2 was observed at oxygen concentrations of 11 and 20%; however, as demonstrated by the optical microscopy results, this material did not ignite until a temperature greater than 825°C was employed. At 1000°C , increased oxygen concentration dramatically increased the combustion rate.

- The effect of oxygen concentration on the ignition and combustion of Lower-Wilcox lignite (PSOC-1443) was examined at 1000°C. Ignition was observed at this temperature. The maximum combustion rate increased and the ignition delay decreased with increased oxygen concentration.
- The characterization of the effects of inorganic constituents on the ignition and combustion of Beulah lignite, Lower-Wilcox lignite, Smith Roland subbituminous coal and Pittsburgh #8 bituminous coal was completed. The effects of demineralization on ignition and combustion were coal-dependent. Demineralization dramatically decreased the reactivity of Beulah lignite, Beulah lignite char, and Smith Roland subbituminous coal, and dramatically increased the reactivity of Lower-Wilcox lignite and its char. The reactivity of Pittsburgh #8 bituminous coal was not significantly affected by this procedure, while the reactivity of its char increased slightly. The various demineralized materials behaved more similarly than the original materials; however, significant differences were still apparent. This result indicates that while the inorganic constituents significantly alter coal reactivities, other parameters are also of importance. The most significant differences observed between the the two demineralized materials studied during combustion (Lower-Wilcox lignite and Pittsburgh #8 bituminous coal) were the larger maximum combustion rates and larger CO₂:CO ratios for the bituminous coal.
- The demineralized coals were reloaded with calcium in amounts proportional to the concentrations of calcium contained in the original coals. This procedure was performed to differentiate between effects produced by inorganic constituents and effects produced by physical changes in the coals resulting from the demineralization procedure. Beulah lignite and Smith Roland subbituminous coal initially contained the highest calcium concentrations and showed the highest reactivities. Demineralization decreased their reactivities. Reloading these materials with approximately one third of their initial calcium concentration increased the reactivity of the demineralized materials, but not to the levels observed for the untreated materials. Since calcium concentration plays a major role in dictating the reactivity of Beulah lignite and Smith Roland subbituminous coal, it appears that heterogeneous reactions are more important than homogeneous reactions to the ignition of the coals. The calcium-reloaded Lower-Wilcox lignite and Pittsburgh #8 bituminous coal showed reactivities similar to those of the demineralized materials--a result consistent with the low levels of calcium initially present in these materials.
- The characterization of the effects of volatile matter on the ignition and combustion of the four coals was completed. This data was obtained by comparing the ignition and combustion behaviors of the coals to their chars. The effects of volatile matter differed between the four coals. Beulah lignite char was found to ignite more rapidly yet burn slower than the original material. The inhibitory effect of volatile matter on the ignition of Beulah lignite is discussed. These results are consistent with the proposed heterogeneous ignition of the lignite. The most significant difference observed between Smith Roland subbituminous coal and its char was the single-staged combustion observed for the char as opposed to the two-staged process observed for the coal. This result was

consistent with the reduced volatile matter in the char and was similar to the Beulah lignite results. The char of Lower-Wilcox lignite was more reactive than the original lignite. The char of Pittsburgh #8 bituminous coal ignited more readily, but burned slower than the original coal.

- The effects of moisture on the ignition and combustion of Beulah lignite were examined. Moisture decreased the combustion rate of the lignite at the least rigorous condition employed; i.e., 650°C and 5% O₂; no other significant effects were observed.
- The effects of gas temperature on the ignition and combustion of Beulah lignite, Lower-Wilcox lignite and Pittsburgh #8 bituminous coal were characterized. As expected, the ignition delays decreased and combustion rates increased with increased gas temperature. The temperature at which ignition occurred was a function of material type. The ignition temperatures increased in the order Beulah lignite < Smith Roland subbituminous coal < Lower-Wilcox lignite < Pittsburgh #8 bituminous coal. For the combustion of Beulah lignite, the CO₂:CO ratios decreased upon increasing the temperature from 500° to 650°C, and increased upon increasing the temperature from 650° to 1000°C. This was interpreted as a result of CO₂ being the favored surface product at low particle temperatures. At low gas temperatures, both the particle and boundary temperatures are low; therefore, the CO₂ predominantly produced at the surface is detected. At the intermediate temperature, the surface temperature is slightly higher, shifting the surface products towards CO; minimal CO oxidation in the boundary occurs and the surface products are detected. At the highest gas temperature, CO is the favored surface product, but now the boundary layer is hot enough to produce significant CO oxidation, resulting in a net increase in CO₂ production.
- The effects of lithotype on the ignition and combustion of Beulah and Lower-Wilcox lignite and Smith Roland subbituminous coal were examined. The fusain lithotype of Beulah lignite ignited the most readily while the attritus lithotype showed the lowest reactivity. The attritus lithotypes of the Lower-Wilcox lignite and Smith Roland subbituminous coal also showed lower reactivities than the vitrains. The differences observed between lithotypes of the same coal were small compared to the differences observed between coals.
- The overall order of reactivity of the materials as determined from their maximum combustion rates was Beulah lignite => Smith Roland subbituminous coal > Pittsburgh # 8 bituminous coal > Lower-Wilcox lignite.
- The feasibility of monitoring the ignition and combustion of single Beulah lignite particles using isothermal DSC was evaluated. The low maximum temperature available with this apparatus, accompanied by the large variation in the results, produced the conclusion that this was not a viable technique for monitoring combustion processes.
- Monitoring events in the ignition apparatus by video imaging was impractical due to sensitivity limits of the video equipment and difficulties in positioning the combusting particles in the focal

volume. The feasibility of obtaining optical pyrometry data through the use of an optical rod inserted into the ignition apparatus was not ascertained.

2.0 GOALS AND OBJECTIVES

The overall objective of the Coal/Char Reactivity Project is to expand the fundamental combustion data base to support existing and advanced atmospheric combustion systems. The investigations will focus primarily on elucidating the burning rates of chars under realistic flame conditions as a function of fuel and system parameters. The chars are mainly derived from low-rank coals. The key issues include the relative contributions of inorganic constituents, and the surface and structural effects on the burning behavior of the low-rank coal-derived chars. Tests will be undertaken to ascertain the limits of bulk diffusion control of the burning rate. The specific objective for this reporting period was to evaluate the burning rates obtained and to determine rate constants based on CO , CO_2 , and CO/CO_2 as primary reaction products.

A second objective was to perform fundamental investigations on the ignition mechanisms of single particles of low-rank coals by measuring rates of carbon monoxide and carbon dioxide production and the onset of light emission. The specific objectives were to determine the effects of oxygen concentration, inorganic constituents, volatile matter, moisture, temperature, and lithotype on the ignition and combustion of Beulah lignite (PSIC-1507), Smith Roland subbituminous coal (PSIC-1520), Lower-Wilcox lignite (PSOC-1443) and Pittsburgh #8 bituminous coal (PSIC-1451).

3.0 EFFECTS OF MINERAL MATTER

3.1 Experimental Equipment

3.1.1 Laminar-Flow Reactor

The laminar-flow reactor enables the examination of single burning particles in an environment where the gas temperature and composition may be carefully controlled. The temperature and size of individual particles are determined simultaneously with three-color optical pyrometry and videomicroscopy, respectively. A detailed description of the laminar-flow reactor, pyrometer, and particle sizing system is given in (1).

In operation, a selected mixture of oxygen and nitrogen is metered from a gas mixing system and introduced through two preheaters into the high-temperature furnace section of the reactor, where the gas is heated by passing over molybdenum disilicide heating elements. The heated gas exits through a nichrome flow straightener and flows upward through a quartz-walled observation chimney. A small portion of the gas mixture is diverted prior to entering the preheaters and is used to entrain particles from a small feeder and inject them into the gas stream. The particles are carried through a water-cooled feed tube and introduced at ambient temperature at the bottom

center of the observation chimney. As the burning particles flow upward along the chimney centerline, they pass the focal point of the optical pyrometer and videomicroscope.

The three-color optical pyrometer consists of the pyrometer optics and a focus detector mounted at right angles to the pyrometer optical axis and focused on the same control volume in the observation chimney. Fiber optic cables connect the pyrometer and focus detector optics to the photomultiplier/amplifier assemblies. Narrow bandpass filters are placed in the optical path immediately before the pyrometer photomultipliers. The amplified photomultiplier signals pass through a coincidence detector to a digital waveform analyzer. Simultaneous signals from the pyrometer and focus detector indicate that a particle is in focus and trigger the capture of the signals by the analyzer. This also triggers the firing of a high-intensity strobelight focused on the control volume. The videomicroscope is focused on the control volume directly opposite the strobelight. The videocamera image is being continually recorded. The illumination from the strobelight momentarily silhouettes the particle, and the camera vidicon tube acts as a storage device, holding the particle image for three to four video frames.

The signals from the three pyrometer channels are stored to disk in their entirety, and later processed to determine particle temperatures. The video frames containing particle images are frozen with the video recorder, captured with a frame-grabber, and processed to determine particle size and shape.

3.1.2 Calcium-Selective Electrode

The calcium-selective electrode, which had been left standing in a saturated calcium acetate solution for about two months, was recalibrated to determine the reproducibility of the previously determined response curve after such a long-term exposure to the calcium acetate solution. The response curve was significantly different, suggesting that the electrode had lost a large degree of its sensitivity. Figure 1 contrasts the response curve determined previously with that of the results from this more recent study, as well as showing more clearly the effects of the presence of ammonium hydroxide on the electrode's response. The reason(s) for the drastic change in the electrode's response is not clear, though a couple of possibilities are known. First, the calcium acetate solution that the electrode was stored in molded after a few weeks. The electrode was placed into fresh calcium acetate solution and, again, after a few more weeks, the solution molded. The electrode was then put into dry storage until shortly before this study was undertaken. Even though no mold appeared to be on or near the electrode in either of the trials, it may have suffered some damage from the mold's presence. It should be noted that the owner's manual for the electrode suggests that the electrode be put into dry storage if it is to sit idle for more than a few days, but it does not clearly state whether this is because of the risk of the solution molding or because of the electrode itself suffering damage from the long exposure.

A second and just-as-likely reason for the change in the electrode's response is the fact that a different potentiometer was used in the earlier study than in the more recent one. The potentiometer used in the earlier study had been replaced with a "better and more sensitive" meter before this study was undertaken. One can reasonably expect some difference in the

Figure 1. Response curve of the calcium-selective electrode.

electrode's response to occur as a result of such a switch, but the magnitude of the observed change (which is indicative of less sensitivity) cannot be due to just a change in potentiometers.

Despite the change in the magnitude of the electrode's response, it was still reasonably linear over three orders of magnitude. As observed previously, the amount of fluctuation in the potential of a solution increased as its calcium concentration decreased, but always was no more than 2mV on either side the nominal value. The effect of the ammonium hydroxide on the potential was also the same as was observed previously: slightly higher than the same solution without the base. The presence of the ammonium hydroxide also tended to stabilize the potential reading for the solution, cutting the fluctuations down to about half that observed in its absence. This stabilization had not been noted in the first calibration.

An interesting observation that may deserve further investigation is the fact that the electrode's response from one-day-old standard solutions was higher than that from freshly prepared solutions. It would be surprising if it took a day for an equilibrium point to be established, and it would be hard to believe that the electrode could degrade so much overnight. The best explanation for this anomaly is that an error was made in the preparation of the two sets of standard solutions such that one of them actually had a slightly greater amount of calcium in it than it should have. Since the sets of standard solutions were made by successive dilution of a carefully measured amount of the initial stock solution, one slightly off measurement of the initial stock solution would carry throughout the whole set, giving the linear, but somewhat different response.

A summary of the predicted and actual calcium concentrations in the solutions from the calcium-loading of the various chars is given in Table 1. The loading procedure consisted of stirring a char sample in a calcium acetate solution using ammonium hydroxide to maintain the pH >8. After removal of the char, the filtrate's potential was measured to determine the extent of loading in the char. The predicted concentrations are determined from the extrapolation of the solutions' calcium-selective electrode potentials to the concentration axis on the standard response curve, while the actual concentrations were determined by either AA analyses or calculations of the dilution of stock solutions.

TABLE 1
CALCIUM-SELECTIVE ELECTRODE RESPONSE DATA

Predicted Ca Conc. (estimated from electrode response) (Molarity)	Actual Ca Conc. (from AA analysis) (Molarity)	Actual Ca Conc. (from dilution calculations) (Molarity)
<u>Standard Solutions</u>		
1.0×10^{-3}	9.5×10^{-4}	8.37×10^{-4}
7.6×10^{-4}	-----	6.03×10^{-4}
4.8×10^{-4}	-----	3.72×10^{-4}
1.6×10^{-4}	1.4×10^{-4}	1.40×10^{-4}
<u>Reaction Solutions</u>		
LWX Chars:		
1.5×10^{-5}	3.5×10^{-5}	--
1.3×10^{-5}	2.7×10^{-5}	--
1×10^{-5}	1.5×10^{-5}	--
1×10^{-5}	1.0×10^{-5}	--
NMB Chars:		
1.0×10^{-5}	2.3×10^{-4}	--
1.8×10^{-5}	8.5×10^{-6}	--
2.4×10^{-5}	3.0×10^{-5}	--
2.4×10^{-5}	2.3×10^{-5}	--

Interestingly enough, the concentrations based on the electrode's response for the standard solutions were always slightly higher than the actual concentrations, while those from the reaction solutions were somewhat lower. This latter observation makes logical sense, if some of the calcium became bound to the humic acids that were extracted into the filtrate from the char. In most of the reactions the filtrates were colored yellow or brown,

indicating that humic acids had been extracted from the chars by the basic solution. Bearing this in mind, in order for one to properly assess the amount of calcium transferred to a char, one should know how much humic acid can be extracted into the aqueous layer from it, the molecular weights and the weight distribution of these humic acids, and the equilibrium constants for their complexation with calcium. These are very likely to vary drastically between char samples and thus would have to be determined for each sample. This would be a formidable, if not impossible, task. The obvious way to eliminate this extra work would be to reacidify the solutions prior to determining their calcium concentration. By acidifying the filtrates, most of the calcium-humic acid complexes would be converted back to free calcium and the humic acids.

Nonetheless, the calcium-selective electrode has been shown to indicate reasonably well when most of the calcium has been loaded onto a char, the lower limit for accurate calcium concentration remaining in the aqueous phase being approximately 1×10^{-5} M.

3.2 Test Plan

The test plan for the current quarter was to examine the effect of alkaline earth cations on char combustion rates and to produce chars from two coals loaded with specific amounts of calcium. The calcium-loaded chars will be used in combustion tests to quantify the effect of calcium on char burning rates.

3.3 Char Preparation

3.3.1 Demineralization Procedure

Samples of Lower-Wilcox (PSOC-1443D) and New Mexico Blue (PSOC-1445D) coals were demineralized by successive treatment with HCl, HF, and HCl and then Soxhlet extracted with water for at least 12 hours to remove the traces of acid. The demineralized coal was then allowed to air dry for several days.

3.3.2 Char Preparation Procedure

The chars were prepared from the demineralized coals in the drop-tube facility. The char production conditions were: gas temperature = 1000°C , mole fraction of oxygen = 0.03, and residence time = 150 ms. The overall yield of char from both of the coals under these conditions was typically less than about 30% of the mass of coal used. In addition to this low yield, typically less than half of the char fell into the desired particle size range of 63-75 μm .

As reported previously (2), attempts to grind either the char or the coal with a mortar and pestle into desirable particle size fractions resulted mostly in the formation of fines. In order to better clarify the swelling and fragmentation of the coal during the charring process, a study consisting of the charring of the <63- μm , 63-75- μm , and 75-90- μm particle sizes of the Lower-Wilcox coal under the above conditions was done. The resultant chars were then resized to determine if the size distribution had changed. The results of this are summarized in Table 2.

TABLE 2

LWX COAL FRAGMENTATION AND SWELLING DURING CHARRING

Initial Size*	Weight % Distribution of Char Particle Sizes					
	<53	53-63	63-75	75-90	90-106	>106
<63	60.6	10.8	9.0	5.5	4.1	10.1
63-75	13.4	13.0	31.2	24.7	10.3	7.1
75-90	1.4	2.4	17.8	38.3	26.7	13.4

*Particle sizes given in microns.

In each case the >106- μ m size fraction appeared to be mostly smaller sized particles that were loosely fused together, which could be broken up by light grinding with a mortar and pestle. The results show that a significant degree of swelling, as well as some particle fragmentation, occurs when all sizes of the coal are charred. The swelling is especially evident, in that the largest size fraction outside the original coal size is the next size range higher. The fact that some material more than two particle size ranges smaller than the initial size was recovered shows that some fragmentation had occurred. Further evidence that fragmentation occurs during the charring is that the total yield of char is less than that expected based on TGA analysis. These analyses show that the percent of volatile matter should be no more than 50% of the total mass. Presumably, the smaller fragmented particles are carried past the collection cyclone with the carrier gas, resulting in the observed lower-than-expected mass recovery.

Since the yield of the 63-75- μ m particle size range was low, the 63-75- μ m, and 75-90- μ m fractions were combined for the calcium-loading study. The fines from the sonic sieving were used to determine the amount of calcium remaining in the demineralized char. It is assumed that the calcium concentration in the fines is representative of that in the larger particles.

3.3.3 Calcium-Loading Procedure

The chars (about 1.8 grams for each run) were mixed with calcium acetate solutions of known concentration (100 ml total volume) to which two milliliters of concentrated ammonium hydroxide had been added, and then rapidly stirred for three days, the pH being maintained above 10. The concentrations of the calcium acetate solutions were chosen such that only specific calcium-loading levels would be obtained, if total calcium uptake occurred. That is, the difference between the desired loading level and the amount of calcium already present was determined and then a solution containing only that much calcium was used. The pH was maintained high so as to ensure rapid, maximum uptake of the calcium (2,3). Only the loading of the LWX char to the 2500-ppm level showed any change in the pH during the loading. Its pH was returned to >10 by the addition of one more milliliter of ammonium hydroxide. After stirring for the desired length of time, the char was removed from the mixture

by vacuum filtration, and the completion of the loading was verified by comparison of the electrical potential between the calcium-selective electrode and a saturated KCl electrode in the filtrate to the standard response curve. The loaded chars were then allowed to air dry for two days before the analysis of their combustibility was done. About one gram of each of the loaded chars and their corresponding filtrates were submitted for AA analysis to verify the calcium-loading levels. Table 3 summarizes the abbreviations used to identify the chars found in Tables 4 and 5. Table 4 lists the resultant calcium-loading levels. In addition to calcium, the demineralized chars were also analyzed for their magnesium concentration, as magnesium was observed to show similar effects on combustion (2), and SEM analysis of the ash recovered from TGA analysis of the coals indicated significant magnesium concentrations. Based on these AA analyses, the concentration of magnesium in Entries 4-10 was about 50 ppm, while that for Entries 12, 14, and 15 was 300 ppm.

In all but one of the chars from this present study [the NMB(2000)], the intended loading levels were nearly obtained, showing the usefulness of this procedure. The reasons for the loading procedure for this one case not working as well as the others is not clear at this time. It appears that as the amount of calcium to be loaded on the chars decreases, so does the rate of loading, thus three days may not have been long enough for complete adsorption to occur. It may also be that an equilibrium point is established, preventing further loading.

3.4 Char Combustion

The demineralized and calcium-loaded chars were combusted in a laminar-flow reactor at 1000 K and 0.06, 0.08, and 0.10 mole percent oxygen with the particle temperatures measured using a three-color detection system set 150 mm above the honeycomb flow straightener of the reactor.

In addition to the above chars, one sample, LWX(NH₄OH), which had been exposed only to dilute ammonium hydroxide (2 ml of concentrated ammonium hydroxide in 100 ml of distilled water) and had not been loaded with more calcium, was combusted to assess the effect of the strong base on the chars.

Table 5 lists the combustion data obtained from this study (Entries 4-10, 12, and 14-15) and from previous studies that employed the same conditions. In the older data, the particle size range was 63 to 75 μm ; due to the small amount of available material, the present study was forced to use the 63- to 90- μm range. These slight variations in particle size are not expected to affect the general comparability of the combustion data. The particle size range used with the LWX(NH₄OH) sample was the 90- to 106- μm size. In order to allow a more valid comparison of this data to the other char samples, a demineralized sample of the LWX char (Entry 9) of the same size range was also combusted. The chi and rho values were calculated from the particle temperatures using rate equations that assume only carbon monoxide formation in the combustion process.

3.5 Data Reduction

Combustion rates were calculated from the measured particle temperatures by applying a steady-state heat analysis to the burning particles. In this analysis, it is assumed that the particles are in thermal equilibrium with the

TABLE 3
EXPLANATION OF ABBREVIATIONS FOR TABLES 4 AND 5

LWX(Ca)	Indicates a Lower-Wilcox char from a previous study that had been loaded with calcium.
LWX(UT)	Indicates a Lower-Wilcox char that was untreated (i.e., not demineralized or calcium-loaded).
LWX(DEM69)	Indicates a demineralized Lower-Wilcox char with a mean particle size of 69 μm .
LWX(2500)	Indicates a Lower-Wilcox char from the present study with an intended calcium-loading level of 2500 ppm.
LWX(2000)	Indicates a Lower-Wilcox char from the present study with an intended calcium-loading level of 2000 ppm.
LWX(1500)	Indicates a Lower-Wilcox char from the present study with an intended calcium-loading level of 1500 ppm.
LWX(1000)	Indicates a Lower-Wilcox char from the present study with an intended calcium-loading level of 1000 ppm.
LWX(DEM76)	Indicates a demineralized Lower-Wilcox char with a mean particle size of 76 μm .
LWX(DEM98)	Indicates a demineralized Lower-Wilcox char with a mean particle size of 98 μm .
LWX(NH_4OH)	Indicates a Lower-Wilcox char that was treated only with ammonium hydroxide.
NMB(Ca)	Indicates a New Mexico Blue char from a previous study that had been loaded with calcium.
NMB(UT)	Indicates a New Mexico Blue char that was untreated (i.e., not demineralized or calcium-loaded).
NMB(2500)	Indicates a New Mexico Blue char from the present study with an intended calcium-loading level of 2500 ppm.
NMB(2000)	Indicates a New Mexico Blue char from the present study with an intended calcium-loading level of 2000 ppm.
NMB(DEM76)	Indicates a demineralized New Mexico Blue char with a mean particle size of 76 μm .
NMB(DEM69)	Indicates a demineralized New Mexico Blue char with a mean particle size of 69 μm .

TABLE 4
CALCIUM CONCENTRATION IN THE CALCIUM-LOADED CHARS (ppm)

<u>Entry No.</u>	<u>Char Sample</u>	<u>Calcium Concentration</u>
1	LWX(Ca)	72400
2	LWX(UT)	29700
3	LWX(DEM69)	7000
4	LWX(2500)	2600
5	LWX(2000)	1900
6	LWX(1500)	1400
7	LWX(1000)	1100
8	LWX(DEM76)	700
9	LWX(DEM98)	700
10	LWX(NH ₄ OH)	700
11	NMB(Ca)	27200
12	NMB(2500)	2500
13	NMB(UT)	1880
14	NMB(2000)	1748
15	NMB(DEM76)	1600
16	NMB(DEM69)	1320

- 1) Entries 1-3, 11, 13, and 16 are from an earlier study.
2) See Table 3 for an explanation of the sample labels.

local surroundings. It is further assumed that the primary reaction product is carbon monoxide. Thus the heat balance is given by Equation 1:

$$\rho \Delta H = \frac{Nu\lambda}{d} (T_p - T_g) + \epsilon \sigma (T_p^4 - T_w^4) \quad [1]$$

where ρ is the overall burning rate, ΔH is the heat of reaction (~2300 cal/mole at 1500 K for CO formation), Nu is the Nusselt number (taken as 2), λ is the gas thermal conductivity, and d is the particle diameter. T_p , T_g , and T_w are the particle, bulk gas, and wall temperatures, respectively; ϵ is the particle emissivity (taken as 0.9); and σ is the Stefan-Boltzmann constant.

A small correction is required for Equation 1 due to Stefan flow (4,5), which arises from the net outflow of molecules from the boundary layer around each particle. The corrected form of Equation 1 is given by Equation 2.

$$x\rho_m \Delta H = \frac{2\lambda}{d} (T_p - T_g) \frac{\ln(1 + X_{O_2}^\infty)}{X_{O_2}^\infty [1 - \frac{(1-x)/Le}{2}] X_{O_2}^\infty} + \epsilon \sigma (T_p^4 - T_w^4) \quad [2]$$

$$x\rho_m \Delta H = \frac{2\lambda}{d} (T_p - T_g) \frac{\ln(1 + X_{O_2}^\infty)}{X_{O_2}^\infty [1 - \frac{(1-x)/Le}{2}] X_{O_2}^\infty} + \epsilon \sigma (T_p^4 - T_w^4) \quad [2]$$

TABLE 5
CHAR COMBUSTION DATA SUMMARY (NEW AND OLD DATA)

Entry No. ^a	Char ^b	Ca concn.	6% O ₂			8% O ₂			10% O ₂		
			T _p	x	p	T _p	x	p	T _p	x	p
1	LWX(Ca)	72400	1386	1.16	0.01				1511	0.96	0.0141
	"	72400	1378	1.16	0.0099						
2	LWX(UT)	29700	1438	1.31	0.0117				1613	1.14	0.0174
3	LWX(DEM69)	7000	1444	1.36	0.012				1622	1.16	0.0175
	"	7000	1465	1.4	0.0126						
4	LWX(2500)	2600	1493	1.55	0.0125	1577	1.35	0.0152	1609	1.19	0.0161
5	LWX(2000)	1900	1489	1.51	0.0122	1552	1.3	0.0141	1641	1.23	0.017
6	LWX(1500)	1400	1442	1.39	0.0111	1463	1.1	0.0117	1612	1.18	0.0163
7	LWX(1000)	1100	1487	1.52	0.0123	1525	1.25	0.0135	1618	1.18	0.0162
8	LWX(DEM76)	700	1487	1.52	0.0124	1498	1.19	0.0128	1617	1.15	0.0161
9	LWX(DEM98)	700	1414	1.52	0.0084	1467	1.16	0.0096	1575	1.17	0.0123
10	LWX(NH ₄ OH)	700				1429	1.05	0.0087	1571	1.14	0.0121
11	NMB(Ca)	27200	1446	1.38	0.0121				1633	1.16	0.0178
12	NMB(2500)	2500	1466	1.44	0.0128				1663	1.23	0.019
13	NMB(UT)	1800				1552	1.26	0.0152	1577	1.24	0.0182
	"	1800							1549	1.02	0.0154
14	NMB(2000)	1748	1461	1.44	0.0116	1590	1.37	0.0153	1657	1.26	0.0177
15	NMB(DEM76)	1600	1469	1.46	0.0119	1544	1.27	0.014	1632	1.21	0.0167
16	NMB(DEM69)	1320	1439	1.39	0.012				1629	1.19	0.0181

^a Entries 1-3, 11, 13, and 16 are from previous studies.

^b Refer to Table 3 for an explanation of the sample labels.

where
$$\chi = \rho/\rho_m \quad [3]$$

and
$$Le = \frac{\lambda}{C_{pg}DC} \quad [4]$$

The χ factor is the ratio of the overall burning rate to the diffusion-limited rate, ρ_m , which is defined by

$$\rho_m = \frac{4M_c DC}{d} \ln (1 + \chi_{O_2}^{\infty}) \quad [5]$$

for the conversion to carbon monoxide. Here, M_c is the molecular weight of carbon and $\chi_{O_2}^{\infty}$ is the mole fraction of oxygen in the bulk gas. Equation 4 defines the Lewis number, C_{pg} is the mean heat capacity of O_2 and CO, D is the bulk diffusion coefficient for oxygen in nitrogen (equivalent to CO in nitrogen), C is the total molar concentration (equal to P_t/RT_m , where P_t is the total pressure, R is the universal gas constant, and $T_m = (T_p + T_g)/2$), i.e., the mean temperature in the boundary layer around the particle).

3.6 Results and Discussion

The combination of the results of this study with those done previously (Figure 2) show that particle temperatures for the LWX chars rise rapidly until the calcium concentration reaches about 2500-2000 ppm. Beyond this concentration, the temperature slowly decreases, becoming significantly different around 30,000 ppm. Similar trends were observed for the NMB chars (Figure 3) except that the magnitude of the particle temperatures was about 20 degrees higher, and the rate of temperature drop with higher calcium concentration was lower. It should be noted that Entry 13 has been deleted from Figure 3 to allow for greater clarity of the data.

The reason(s) for the differences between the LWX and NMB chars is not clear. It may be that the NMB char's slightly greater reactivity is due to inherent differences in its chemical structures. Figures 4-6, which contrast the combustion of the calcium-loaded chars at different oxygen mole fractions, verify this possibility. In Figure 4 it can be seen that at low oxygen concentrations the LWX chars exhibited greater particle temperatures than the NMB chars at similar calcium concentration, while at higher oxygen concentrations (Figure 6) the opposite was true. At the intermediate oxygen concentrations (Figure 5) little difference between the two chars was observed. Since the form of the calcium in the calcium-loaded chars (calcium acetate) was the same, the same mechanism of combustion and/or calcium-catalysis of that combustion should be occurring in all of the samples. Thus, the best explanation for the above observations is that the two chars have inherently different chemical reactivities.

Another possibility is that the greater amount of magnesium in a char creates a secondary avenue for combustion to occur. In order for this to be true, there must be some difference in the combustion mechanism associated with magnesium since, if the same mechanism was involved, the magnesium would

Figure 2. Combustion of LWX calcium-loaded chars.

Figure 3. Combustion of NMB calcium-loaded chars.

Figure 4. Contrast of LWX and NMB chars at 6% O₂.

Figure 5. Contrast of LWX and NMB chars at 8% O₂.

Figure 6. Contrast of LWX and NMB chars at 10% O₂.

give the same effect as a somewhat greater calcium concentration. Since a greater calcium concentration wouldn't necessarily give higher particle temperatures, there is room for doubt as to the validity of this proposed possibility.

The reason(s) for the particle temperatures peaking at such low calcium concentrations is not clear. If one assumes that the chars have about 3 milliequivalents of acid per gram of char and that calcium has 2 equivalent weights per mole of acid in the neutralization of the acid functionalities, then one could expect a maximum calcium-loading of about 60,000 ppm. This may not even include association of the calcium with phenolate ions. It has been proposed that calcium facilitates the crosslinking and polymerization reactions in chars (6). Thus it may be that at higher calcium concentrations, the "holes" left after elimination of carbon monoxide or carbon dioxide are rapidly healed by the calcium by reforming thermally stable products. In effect, this would reduce the rate of reaction and give lower particle temperatures. Some caution should be taken in comparing the data from the present study to those from previous studies since the calcium-loading procedures were different. In the present study, all of the chars were loaded under basic conditions, while those in the past were done under nearly neutral conditions. Since the chars were not neutralized after being loaded with calcium, all acid functionalities (both carboxylic acids and phenolics) not converted to calcium salts must be ammonium salts rather than free acids.

In the same train of thought, comparison of the loaded chars to the demineralized chars must be made with caution. Figure 7 contrasts the combustion of the LWX(NH₄OH) char to that of the LWX without exposure to the

Figure 7. Combustion of LWX(DEM) and LWX(NH₄OH) chars.

basic conditions. It also depicts the effects of particle size by contrasting the combustion of the 63-90-μm and 90-106-μm particle sizes of the demineralized chars. The results show that the effect of treating the chars with ammonium hydroxide strongly reduces their combustibility. This is borne out by the facts that the LWX(NH₄OH) char's particle temperature at 0.06 mole percent oxygen was unmeasurable with our apparatus, while those of the LWX(DEM76) and LWX(DEM98) readily were, and that at 0.08 mole percent oxygen, the LWX(NH₄OH) char's particle temperature was 38 degrees lower than the corresponding demineralized char. Only under the more vigorous combustion conditions at 0.10 mole percent oxygen were the effects of the base nearly eliminated. Undoubtedly, the reasons for these decreases in particle temperatures are due to the greater ease of eliminating carbon dioxide from a neutrally charged acid than from a carboxylate anion, or the elimination of carbon monoxide from a neutral phenol rather than a phenolate anion. Comparison of Entry 8 with Entry 9 from Table 5 would suggest that the effect of the NH₄OH is equivalent to about 400 ppm of calcium (when the initial concentration is less than 2500 ppm). Based on the above observations, it is reasonable to assume that had the chars been neutralized prior to combustion analysis, the resultant particle temperatures would have been significantly higher than they actually were.

Another example of where caution must be used in comparing the new and the old data is borne out by looking again at Figure 6. Here, the two lowest particle temperatures shown for the NMB char are those that correspond to the combustion data of the untreated char (Entries 15 and 16 in Table 5). Even though the amount of calcium was low and reasonably comparable to the most

reactive of the chars in the present study, the form of the calcium very likely was not the same, and very likely its distribution was not as even as in the loaded chars. The combination of these factors explains why the particle temperatures were so much lower than those from the present study.

The data also shows that as the particle size gets larger, the particle temperatures decrease. This is consistent with what has been observed previously (7). This suggests that when comparing the new data with the old, the particle temperatures for the new samples may be slightly lower than the old at similar calcium concentrations.

Figure 8 presents the combustion data in a somewhat different fashion. Here we see clearly that the rate of reaction of the chars is not necessarily linear with respect to the oxygen concentration. In fact, the data suggests that the increase in the reaction rate due to an increase in oxygen concentration follows a smooth curve which increases sharply as it approaches 10 mole percent. At this oxygen concentration, the reaction controlled by the diffusion of oxygen to the char surface is probably at or nearly at its maximum rate. Prior to an oxygen concentration of 9 mole percent, the rate of reaction of the char with oxygen is not so rapid as to mask the catalytic effects associated with the presence of calcium.

In direct correlation to the particle temperatures, the χ and ρ values for the calcium-loaded chars increase as the calcium concentration approaches about 2500 ppm and then slowly decrease as the calcium concentration increases further (Figures 9-12). The magnitudes of the χ values, being greater than

Figure 8. Char combustion vs. oxygen concentration.

Figure 9. LWX char combustion: χ values vs. calcium concentration.

Figure 10. LWX char combustion: ρ values vs. calcium concentration.

Figure 11. NMB char combustion: χ values vs. calcium concentration.

Figure 12. NMB char combustion: ρ values vs. calcium concentration.

the theoretical value of unity, show that at the lower oxygen concentrations significant amounts of carbon dioxide is being formed. Even at the higher oxygen concentrations, where diffusion-controlled conditions predominate, the x values are greater than unity, showing that the catalytic effect of calcium is not absent.

The x and p values observed here are significantly higher than those from other studies involving noncalcium-loaded chars. That is, the only previously studied chars to give x values as high as the present ones were ion-exchanged, calcium-loaded chars. This shows that the present combustion behavior is at least consistent with that observed in the past.

4.0 IGNITION BEHAVIOR

4.1 Introduction

An important consideration in designing any combustion system is the ignition delay. The ignition delay can generally be defined as the time elapsed between the combining of a fuel/oxidant mixture with an activation energy source and the beginning of this mixture's rapid exothermic transition. In the field of coal combustion, knowledge of the ignition characteristics of a given coal are important in the prevention of spontaneous ignition, in the production of stable flames, and in the optimization of combusting fluidized-bed temperatures. Ignition mechanisms may also influence NO_x formation rates (8).

Several reviews of coal combustion behavior have been written that include summaries of coal ignition processes (9,10,11). The ignition behavior of a coal has been shown to depend on a variety of coal characteristics and combustion conditions. Ignition delays of coals have been shown to increase with increasing rank (12) as have ignition temperatures (13). The chars of lignites have also been shown to be more reactive than their higher-rank counterparts (14). The inherent mineral matter in low-rank chars has been ascribed promotional properties (9,14,15,16). The effect of volatile matter on the ignition mechanism of lignites and subbituminous and bituminous coals (17,18,19) has also been emphasized. Others emphasize the effects of surface area (20).

The objective of this study is to define the effects of basic coal characteristics such as moisture content, lithotype, volatile matter concentration and inorganic constituents, and combustion conditions such as oxygen concentration and temperature on the ignition delays and combustion rates of coals. Two lignites, one subbituminous coal, and one bituminous coal were chosen. Low-rank materials were concentrated upon since they have been studied far less extensively than high-rank coals, and interest is growing in the usage of low-rank coals for power generation.

The most commonly monitored events used to determine coal ignition points are light production, mass loss, heat production, and combustion product detection. The detection of CO_2 and CO evolution was chosen as one method of determining ignition for the present study. This procedure was selected since it is relatively unresponsive to the production of volatile pyrolysis products

and allows a mass balance to be performed on the overall combustion process. The second method chosen for determining the ignition point was the observation of light emission. These two methods provide complementary data.

4.2 Experimental Equipment and Procedures

A schematic of the ignition apparatus is shown in Figure 13. A listing of the major components is presented in Table 6. All components of this apparatus are operational; however, the optical pyrometer was not integrated into the system. Attempts to obtain video images of particles combusting in the ignition apparatus were unsuccessful. These two pieces of equipment are the same as those described in Subsection 2.1.

The combustion zone furnace is detailed in Figures 14 and 15. Gas temperatures were measured by a thermocouple inserted into the sample zone. Wall temperatures were measured by a thermocouple glued to the quartz tube directly under the particle. The wall temperature is reported in the text. The gas temperatures were within 1% of the wall temperatures.

The particle drop tube consists of a stainless steel tube with a quartz window glued into a position that coincides with the optical trigger. The steel portion of the tube is grounded. This modification prevents the coal particles from sticking to the drop tube as a result of static charging.

Figure 13. Layout of ignition apparatus.

TABLE 6
MAJOR COMPONENTS OF THE IGNITION APPARATUS

-
1. Beckman model 868 nondispersive infrared CO analyzer with 36.48-cm³ detection chamber.
 2. Beckman model 868 nondispersive infrared CO₂ analyzer with 18.24-cm³ detection chamber.
 3. Standard 286 microcomputer.
 4. Gas mixing system:
 - a) Brooks N₂ mass flow controller model 5851.
 - b) Brooks O₂ mass flow controller model 5851.
 - c) Brooks control and readout model 5876.
 5. A/D converter (Techmar Incorporated).
 6. Omega model 660 thermocouple thermometer.
 7. Omega model 6000 furnace controller.
 8. Omega model CN-2010 programmable furnace controller.
 9. Type S thermocouples.
 10. Trigger:
 - a) Micronta low-voltage DC power supply.
 - b) Infrared-emitting diode M10E71 (Radio Shack).
 - c) Photodetector MF0D72 (Radio Shack).
 - d) Type 324 quad operational amplifier.
-

Figure 14. Detailed front view of the ignition apparatus combustion zone furnace.

Figure 15. Detailed side view of the ignition apparatus combustion zone furnace.

The operational procedure for the ignition apparatus is as follows. The coal particle is picked up with a suction bulb attached to a capillary tube and sized under a microscope. It is then placed in the 0.5-mm-O.D. syringe needle. The needle is inserted into the air-tight chamber containing the top of the 1-mm-I.D., 2-mm-O.D. drop tube as shown in Figures 14 and 15. The particle is pushed into the tube with a wire plunger and falls through the drop tube into the flowing oxidant gas stream. The particle comes to rest at the spot determined by the ZrO_2 particle stop screen shown in Figure 15. Passage of the particle through the detection system triggers data accumulation from the CO and CO₂ analyzers.

The flow rate through the combustion zone was 200 ± 1 ml/min; the gas composition was varied as noted. The pressure in the combustion zone was 102 kPa (14.8 psi) for the 650°C runs and 103 kPa (14.9 psi) for the 1000°C runs. The flow rates through the CO₂ and CO analyzers were 100 ± 0.5 mL/min.

The time scale used to collect the CO and CO₂ analyses was based on the A/D conversion board clock, which was calibrated with a sine wave generator.

The coal samples used, Beulah lignite (PSOC-1507), Lower-Wilcox lignite (PSOC-1443), Smith Roland subbituminous coal (PSOC-1520) and Pittsburgh #8 bituminous coal (PSOC-1451), were obtained from the Pennsylvania State Sample Bank. The original samples consisted of pieces <0.25 inch in diameter. These pieces were separated according to lithotype using the following criteria. Vitrain was categorized by its hard texture and glassy appearance, attritus by its hard texture and grainy appearance, and fusain by its brittleness and tendency to fracture into needle-like fragments (21). The major lithotype in all four samples was vitrain.

The moisture content of the particles was established by storing them either over water or concentrated sulfuric acid at 30°C for a period of two weeks or greater. This procedure establishes the relative moisture content as 100% or 0%, respectively (22).

The demineralized coals examined in the ignition apparatus or used to produce the demineralized chars were produced by treatment with hydrochloric and hydrofluoric acids, followed by water washing to remove residual acid, according to the procedure described previously (23). Portions of the demineralized coals were reloaded with calcium by ion-exchanging the demineralized coal in a solution of calcium acetate, using a procedure adapted from that used to determine the carboxylic acid groups in coal (24). The analyses of the cation concentrations present in the materials examined are shown in Table 7.

TABLE 7
CATION CONCENTRATIONS OF COALS USED IN THE IGNITION STUDIES

		Concentration ^a			
		Ca (ppm)	K (ppm)	Na (ppm)	Wt% Ash ^b
Beulah	(UT)	31,000	400	4,600	--
Lower-Wilcox	(UT)	700	2,000	500	--
Smith Roland	(UT)	15,000	700	900	--
Pittsburgh #8	(UT)	2,000	1,200	400	--
Beulah	(DM)	31	4	4	0.09
Lower-Wilcox	(DM)	240	65	37	1.23
Smith Roland	(DM)	112	18	61	0.22
Pittsburgh #8	(DM)	110	30	39	0.24
Beulah	(Ca)	10,518	--	--	--
Lower-Wilcox	(Ca)	555	--	--	--
Smith Roland	(Ca)	7,350	--	--	--
Pittsburgh #8	(Ca)	372	--	--	--

^a Determined by flame AA.

^b ASTM.

UT = Untreated.

DM = Demineralized.

Ca = Calcium-reloaded.

The chars were prepared from sized fractions of the whole coals. A drop-tube furnace was used to prepare the chars. The conditions used were: 1275 K, a residence time of 150 ms, and an O₂ concentration of 3%. The densities of the chars, original coals, demineralized chars, and demineralized coals are shown in Table 8.

Each particle was sized under a microscope immediately preceding combustion. Due to the asymmetrical nature of the coal particles, three axes per particle were measured. The reported particle volumes were based on this data by assuming a rectangular shape. The particle aspect ratios were calculated by dividing the length of the longest axis by the average of the two smaller.

TABLE 8
DENSITIES OF THE MATERIALS USED IN IGNITION EXPERIMENTS

<u>Material</u>	<u>Density (g/ml)</u>
p ^a #8 UT ^b Coal	1.29
P #8 DM ^c Coal	1.20
P #8 UT Char	0.59
P #8 DM Char	0.26
LW ^d UT Coal	1.54
LW DM Coal	1.48
LW UT Char	1.37
LW DM Char	1.33
SR ^e UT Coal	1.23
SR DM Coal	1.10
SR UT Char	0.85
SR DM Char	0.28
B ^f UT Coal	1.23
B DM Coal	1.14
B UT Char	0.90
B DM Char	0.28

- ^a P = Pittsburgh
^b UT = Untreated
^c DM = Demineralized
^d LW = Lower-Wilcox
^e SR = Smith Roland
^f B = Beulah

Dispersion produced during the transition of the gas samples from the combustion zone to the gas analyzers can produce significant differences between the recorded analyzer responses and the events originally occurring in the combustion zone. In order to correlate the analyzer responses to actual events in the combustion zone, the analyzers were calibrated with gas samples of known volume and concentration via the flow system calibrator shown in Figure 16.

The operational procedure for the flow system calibrations was as follows. The calibrator was substituted for the combustion zone furnace with the outlet positioned to mimic the particle position in the ignition studies. The CO/CO₂ cell, the region between the top two solenoid valves pictured in Figure 16, was filled with specific concentrations of CO and/or CO₂, while the gas stream passed through the zero gas cell, the region between the solenoid valves of Figure 16. The gas stream was then switched to flow through the CO/CO₂ cell while simultaneously triggering the data acquisition. The same oxidant gas flow rate and composition used in the ignition studies was employed during the calibrations. The volumes of the standard gas plugs were varied as necessary.

Figure 16. Flow system calibrator for the ignition apparatus.

The procedure for calculating the ignition delay consists of using malonic acid particles to define a single operational constant for the ignition apparatus (see Figure 17). Malonic acid particles were injected into the ignition apparatus and the delay between the trigger and initial CO_2 detection measured. Since malonic acid decarboxylates at the relatively low temperature of 140°C , it is assumed that the decarboxylation time (time E in Figure 17) is essentially zero. Subtraction of the malonic acid response time from the total delays of the various coal particles yields their ignition delays. This procedure also assumed that the malonic acid particles had particle drop times equivalent to those of the coal particles; hence malonic acid particles similar in size to the coal particles were used for the calibration. The ignition apparatus was calibrated daily using the malonic acid particles. The average malonic acid response times measured at 650° and 1000°C were 4.266 ± 0.051 sec and 4.218 ± 0.071 sec, respectively. The ignition delays are calculated from the CO_2 analyses and not the CO because of the fourfold greater sensitivity of the CO_2 analyzer.

An optical microscope coupled with a heated stage was also used to study factors that influence the ignition and combustion of coal particles. A schematic diagram of the optical microscopy apparatus is shown in Figure 18. This system consists of three major components: a heated stage, a microscope, and a video camera. The stage was a modified Lietz Westlar Microscope Heating Stage, model-1750. The modification consisted of adding an adaptor between the cover and the stage. This adaptor contained a small access hole for the particle injector and is shown in Figure 19. The hole was sealed with silicone to produce an airtight seal. The stage temperature is monitored with a type "S" thermocouple.

Figure 17. Modified timing chart: A) software delay, B) malonic acid response time, C) total coal delay, D) coal particle ignition delay = C-B, and E) decarboxylation delay.

Figure 18. Schematic of optical microscopy apparatus.

Figure 19. Diagram of modified heated stage.

The particle injector consisted of a 0.56-mm-O.D., 0.31-mm-I.D. needle. A 0.25-mm-diameter wire was used to push the particles onto the heated stage. The needle was curved to minimize the distance between the end of the needle and the stage.

The microscope used was a Carl Zeiss Tessovar Zoom System. A video camera was attached to the view port to monitor particle combustion. The video output was recorded on a VCR. Since a light background is needed to view the coal particles, a thin layer of Al_2O_3 cement was applied to the heated stage.

The following procedure was used for the optical microscopy studies. The desired atmosphere was introduced into the stage. Six to ten particles were placed into the particle injector and the injector inserted into the hot stage. The stage was brought to temperature and the particles were then pushed out of the injector onto the stage. Each event was recorded by the video camera.

The differential scanning calorimetry (DSC) experiments were performed using a Du Pont Industries model 910 DSC. A hole was drilled in the lid of the DSC cell, and a 41-mm-long, 1-mm-I.D. stainless steel tube was welded to the lid to coincide with the hole. The operational procedure consists of preheating the DSC to 500°C, introducing the desired atmosphere, closing the gas inlet valve, and dropping a single particle through the 1-mm tube onto the sample pan.

4.3 Data Analyses

Four separate pieces of information can be directly extracted from the CO and CO₂ analyzer responses obtained from the ignition apparatus: the ignition delay, the total moles of CO and CO₂ produced, the duration of combustion and the maximum rate of CO and CO₂ production. The ignition delay is defined as the time from injection of a particle into the furnace until its initial production of CO₂. The procedure for calculating this value has been described in the experimental section.

In order to determine the other three parameters, moderate manipulation of the initially recorded detector responses is necessary. Figure 20 describes the response of an integral detector to the movement of sample plug through its detection chamber (11). From this result, it can be seen that the total moles of the sample plug can be calculated from the peak deflection of the analyzer. Tests performed with the flow system calibrator resulted in the establishment of equations capable of accurately ($\pm 5\%$) quantifying the amount of CO₂ and CO present in a sample as small as 2×10^{-8} moles. These calculations are valid as long as the sample combustion time does not exceed the detection chamber residence time. The flow system calibrator results indicated that the residence time of a sample in the smaller (and therefore limiting) CO₂ detection chamber was approximately 6.5 seconds at the flow rate employed. Most of the coal particles studied had total burnout times of less than 6.5 seconds, and hence accurate quantitation of the CO₂ evolved during combustion was possible. The fact that the CO detection chamber is larger than the CO₂ detection chamber produces the result that particles with burnout times of greater than 6.5 seconds will have both their CO₂:CO product ratios and their carbon recoveries underestimated. The range of error reported in the data tables is the standard deviation observed between particles in a data set.

The carbon recovery was calculated by summing the amounts of CO₂ and CO detected and dividing this value by the amount of carbon estimated to be contained in the initial coal/char sample. This latter value was calculated from the average density, the estimated carbon percentage and the particle volume.

In order to obtain the combustion duration and maximum CO₂ and CO production rates, the initial analyzer responses were converted to moles of gas detected and differentiated with respect to time. The CO/CO₂ rate profiles presented were obtained using this direct differentiation technique. The time constants used in the differentiation of the CO₂ and CO analyses were 100 and 400 ms, respectively. The larger differentiation time used for the CO analyses was necessitated by this detector's lower sensitivity. The high degree of noise present in the CO analysis is a result of this lower sensitivity. The results of differentiating the analyzer response from a standard gas plug is compared with the initial plug shape in Figure 21. It can be seen that the analyzer response and initial plug shape differ in length and peak height. Therefore, the presented CO/CO₂ rate profiles only qualitatively describe the combustion process occurring in the combustion zone.

Figure 20. Response of integral detector to a pulse-type signal.

Figure 21. Evaluation of sample distortion.

To estimate the actual combustion durations and maximum combustion rates, calibrations were defined using the measured analyzer responses and the known lengths and concentrations of standard gas plugs. A diffusion-broadening constant was defined to subtract from the analyzer deflection duration to produce the combustion duration. This procedure is accurate (± 0.2 sec) for combustion durations of 0.543 sec or larger. The reported combustion durations represent the duration of CO_2 production from the burning coal particles. Two times are reported because two-stage combustion was observed for some particles. These times are the total combustion time and the first-stage combustion time.

The equations defined to yield the initial plug concentrations, which would correlate to gas production rates for a combustion event, were obtained by comparing the known CO_2 and CO concentrations of sample plugs with the peak heights of the differentiated analyzer responses, as shown in Figure 20. This procedure was straightforward for lengthy samples, since the central portions of such samples are not greatly changed in their transition from the sample zone to the detection chamber. However, when the plug is short, a condition mimicking rapidly-burning coal particles, the maximum detected concentration becomes a function of sample length. Calibrations producing accurate ($\pm 5\%$) quantitation of plug concentrations were established for sample lengths of 0.543 sec or greater.

The calibration equations established from the standard gas plug concentrations were used to calculate the tabulated maximum rates of CO_2 and CO production from the combusting coal particles. This analysis is valid for sample lengths between 6.5 and 0.543 seconds, and assumes a rapidly established, constant, particle combustion rate. The maximum carbon conversion rates reported are the sum of the peak CO_2 and CO production rates corrected for dispersion. A carbon conversion rate per unit surface area, ρ , was calculated from the conversion rate according to Equation 6, where m is the

$$-dm/dt = \rho A_s \quad [6]$$

mass of carbon, A_s is the initial surface area, and t is time.

Three possible mechanisms exist for the formation of CO_2 : initial production at the particle surface, oxidation of CO to CO_2 in the boundary layer of the particle where the gas temperature is influenced by the particle, and CO oxidation in the bulk gas phase during the transition of the gas sample through the combustion zone furnace. In order to remove the latter mechanism from consideration, its magnitude was estimated by introducing CO/air mixtures into the combustion furnace at various temperatures. No significant CO oxidation was observed at or below 825°C . At 1000°C , significant CO conversion was observed and an overall rate constant was estimated for this reaction. The CO_2 :CO product and rate ratios reported were corrected for conversion of CO to CO_2 in the bulk gas stream.

Evaluation of the particle heating rates in the ignition apparatus was performed via the following procedure. A spherical particle in contact with a hot gas was assumed (25,26) and the rate of reaction, ρ , was assumed to be zero. The particle temperature as a function of time is determined from the unsteady-state energy balance, Equation 7.

$$mC_p(dT_p/dt) = A_s\rho\Delta H - hA_s(T_p - T_g) - \epsilon\sigma A_s(T_p^4 - T_w^4) \quad [7]$$

Here m is the mass of the particle, while A_s is the surface area. The energy balance equation accounts for the heating of the particle by reaction (where ρ is the overall rate of reaction and ΔH is the enthalpy of reaction) and the loss of heat by conduction to the ambient gas and by radiation to surrounding walls. The temperatures of the particle, wall, and gas are T_p , T_w , and T_g , respectively. The heat transfer coefficient, h , is determined from the Nusselt number, Nu , which is given by

$$Nu = hd/\lambda \quad [8]$$

The limiting value of the Nu is two and depends on d , the particle diameter, and λ , the thermal conductivity of the gas, which is a function of temperature. The emissivity, ϵ , is taken to be unity, and σ is the Stefan-Boltzmann constant.

Mass and area are related to the diameter through

$$m = \pi\rho'd^3/6 \quad [9]$$

and

$$A_s = \pi d^2 \quad [10]$$

where ρ' is the density. The calculated particle temperature-versus-time curves are shown in Figure 22 for 240- μm particles at gas temperatures of 650° and 1000°C.

The data analysis procedure for the video recordings obtained from the optical microscopy studies was as follows. The recordings were analyzed by first calibrating the slow motion playback and then viewing the recording at slow motion to observe and note significant events. The error in the timing of each event is no more than 0.02 seconds. The events recorded consisted of: 1) the ignition delay, the time from when the particle contacted the stage until its light emission was observed; 2) the combustion duration, the time from initial light emission to burnout; 3) the cloud duration, the time from the appearance of a volatile cloud until its subsequent disappearance; and 4) the shrinkage duration, the time from when a nonigniting particle contacted the heated stage and began to shrink until its size ceased to diminish.

Figure 22. Calculated particle temperature profiles for 240- μ m particles in the ignition apparatus.

4.4 Results and Discussion

4.4.1 General

The operational procedure and experimental design of the ignition apparatus was optimized for the examination of 240- μ m coal particles. Ignition and combustion characteristics of four coals were examined using this procedure and design. The sensitivity of the ignition apparatus was also evaluated. It was determined that particles as small as 50 μ m could be examined using the CO₂ analyzer employed. The practical minimal particle size was determined to be 200 μ m due to limitations in the particle handling techniques and optical detector. The average particle examined had a volume similar to that of a 240- μ m sphere.

An apparatus for visually monitoring combusting coal and char particles was assembled. This apparatus consists of a video camera, microscope and heated stage. An Associated Western Universities (AWU) fellow used this apparatus to examine the same suite of coals characterized in the ignition apparatus. The optical microscopy observations were complementary to those obtained in the ignition apparatus.

A knowledge of the particle heating rate and mechanism in the ignition apparatus and optical microscope is essential if comparisons are to be made and if extrapolation of the results to larger, more applied systems is desired. Both surface reactions and the experimental apparatus contribute to the particle heating rates. Prior to ignition, the contributions from the experimental apparatus predominate. This source has three components: conduction from the gas phase, radiation from the furnace walls, and conduction from the solid in contact with the particle. In the ignition apparatus, conduction from the surface in contact with the particle is assumed to be minimal, because it is ZrO_2 felt, which has a low thermal conductivity and high porosity.

The heating rate of 240- μm particles in the ignition furnace was experimentally determined by comparing the delay in CO_2 production from CaCO_3 and malonic acid at a furnace temperature of 1000°C . The decomposition temperatures of CaCO_3 and malonic acid are 899° and 140°C , respectively (27). A 0.220-second difference was measured between the initial CO_2 production from these materials. This corresponds to a average particle heating rate of 3.5×10^3 $^\circ\text{C}/\text{sec}$ for this material.

Temperature-versus-time profiles for 240- μm carbon particles heated by gas conduction and radiation from the furnace walls were calculated using the energy balance (see Figure 22). The average heating rates of the particles during the initial 0.160 seconds are 5.8×10^3 $^\circ\text{C}/\text{sec}$ at 1000°C and 3.4×10^3 $^\circ\text{C}/\text{sec}$ at 650°C . These values are similar to the experimentally determined values. Hence, it appears that the heating rate in the ignition apparatus is dictated by conduction from the surrounding gas with a smaller contribution from the radiative heating from the furnace walls.

Conti and Zlochower (28) have calculated the time needed to heat polymethylmethacrylate (PMMA) particles to 400°C in air. These times were found to be similar to the ignition delays observed for this material in a Bureau of Mines 1.2-L furnace. The heating times and ignition delays for 180- μm particles were 0.835 and 0.67 seconds, respectively, at gas temperatures of 600°C , 0.321 and 0.27 at 700°C , and .087 and .092 at 900°C . The reactivity of PMMA is between that of Pittsburgh seam bituminous coal particles and Beulah lignite (19). The ignition delays of the 180- μm PMMA particles are similar to those observed for the 240- μm Beulah lignite particles in the ignition apparatus (see Tables 9 and 10). The ignition delays measured in the ignition apparatus are similar to those measured in the Bureau of Mines furnace; particle heating rates primarily dictated by gas conduction are indicated for both systems.

TABLE 9

IGNITION AND COMBUSTION PARAMETERS OF DRY BEULAH LIGNITE (PSOC-1507) VITRAIN:
THE EFFECTS OF OXYGEN CONCENTRATION, INORGANIC CONSTITUENTS AND VOLATILES

Data Set ^a	T (°C)	O ₂ (%)	Moist. (%)	No. of Particles	Particle Vol. (cm ³)	Carbon Recovery (%)	CO ₂ :CO Prod. Ratio	CO ₂ /CO Release Stages	Maximum Conversion Rate (g/s)
Oxygen Concentration									
BVLC	650	0	0	6	1.3 ± 0.5x10 ⁻⁵	3 ± 1 ^a	0.98 ± 0.39	1	6.7 ± 2.3x10 ⁻⁷
BVLE	650	5	0	7	8.0 ± 3.0x10 ⁻⁶	65 ± 22	7.23 ± 4.14	2	1.5 ± 0.7x10 ⁻⁶
BVLD	650	11	0	7	8.7 ± 1.5x10 ⁻⁶	76 ± 11	1.56 ± 0.36	1	4.4 ± 1.2x10 ⁻⁶
BVLA	650	20	0	11	5.4 ± 1.3x10 ⁻⁶	90 ± 21	0.84 ± 0.16	1	4.5 ± 1.1x10 ⁻⁶
BVLH	650	28	0	9	1.1 ± 0.2x10 ⁻⁵	70 ± 22	0.96 ± 0.22	1	6.9 ± 2.0x10 ⁻⁶
BVLJ	650	50	0	10	9.6 ± 1.6x10 ⁻⁶	82 ± 17	0.46 ± 0.08	1	9.8 ± 2.2x10 ⁻⁶
BVLK	650	100	0	10	1.2 ± 0.4x10 ⁻⁵	101 ± 40	0.99 ± 0.55	1	8.3 ± 2.4x10 ⁻⁶
Inorganic Constituents									
BVLE	650	5	0	7	8.0 ± 3.0x10 ⁻⁶	65 ± 22	7.23 ± 4.14	2	1.5 ± 0.7x10 ⁻⁶
BDLA	650	5	0	11	6.8 ± 1.1x10 ⁻⁶	23 ± 4	0.66 ± 0.09	1	1.1 ± 0.2x10 ⁻⁶
BRLA	650	5	0	9	8.7 ± 2.7x10 ⁻⁶	64 ± 10	4.22 ± 1.11	2	9.9 ± 2.9x10 ⁻⁷
BCLB	650	5	0	9	1.0 ± 0.2x10 ⁻⁵	63 ± 18	9.92 ± 4.20	1-2	1.2 ± 0.4x10 ⁻⁶
BCLC ^d	650	5	0	5	1.2 ± 0.4x10 ⁻⁵	31 ± 6	0.75 ± 0.37	1	1.2 ± 0.6x10 ⁻⁶
Volatiles									
BV5A	500	20	0	8	1.1 ± 0.3x10 ⁻⁵	39 ± 10	3.67 ± 1.15	2	2.4 ± 1.1x10 ⁻⁶
BC5A	500	20	0	6	1.2 ± 0.2x10 ⁻⁵	53 ± 14	2.55 ± 1.20	2	2.6 ± 0.3x10 ⁻⁶
BVLE	650	5	0	7	8.0 ± 3.0x10 ⁻⁶	65 ± 22	7.23 ± 4.14	2	1.5 ± 0.7x10 ⁻⁶
BCLB	650	5	0	9	1.0 ± 0.2x10 ⁻⁵	63 ± 18	9.92 ± 4.20	1-2	1.2 ± 0.4x10 ⁻⁶

^a The first letter indicates a Beulah lignite coal; the second letter indicates the sample form: V = Vitrain, D = Demineralized, R = demineralized and Reloaded with calcium, C = Char; the third letter indicates the

temperature: L = 650°C.

^b The combustion duration was too short to accurately quantitate p.

^c The mass recoveries were lower than the calibrated range.

^d Demineralized.

Continued ...

TABLE 9 (CONT.)

IGNITION AND COMBUSTION PARAMETERS OF DRY BEULAH LIGNITE (PSOC-1507) VITRAIN:
THE EFFECTS OF OXYGEN CONCENTRATION, INORGANIC CONSTITUENTS AND VOLATILES

Data Set ^a	p max g/cm ² s	Combustion Stage Used for p max	CO ₂ :CO p max Ratio	Total Combustion Duration (s)	First-stage Combustion Duration (s)	First-stage Ignition Delay (s)
Oxygen Concentration						
BVLC	2.1 ± 0.9×10 ⁻⁴ ^b	1	0.95 ± 0.48	0.3 ± 0.2	0.3 ± 0.2	0.430 ± 0.028
BVLE	6.3 ± 2.4×10 ⁻⁴	2	2.68 ± 0.32	4.8 ± 1.8	0.5 ± 0.2	0.382 ± 0.062
BVLD	1.6 ± 0.5×10 ⁻³	1	1.56 ± 0.36	1.6 ± 0.6	1.6 ± 0.6	0.363 ± 0.076
BVLA	2.4 ± 0.6×10 ⁻³	1	0.59 ± 0.13	1.0 ± 0.6	1.0 ± 0.6	0.419 ± 0.051
BVLH	2.3 ± 0.6×10 ⁻³	1	0.69 ± 0.16	0.9 ± 0.3	0.9 ± 0.3	0.140 ± 0.046
BVLJ	3.5 ± 0.7×10 ⁻³	1	0.35 ± 0.09	0.6 ± 0.1	0.6 ± 0.1	0.234 ± 0.070
BVLK	2.7 ± 0.6×10 ⁻³	1	0.74 ± 0.42	0.9 ± 0.4	0.9 ± 0.4	0.109 ± 0.045
Inorganic Constituents						
BVLE	6.3 ± 2.4×10 ⁻⁴	2	2.68 ± 0.32	4.8 ± 1.8	0.5 ± 0.2	0.382 ± 0.062
BDLA	5.1 ± 1.0×10 ⁻⁴	1	1.20 ± 0.25	0.4 ± 0.4	0.4 ± 0.4	0.371 ± 0.119
BRLA	3.8 ± 1.1×10 ⁻⁴	2	2.23 ± 0.70	7.0 ± 1.0	0.4 ± 0.2	0.275 ± 0.059
BCLB	4.2 ± 1.4×10 ⁻⁴	1	4.50 ± 1.46	4.8 ± 2.4	4.8 ± 2.4	0.364 ± 0.080
BCLC ^d	3.9 ± 2.3×10 ⁻⁴	1	1.64 ± 0.68	0.4 ± 0.1	0.4 ± 0.1	0.358 ± 0.072
Volatiles						
BV5A	7.9 ± 2.6×10 ⁻⁴	2	2.39 ± 1.08	1.2 ± 0.7	--	0.521 ± 0.090
BC5A	8.9 ± 0.7×10 ⁻⁴	2	1.85 ± 0.65	1.4 ± 0.9	--	0.561 ± 0.068
BVLE	6.3 ± 2.4×10 ⁻⁴	2	2.68 ± 0.32	4.8 ± 1.8	0.5 ± 0.3	0.382 ± 0.062
BCLB	4.2 ± 1.4×10 ⁻⁴	i	4.50 ± 1.46	4.8 ± 2.4	4.8 ± 2.4	0.364 ± 0.080

^a The first letter indicates a Beulah lignite coal; the second letter indicates the sample form:

V = Vitrain, D = Demineralized, R = demineralized and Reloaded with calcium, C = Char; the third

letter indicates the temperature: L = 650°C.

^b The combustion duration was too short to accurately quantitate p.

^c The mass recoveries were lower than the calibrated range.

^d Demineralized.

TABLE 10

IGNITION AND COMBUSTION PARAMETERS OF BEULAH LIGNITE (PSOC-1507) VITRAIN:
THE EFFECTS OF MOISTURE, TEMPERATURE, AND LITHOTYPE

Data Set ^a	T (°C)	O ₂ (%)	Moist. (%)	No. of Particles	Particle Vol. (cm ³)	Carbon Recovery (%)	CO ₂ :CO Prod. Ratio	CO ₂ /CO Release Stages	Maximum Conversion Rate (g/s)
Moisture									
BVHB	1000	20	100	8	1.1 ± 0.5x10 ⁻⁵	68 ± 27	2.15 ± 0.72	1	5.7 ± 0.6x10 ⁻⁶
BVHA	1000	20	0	8	6.9 ± 2.0x10 ⁻⁶	75 ± 23	1.18 ± 0.36	1	5.1 ± 1.2x10 ⁻⁶
BVLB	650	20	100	7	8.3 ± 1.5x10 ⁻⁶	47 ± 19	0.99 ± 0.21	1	3.9 ± 1.1x10 ⁻⁶
BVLA	650	20	0	11	5.4 ± 1.3x10 ⁻⁶	90 ± 21	0.84 ± 0.16	1	4.5 ± 1.1x10 ⁻⁶
BVLF	650	5	100	10	1.0 ± 0.2x10 ⁻⁵	61 ± 14 ^b	4.76 ± 0.93 ^b	2	1.2 ± 0.3x10 ⁻⁶
BVLE	650	5	0	7	8.0 ± 3.0x10 ⁻⁶	65 ± 22	7.23 ± 4.14	2	1.5 ± 0.7x10 ⁻⁶
Temperature									
BV5A	500	20	0	8	1.1 ± 0.3x10 ⁻⁵	39 ± 10	3.67 ± 1.15	2	2.4 ± 1.1x10 ⁻⁶
BVLA	650	20	0	11	5.4 ± 1.3x10 ⁻⁶	90 ± 21	0.84 ± 0.16	1	4.5 ± 1.1x10 ⁻⁶
BVHA	1000	20	0	8	6.9 ± 2.0x10 ⁻⁶	75 ± 23	1.19 ± 0.36	1	5.3 ± 1.2x10 ⁻⁶
Lithotype									
BALA	650	20	0	9	9.8 ± 5.1x10 ⁻⁶	80 ± 31	0.78 ± 0.25	1	7.2 ± 2.7x10 ⁻⁶
BFLA	650	20	0	7	6.7 ± 1.9x10 ⁻⁶	94 ± 22	0.88 ± 0.33	1	6.3 ± 1.4x10 ⁻⁶
BVLA	650	20	0	11	5.4 ± 1.3x10 ⁻⁶	90 ± 21	0.84 ± 0.16	1	4.5 ± 1.1x10 ⁻⁶

^a The first letter indicates a Beulah lignite coal; the second letter indicates the sample form: V = Vitrain, A = Attritus, F = Eusain; the third letter indicates the temperature: H = 1000°C, L = 650°C.

^b Underestimated since the combustion duration exceeded the residence time of the CO₂ analyzer.

Continued ...

TABLE 10 (CONT.)

IGNITION AND COMBUSTION PARAMETERS OF BEULAH LIGNITE (PSOC-1507) VITRAIN:
THE EFFECTS OF MOISTURE, TEMPERATURE, AND LITHOTYPE

Data Set ^a	p max g/cm ² s	Combustion Stage Used for p max	CO ₂ :CO p max Ratio	Total Combustion Duration (s)	First-Stage Combustion Duration (s)	First-Stage ignition Delay (s)
Moisture						
BVHB	2.2 ± 0.6×10 ⁻³	1	1.45 ± 0.58	0.8 ± 0.1	0.9 ± 0.1	0.170 ± 0.053
BVHA	2.5 ± 0.6×10 ⁻³	1	0.75 ± 0.31	0.8 ± 0.1	0.8 ± 0.1	0.137 ± 0.038
BVLB	1.6 ± 0.5×10 ⁻³	1	0.74 ± 0.14	0.7 ± 0.3	0.7 ± 0.3	0.376 ± 0.062
BVLA	2.4 ± 0.6×10 ⁻³	1	0.59 ± 0.13	1.0 ± 0.6	1.0 ± 0.6	0.419 ± 0.051
BVIF	4.0 ± 1.2×10 ⁻⁴	2	2.49 ± 0.44	12.0 ± 3.1 ^b	1.9 ± 0.3	0.378 ± 0.076
BVLE	6.3 ± 2.4×10 ⁻⁴	2	2.68 ± 0.32	4.8 ± 1.8	0.5 ± 0.3	0.382 ± 0.062
Temperature						
BV5A	7.9 ± 2.6×10 ⁻⁴	2	2.39 ± 1.08	1.2 ± 0.7	--	0.521 ± 0.090
BVLA	2.4 ± 0.6×10 ⁻³	1	0.59 ± 0.13	1.0 ± 0.6	1.0 ± 0.6	0.419 ± 0.051
BVHA	2.5 ± 0.6×10 ⁻³	1	0.89 ± 0.31	0.8 ± 0.1	0.8 ± 0.1	0.137 ± 0.038
Lithotype						
BALA	2.4 ± 0.7×10 ⁻³	1	0.54 ± 0.16	1.2 ± 0.4	1.2 ± 0.4	0.371 ± 0.036
BFLA	2.8 ± 0.5×10 ⁻³	1	0.60 ± 0.17	0.8 ± 0.1	0.8 ± 0.1	0.302 ± 0.051
BVLA	2.4 ± 0.6×10 ⁻³	1	0.59 ± 0.13	1.0 ± 0.6	1.0 ± 0.6	0.419 ± 0.051

^a The first letter indicates a Beulah coal; the second letter indicates the sample form: V = Vitrain,

A = Attritus, F = Eusain; the third letter indicates the temperature: H = 1000°C, L = 650°C.

^b Underestimated since the combustion duration exceeded the residence time of the CO₂ analyzer.

Huang et al. (29) have measured gas temperatures and estimated particle temperatures as a function of time in an apparatus similar to the ignition apparatus. The material studied was 800- to 500- μm Texas subbituminous coal particles. These workers reported heterogeneous ignition delays of 3.85 sec and homogeneous ignition delays of 0.690 sec for 800- μm particles at 700°C. These long delays are a result of the low heating rates (900°-50°C/sec) calculated for these large particles. The homogenous ignition delay decreased with decreasing particle size, but not as rapidly as the heterogeneous ignition delay. Extrapolation of these ignition delays to 240- μm particles yields homogeneous ignition delays of approximately 0.500 sec, and heterogeneous ignition delays of approximately 1.000 sec. These values are larger than those observed for the Beulah lignite and the Smith Roland subbituminous coal at 650°C (see Tables 9, 10 and 11). The other two materials studied in the ignition apparatus, i.e., Lower-Wilcox lignite and Pittsburgh #8 bituminous coal, did not ignite until temperatures greater than 650°C were employed (see Tables 12-13). Detailed comparison between the results of the two studies is difficult because different particle sizes and materials were used. However, the ignition delays obtained in the two systems appear to be complementary and consistent with the similarities in the apparatuses used to obtain them.

The relative trends of the ignition delays obtained from the optical microscopy studies have been in general agreement with those obtained in the ignition apparatus; however, the exact ignition delays measured by optical microscopy were usually shorter than those measured in the ignition apparatus (see Tables 11-14). This is either a result of the different parameters used to define ignition, i.e., light emission versus CO_2 production, or a result of differences in the particle heating rates experienced by the particles in the two different experiments. Wall et al. (30) have measured the ignition temperatures of pulverized coal clouds by both light emission and CO_2 production. Initial light emission was observed at a temperature much lower than that at which significant quantities of CO_2 were detected. Since it is expected that a light-producing reaction would generate CO and/or CO_2 , this result was attributed to the ignition of small numbers of particles in the cloud. Since the present experiments are performed on single particles, it is expected that light emission and CO_2/CO production would occur simultaneously.

The heating rates of the particles in the optical microscopy experiments are primarily dictated by the energy transfer from the heated stage to the particle. In the optical microscopy experiments the heated stage was painted with a smooth layer of Al_2O_3 prior to the ignition tests. The thermal conductivity of Al_2O_3 is approximately 15.6 times greater than that of ZrO_2 , the solid material in contact with the particle in the ignition apparatus, and approximately 500 times that of N_2 at 657°C. The percentage of the particle in contact with the smooth solid surface in the optical microscopy experiments is expected to be greater than that in contact with the porous ZrO_2 plug in the ignition apparatus. It is also significant that the coal particles studied are not spherical but rectangular. Therefore, it is reasonable that the heating rate in the optical microscopy studies could exceed that of the ignition apparatus, which would account for the shorter ignition delays in the optical microscopy experiments. Having defined the relationship between the ignition delays measured in the ignition apparatus and those measured by optical microscopy, it is possible to examine the ignition results in detail.

TABLE 11

IGNITION AND COMBUSTION PARAMETERS OF SMITH ROLAND SUBBITUMINOUS COAL (PSOC-1520) VITRAIN:
THE EFFECTS OF LITHOTYPE, INORGANIC CONSTITUENTS, AND OXYGEN CONCENTRATION

Data Set ^a	T (°C)	O ₂ (%)	Moist. (%)	No. of Particles	Particle Vol. (cm ³)	Carbon Recovery (%)	CO ₂ :CO Prod. Ratio	CO ₂ /CO Release Stages	Maximum Conversion Rate (g/s)
Lithotype									
SALA	650	20	0	8	$7.7 \pm 1.8 \times 10^{-6}$	61 ± 19	1.10 ± 0.44	1	$4.6 \pm 1.5 \times 10^{-6}$
SVLA	650	20	0	10	$7.2 \pm 2.4 \times 10^{-6}$	87 ± 17	0.88 ± 0.36	1	$6.1 \pm 1.2 \times 10^{-6}$
Inorganic Constituents									
SVLB	650	5	0	9	$8.5 \pm 1.9 \times 10^{-6}$	53 ± 10	5.03 ± 0.47	2	$9.3 \pm 2.0 \times 10^{-7}$
SDLA	650	5	0	10	$9.0 \pm 4.4 \times 10^{-6}$	25 ± 13	1.74 ± 0.34	1	$1.2 \pm 0.2 \times 10^{-6}$
SRLA	650	5	0	11	$8.1 \pm 6.0 \times 10^{-10}$	43 ± 23	1.57 ± 0.37	2	$9.4 \pm 2.7 \times 10^{-7}$
O ₂ conc.									
SVLC	650	0	0	5	$9.3 \pm 1.5 \times 10^{-6}$	6 ± 1	1.12 ± 0.14	1	$8.2 \pm 2.5 \times 10^{-7}$
SVLB	650	5	0	9	$8.5 \pm 1.9 \times 10^{-6}$	53 ± 10	5.03 ± 0.47	2	$9.3 \pm 1.9 \times 10^{-7}$
SVLA	650	20	0	10	$7.2 \pm 2.4 \times 10^{-6}$	87 ± 17	0.88 ± 0.36	1	$6.1 \pm 1.2 \times 10^{-6}$
Volatiles									
SVLB	650	5	0	9	$8.5 \pm 1.9 \times 10^{-6}$	53 ± 10	5.03 ± 0.47	2	$9.3 \pm 1.9 \times 10^{-7}$
SCLA	650	5	0	9	$4.5 \pm 0.6 \times 10^{-6}$	80 ± 16	5.02 ± 1.07	1	$1.3 \pm 0.4 \times 10^{-6}$

^a The first letter indicates a Smith-Roland subbituminous coal; the second letter indicates the sample form: A = Attritus, V = Vitrain, D = Demineralized, C = Char, R = demineralized and Reloaded with calcium; the third letter indicates the temperature: L = 650°C.

^b The combustion duration was too small to accurately quantitate p.

Continued ...

TABLE 11 (CONT.)

IGNITION AND COMBUSTION PARAMETERS OF SMITH ROLAND SUBBITUMINOUS COAL (PSOC-1520) VITRAIN:
THE EFFECTS OF LITHOTYPE, INORGANIC CONSTITUENTS, AND OXYGEN CONCENTRATION

Data Set ^a	p max g/cm ² s	Combustion Stage Used For p Max	CO ₂ :CO p max Ratio	Total Combustion Duration (s)	First-Stage Combustion Duration (s)	First-Stage ignition Delay (s)
Lithotype						
SALA	1.9 ± 0.7x10 ⁻³	1	1.06 ± 0.55	0.9 ± 0.2	0.9 ± 0.2	0.323 ± 0.045
SVLA	2.5 ± 0.6x10 ⁻³	1	0.66 ± 0.28	1.0 ± 0.3	1.0 ± 0.3	0.359 ± 0.062
Mineral Matter						
SVLB	3.5 ± 0.4x10 ^{-4b}	1	2.71 ± 0.68	5.7 ± 1.4	0.5 ± 0.2	0.375 ± 0.071
SDLA	4.9 ± 1.5x10 ^{-4b}	1	2.80 ± 0.47	1.2 ± 0.8	1.2 ± 0.8	0.282 ± 0.062
SRLA	3.9 ± 1.4x10 ^{-4b}	1	0.97 ± 0.36	>10.0	0.4 ± 0.4	0.331 ± 0.081
O ₂ conc.						
SVLC	3.0 ± 0.9x10 ^{-4b}	1	1.24 ± 0.17	<0.1	<0.1	0.426 ± 0.114
SVLB	3.5 ± 0.4x10 ⁻⁴	2	2.71 ± 0.68	5.7 ± 1.4	0.5 ± 0.2	0.375 ± 0.071
SVLA	2.5 ± 0.6x10 ⁻³	1	0.66 ± 0.28	1.0 ± 0.3	1.0 ± 0.3	0.359 ± 0.062
Volatiles						
SVLB	3.5 ± 0.4x10 ⁻⁴	2	2.71 ± 0.68	5.7 ± 1.4	0.5 ± 0.2	0.375 ± 0.071
SCLA	4.6 ± 1.3x10 ⁻⁴	1	3.43 ± 0.88	5.1 ± 1.3	5.1 ± 1.3	0.308 ± 0.089

^a The first letter indicates a Smith-Roland subbituminous coal; the second letter indicates the sample form:
A = Attritus, V = Vitrain, D = Demineralized, C = Char, R = demineralized and Beloaded with calcium; the
third letter indicates the temperature: L = 650°C.

^b The combustion duration was too small to accurately quantitate p.

TABLE 12

IGNITION AND COMBUSTION PARAMETERS OF LOWER-WILCOX LIGNITE (PSOC-1443) VITRAIN:
THE EFFECTS OF LITHOTYPE, TEMPERATURE, AND OXYGEN CONCENTRATION

Data Set ^a	T (°C)	O ₂ (%)	Moist. (%)	No. of Particles	Particle Vol. (cm ³)	Carbon Recovery (%)	CO ₂ :CO Prod. Ratio	CO ₂ /CO Release Stages	Maximum Conversion Rate (g/s)
Lithotype									
LVLA	650	20	0	4	$8.8 \pm 1.5 \times 10^{-6}$	$< 1^b, c$	--	1	2.4×10^{-8}
LALA	650	20	0	4	$7.4 \pm 1.8 \times 10^{-6}$	3 ± 1^c	--	1	$7.1 \pm 3.1 \times 10^{-8}$
LVHB	1000	5	0	8	$8.0 \pm 1.6 \times 10^{-6}$	45 ± 11^b	0.35 ± 0.18	1	$2.8 \pm 0.3 \times 10^{-7}$
LAHA	1000	5	0	8	$7.1 \pm 0.9 \times 10^{-6}$	25 ± 5^b	0.00 ± 0.06	1	$1.5 \pm 0.2 \times 10^{-7}$
Temperature									
LVLA	650	20	0	4	$8.8 \pm 1.5 \times 10^{-6}$	$< 1^b, c$	--	1	2.4×10^{-8}
LVHA	1000	20	0	9	$8.1 \pm 3.1 \times 10^{-6}$	102 ± 33^b	0.40 ± 0.27	1	$1.0 \pm 0.3 \times 10^{-6}$
O ₂ conc.									
LVHB	1000	5	0	8	$8.0 \pm 1.6 \times 10^{-6}$	45 ± 11^b	0.35 ± 0.18	1	$2.8 \pm 0.3 \times 10^{-7}$
LVHA	1000	20	0	9	$8.1 \pm 3.1 \times 10^{-6}$	102 ± 33^b	0.40 ± 0.27	1	$1.0 \pm 0.3 \times 10^{-6}$

^a The first letter indicates a Lower-Wilcox lignite; the second letter indicates the sample form: V = Vitrain, A = Attritus; the third letter indicates the temperature: L = 650°C, H = 1000°C.

^b Underestimated since the combustion duration exceeded the residence time of the CO₂ analyzer.

^c The mass recoveries were lower than the calibrated range.

Continued ...

TABLE 12 (CONT.)

IGNITION AND COMBUSTION PARAMETERS OF LOWER-WILCOX LIGNITE (PSOC-1443) VITRAIN:
THE EFFECTS OF LITHOTYPE, TEMPERATURE, AND OXYGEN CONCENTRATION

Data Set ^a	p max g/cm ² s	Combustion Stage Used For p max	CO ₂ :CO p max Ratio	Total Combustion Duration (s)	First-Stage Combustion Duration (s)	First-Stage Ignition Delay (s)
Lithotype						
LVLA	8.3 ± 1.0 × 10 ⁻⁶	1	--	>10 ^b	>10 ^b	0.923 ± 0.328
LALA	2.9 ± 1.6 × 10 ⁻⁵	1	--	5.0 ± 2.5	5.0 ± 2.5	0.702 ± 0.071
LVHB	1.1 ± 0.2 × 10 ⁻⁴	1	0.35 ± 0.32	18.7 ± 3.5 ^b	18.7 ± 3.5 ^b	0.584 ± 0.161
LAHA	6.2 ± 0.8 × 10 ⁻⁵	1	0.14 ± 0.07	18.4 ± 1.1 ^b	18.4 ± 1.1 ^b	0.738 ± 0.179
Temperature						
LVLA	8.3 ± 1.0 × 10 ⁻⁶	1	--	>10 ^b	>10 ^b	0.923 ± 0.328
LVHA	4.3 ± 1.5 × 10 ⁻⁴	1	0.68 ± 0.42	8.1 ± 1.2 ^b	8.1 ± 1.2 ^b	0.469 ± 0.092
O ₂ conc.						
LVHB	1.1 ± 0.2 × 10 ⁻⁴	1	0.35 ± 0.32	18.7 ± 3.5 ^b	18.7 ± 3.5 ^b	0.584 ± 0.161
LVHA	4.3 ± 1.5 × 10 ⁻⁴	1	0.68 ± 0.42	8.1 ± 1.2 ^b	8.1 ± 1.2 ^b	0.469 ± 0.092

^a The first letter indicates a Lower-Wilcox lignite; the second letter indicates the sample form:

V = Vitrain, A = Attritus; the third letter indicates the temperature: L = 650°C, H = 1000°C.

^b Underestimated since the combustion duration exceeded the residence time of the CO₂ analyzer.

^c The mass recoveries were lower than the calibrated range.

TABLE 13

IGNITION AND COMBUSTION PARAMETERS OF LOWER-WILCOX LIGNITE (PSOC-1443) VITRAIN:
THE EFFECTS OF INORGANIC CONSTITUENTS AND VOLATILE MATTER

Data Set ^a	T (°C)	O ₂ (%)	Moist. (%)	No. of Particles	Particle Vol. (cm ³)	Carbon Recovery (%)	CO ₂ :CO Prod. Ratio	CO ₂ /CO Release Stages	Maximum Conversion Rate (g/s)
Inorganic Constituents									
LVHA	1000	20	0	9	$8.1 \pm 3.1 \times 10^{-6}$	102 ± 33^b	0.40 ± 0.27	1	$1.0 \pm 0.3 \times 10^{-6}$
LDHA	1000	20	0	7	$8.9 \pm 3.2 \times 10^{-6}$	96 ± 35	0.78 ± 0.26	1	$4.6 \pm 1.5 \times 10^{-6}$
LRHA	1000	20	0	8	$5.0 \pm 1.7 \times 10^{-6}$	138 ± 38	1.23 ± 0.21	1	$4.4 \pm 1.5 \times 10^{-6}$
Volatile Matter									
LVHA	1000	20	0	9	$8.1 \pm 3.1 \times 10^{-6}$	102 ± 33^b	0.40 ± 0.27	1	$1.0 \pm 0.3 \times 10^{-6}$
LCHA	1000	20	0	6	$1.2 \pm 0.3 \times 10^{-5}$	123 ± 66	0.31 ± 0.20	1	$2.0 \pm 0.4 \times 10^{-6}$

^a The first letter indicates a Lower-Wilcox lignite; the second letter indicates the sample form: V = Vitrain,
D = Demineralized, R = demineralized and Beloaded with calcium, C = Char; the third letter indicates the temperature:

H = 1000°C.

^b Underestimated since the combustion duration exceeded the residence time of the CO₂ analyzer.

Continued ...

TABLE 13 (CONT.)

IGNITION AND COMBUSTION PARAMETERS OF LOWER-WILCOX LIGNITE (PSOC-1443) VITRAIN:
THE EFFECTS OF INORGANIC CONSTITUENTS AND VOLATILE MATTER

Data Set ^a	p_{max} g/cm ² s	Combustion Stage Used for p_{max}	CO ₂ :CO p_{max} Ratio	Total Combustion Duration (s)	First-Stage Combustion Duration (s)	First-Stage Ignition Delay (s)
Inorganic Constituents						
LVHA	$4.3 \pm 1.5 \times 10^{-4}$	1	0.68 ± 0.42	8.1 ± 1.2^b	8.1 ± 1.2^b	0.469 ± 0.092
LDHA	$1.9 \pm 0.8 \times 10^{-3}$	1	0.79 ± 0.07	2.8 ± 1.3	2.8 ± 1.3	0.391 ± 0.096
LRHA	$2.2 \pm 0.7 \times 10^{-3}$	1	1.17 ± 0.17	2.5 ± 0.9	2.5 ± 0.9	0.546 ± 0.091
Volatile Matter						
LVHA	$4.3 \pm 1.5 \times 10^{-4}$	1	0.68 ± 0.42	8.1 ± 1.2^b	8.1 ± 1.2^b	0.469 ± 0.092
LCHA	$6.3 \pm 1.4 \times 10^{-4}$	1	0.32 ± 0.09	4.6 ± 2.5	4.6 ± 2.5	0.533 ± 0.093

^a The first letter indicates a Lower-Wilcox lignite; the second letter indicates the sample form:
V = Vitrain, D = Demineralized, R = demineralized and Beloaded with calcium, C = Char; the third
letter indicates the temperature: H = 1000°C.

^b Underestimated since the combustion duration exceeded the residence time of the CO₂ analyzer.

TABLE 14

IGNITION AND COMBUSTION PARAMETERS OF PITTSBURGH #8 BITUMINOUS COAL (PSOC-1451) VITRAIN:
THE EFFECTS OF TEMPERATURE AND OXYGEN CONCENTRATION

Data Set ^a	T (°C)	O ₂ (%)	Moist. (%)	No. of Particles	Particle Vol. (cm ³)	Carbon Recovery (%)	CO ₂ :CO Prod. Ratio	CO ₂ /CO Release Stages	Maximum Conversion Rate (g/s)
Temperature									
PVHB	1000	20	0	7	6.2 ± 1.8x10 ⁻⁶	70 ± 23	2.01 ± 0.53	1	4.5 ± 1.8x10 ⁻⁶
PVLB	650	20	0	8	6.5 ± 2.9x10 ⁻⁶	40 ± 17	0.62 ± 0.10	2	9.9 ± 2.5x10 ⁻⁷
O ₂ conc.									
PVLC	650	0	0	8	9.2 ± 3.6x10 ⁻⁶	4 ± 2 ^b	---	1	3.2 ± 0.6x10 ⁻⁷
PVLD	650	11	0	8	1.0 ± 0.2x10 ⁻⁵	36 ± 13 ^c	0.76 ± 0.06 ^c	2	1.5 ± 0.2x10 ⁻⁶
PVLB	650	20	0	8	6.5 ± 2.9x10 ⁻⁶	40 ± 17	0.62 ± 0.10	2	9.9 ± 2.5x10 ⁻⁷
Inorganic Constituents									
PVHB	1000	20	0	7	6.2 ± 1.8x10 ⁻⁶	70 ± 23	2.01 ± 0.53	1	4.5 ± 1.8x10 ⁻⁶
PDHA	1000	20	0	11	9.3 ± 1.4x10 ⁻⁶	84 ± 24	4.1 ± 1.03	1	6.7 ± 1.9x10 ⁻⁶
PRHA	1000	20	0	11	6.2 ± 2.3x10 ⁻⁶	72 ± 36	3.89 ± 1.30	1	4.2 ± 2.0x10 ⁻⁶
Volatile Matter									
PVHB	1000	20	0	7	6.2 ± 1.8x10 ⁻⁶	70 ± 23	2.01 ± 0.53	1	4.5 ± 1.8x10 ⁻⁵
PCHA	1000	20	0	9	1.8 ± 0.3x10 ⁻⁵	56 ± 23	3.83 ± 0.99	1	4.1 ± 2.1x10 ⁻⁶

^a The first letter indicates a Pittsburgh #8 bituminous coal; the second letter indicates the sample form: V = Vitrain, D = Demineralized, R = demineralized and Beloaded with calcium, C = Char (mostly cenospheres); the third letter indicates the temperature: L = 650°C, H = 1000°C.

^b The mass recoveries were lower than the calibrated range.

^c Underestimated since the combustion duration exceeded the residence time of the CO₂ analyzer.

^d The combustion duration was too short to accurately quantitate p.

Continued ...

TABLE 14 (CONT.)

IGNITION AND COMBUSTION PARAMETERS OF PITTSBURGH #8 BITUMINOUS COAL (PSOC-1451) VITRAIN:
THE EFFECTS OF TEMPERATURE AND OXYGEN CONCENTRATION

Data Set ^a	p max g/cm ² s	Combustion		CO ₂ :CO p: max Ratio	Total Combustion Duration (s)	First-Stage Combustion Duration (s)	First-Stage Ignition Delay (s)
		Stage Used for	p max				
Temperature							
PVHB	2.3 ± 0.7x10 ⁻³	1		1.66 ± 0.41	1.1 ± 0.3	1.1 ± 0.3	0.120 ± 0.079
PVLB	4.7 ± 1.1x10 ⁻⁴	1		1.59 ± 0.26	6.9 ± 0.5	0.7 ± 0.1	0.480 ± 0.034
O ₂ Conc.							
PVLC	1.2 ± 0.4x10 ^{-4d}	1		0.43 ± 0.12	<0.300	<0.300	0.638 ± 0.050
PVLD	5.2 ± 1.1x10 ⁻⁴	1		2.09 ± 0.26	>10	1.0 ± 0.3	0.390 ± 0.096
PVLB	4.7 ± 1.1x10 ⁻⁴	1		1.59 ± 0.26	6.9 ± 0.5	0.7 ± 0.1	0.480 ± 0.034
Inorganic Constituents							
PVHB	2.3 ± 0.7x10 ⁻³	1		1.66 ± 0.41	1.1 ± 0.3	1.1 ± 0.3	0.120 ± 0.079
PDHA	2.4 ± 0.8x10 ⁻³	1		3.30 ± 0.90	1.5 ± 0.4	1.5 ± 0.4	0.065 ± 0.035
PRHA	1.8 ± 0.7x10 ⁻³	1		3.67 ± 1.63	1.3 ± 0.8	1.3 ± 0.8	0.108 ± 0.057
Volatile Matter							
PVHB	2.3 ± 0.7x10 ⁻³	1		1.66 ± 0.41	1.1 ± 0.3	1.1 ± 0.3	0.120 ± 0.079
PCHA	9.9 ± 4.7x10 ⁻⁴	1		3.04 ± 1.18	1.1 ± 0.4	1.1 ± 0.4	0.203 ± 0.095

^a The first letter indicates a Pittsburgh #8 bituminous coal; the second letter indicates the sample form: V = Vitrain, D = Demineralized, R = demineralized and Reloaded with calcium, C = Char (mostly cenospheres); the third letter indicates the temperature: L = 650°C, H = 1000°C.

^b The mass recoveries were lower than the calibrated range.

^c Underestimated since the combustion duration exceeded the residence time of the CO₂ analyzer.

^d The combustion duration was too short to accurately quantitate p.

The combustion of Beulah lignite vitrain and Beulah lignite char particles were also monitored by DSC. This work was performed by an Associated Western Universities fellow. The maximum temperature attainable in this apparatus was 500°C; therefore, only the most reactive material, i.e., Beulah lignite, was examined. Large variations in response were observed from particle to particle; this fact, accompanied by the low maximum employable temperature, limits the usefulness of this technique for evaluating the reactivity of coals. Therefore, the specific results previously reported (31) are presented herein.

It was determined that the monitoring of events in the ignition apparatus by video imaging was impractical due to the low sensitivity of the video equipment and difficulties in positioning the combusting particles in the focal volume. The feasibility of obtaining optical pyrometry data through the use of an optical rod inserted into the ignition apparatus has not yet been ascertained.

4.4.2 Effects of Oxygen Concentration

The ignition and combustion of Beulah lignite (PSOC-1507) vitrain was examined in the ignition apparatus at oxygen concentrations of 0%-100% at 650°C. The overall results are shown in Table 9. In general, increasing the oxygen concentration increased the maximum combustion rate per unit surface area (ρ maximum), decreased the combustion duration, decreased the ignition delay and decreased the CO_2 :CO product and rate ratios.

The CO_2 production profiles of Figure 23 show both the increased combustion rate with increased oxygen concentration as evidenced by the shorter combustion durations, as well as the shift towards CO_2 production at lower oxygen concentrations. The decreased maximum CO_2 production rates at high O_2 concentrations are due to a shift in the product ratio towards CO. When first considering this figure, it appears that the combustion rate is decreased at higher oxygen concentrations; this is a result of the shift in products away from CO_2 towards CO at higher oxygen concentrations. The sum of the rates of CO_2 and CO production, shown in Table 9, did, in general, increase with increased oxygen concentration. Figure 23 also shows that at an oxygen concentration of 5%, CO_2 is produced in two distinct stages. The optical microscopy studies also showed the ignition delay and combustion duration to decrease with increased oxygen concentration (see Table 15). The study performed at an oxygen concentration of 100% showed some discrepancies with the trends noted between concentrations of 0 and 50%. A lower ρ maximum, longer combustion duration, and higher CO_2 :CO ratios were observed than for the 50% oxygen studies. The results of the 100% concentration studies were, in fact, similar to those of the 28% study. Increased ρ maximum values and accompanying decreased combustion durations produced by increased oxygen concentrations are consistent with current combustion theory. The increase in the proportion of CO produced with increased oxygen concentration is thought to be a result of higher particle temperatures produced by the larger combustion rates. The CO: CO_2 product ratios during the combustion of solid carbonaceous particles have been correlated with particle temperature (32,33). To obtain a similar correlation for the present data, particle

TABLE 15

OPTICAL MICROSCOPY RESULTS FROM THE COMBUSTION OF DRY
180- TO 250- μm BEULAH LIGNITE (PSOC-1507) PARTICLES

	Temp. (°C)	O ₂ (%)	Ignition Delay (s)		Combustion Duration (s)		Cloud Duration (s)	
Particle Size			Avg.	Std. D.	Avg.	Std. D.	Avg.	Std. D.
Vitrain	650	5	0.53	0.16	2.16	0.76	0.59	0.12
Vitrain ^a	650	5	0.31	0.09	0.99	0.31	0.58	0.14
Temperature								
Vitrain	650	20	0.09	0.03	0.70	0.30	0.18	0.05
Vitrain	825	20	0.05	0.03	0.51	0.17	--	--
Vitrain	1000	20	<0.05	--	<0.05	--	--	--
Vitrain	650	5	0.53	0.16	2.16	0.76	0.59	0.12
Vitrain	825	5	0.13	0.02	1.05	0.60	--	--
Vitrain	1000	5	<0.05	--	0.37	0.05	--	--
Moisture								
Vitrain	650	20	0.09	0.03	0.70	0.30	0.18	0.05
Vitrain ^b	650	20	0.05	0.03	0.66	0.33	--	--
Vitrain	650	5	0.53	0.16	2.16	0.76	0.59	0.12
Vitrain ^b	650	5	0.30	0.11	3.79	1.14	--	--
Lithotype								
Vitrain	650	20	0.09	0.03	0.70	0.30	0.18	0.05
Attritus	650	20	0.17	0.05	1.60	0.49	--	--
Fusain	650	20	0.14	0.04	0.57	0.12	--	--
Vitrain	650	5	0.53	0.16	2.16	0.76	0.59	0.12
Attritus	650	5	0.42	0.02	5.71	0.97	--	--
Fusain	650	5	0.26	0.03	2.79	0.72	--	--

^a Particle size = 120- to 170- μm diameter.^b Moisture = 100%.

Figure 23. Effect of O_2 concentration on the production of CO_2 from Beulah lignite vitrain at $650^\circ C$ (BVLG, 0% O_2 ; BVLE, 5% O_2 ; BVLD, 11% O_2 ; BVLA, 20% O_2 ; BVLJ, 50% O_2).

temperatures were estimated for oxygen concentrations from 5% to 50% using the steady-state form of Equation 7 and the measured ρ_{max} values. The correlation with the measured $CO:CO_2$ product ratios is shown in Equation 11.

$$CO:CO_2 = 44,000 \exp(-28,00/1.987T_p) \quad [11]$$

Further details of this calculation are available (34). A plot of this correlation and those of Arthur (32) and Hardesty (33) are shown in Figure 24. This correlation is seen to be intermediate to those previously reported. The maximum error which could be incurred in the correlation of Equation 11 by the assumption that the product ratios measured at $650^\circ C$ are representative of the surface reactions is demonstrated by the results obtained at the oxygen concentration of 50%. Under this condition, CO_2 comprised 30% of the products. Since the particle temperature is highest at this condition, the boundary layer temperature is also highest; therefore, the maximum amount of CO that could be oxidizing in the boundary layer is 30%. Since the amount of CO produced decreases at the lower oxygen concentrations, the maximum possible error is also reduced at the lower oxygen concentrations.

Figure 24. Correlations of CO:CO₂ product ratios with particle temperature: a) Arthur (32), b) this work, c) Hardesty (33).

The results obtained at oxygen concentrations of 100% are of interest, although not included in the above correlation. Examination of these results shows that the CO₂:CO ratio was higher for this case than at the 50% oxygen study, and further, that the ρ maximum was lower. A large standard deviation in the measurements was also observed. It is suggested that these results are produced by significant CO oxidation occurring in the boundary layer under these conditions; this reaction would increase CO₂ production and decrease the oxygen concentration at the particle surface and, hence, decrease ρ maximum.

The shift from single- to two-stage CO₂ release upon decreasing the oxygen concentration to 5% is interpreted as resulting from devolatilization of the lignite prior to ignition at the low oxygen concentration. This conclusion is based on the similarity in position and magnitude of the CO₂ peak produced during pyrolysis, with the initial peak observed at the low oxygen concentration (see Figure 23). The decrease in ignition delays and the shift towards single-stage combustion at higher oxygen concentrations is interpreted as resulting from increased particle surface oxidation rates producing rapid heterogeneous ignition at the higher oxygen concentrations. The promotion of heterogeneous Beulah lignite ignition by increased oxygen concentration has been previously reported (35).

The effect of oxygen concentration on the ignition and combustion of Smith Roland subbituminous coal at 650°C was examined in the ignition apparatus. The results are shown in Table 11. The CO/CO₂ profiles of the 5% and 20% oxygen studies are shown in Figures 25 and 26, respectively. This material behaved similarly to the Beulah lignite, i.e., the ρ maximum increased, the ignition delay decreased and the CO₂:CO ratios decreased with increased oxygen concentration. The transfer from two-staged to single-staged CO₂ production was also observed at the 5% oxygen concentration. As with Beulah lignite, heterogeneous ignition is indicated to precede pyrolysis at oxygen concentrations greater than 5%.

The effect of oxygen concentration on the ignition and combustion of Lower-Wilcox lignite was examined in the ignition apparatus at 1000°C (see Table 12 and Figures 27 and 28). The ρ maximum increased, the combustion duration decreased, the ignition delay decreased slightly and the CO₂:CO ratios were not significantly affected by increased oxygen concentration. The optical microscopy studies showed that ignition of this lignite did not occur until oxygen concentrations of 20% were employed at a gas temperature of 825°C. Single-staged slow combustion was observed even at 1000°C in 20% O₂ (see Figure 28). The reactivity of this material is dramatically lower than that of the Beulah lignite and the Smith Roland subbituminous coal.

The effect of oxygen concentration on the ignition and combustion of Pittsburgh #8 bituminous coal was examined at 650°C in the ignition apparatus (see Table 14 and Figure 29). The process observed at this temperature was not the same as that observed for the more highly reactive Beulah lignite or Smith Roland subbituminous coal, as indicated by the lower mass recoveries and much lower ρ maximum values observed for this material. In fact, the optical microscopy studies showed that light emission did not occur from this material until temperatures of 1000°C were employed. Therefore, the oxygen concentration study at 650°C, while monitoring an oxidation rate (indicated by the increase in products with increased oxygen concentration) is not monitoring sustained combustion. In general, the ρ maximum increased, and the CO₂:CO rate ratio decreased with increased oxygen concentration. The fact that larger CO₂ production rates were observed at an oxygen concentration of 11% than at 20% (see Figure 29) is a result of not only decreasing CO₂:CO ratios with higher oxygen concentration, but also the larger particle size used for the 11% studies. It is recalled that the CO₂ and CO production profiles, unlike ρ maximum, are total production rates not normalized to particle size.

Figure 25. Rates of CO and CO₂ production from dry Smith Roland subbituminous coal vitrain at 650°C, 5% O₂ (SVLB).

Figure 26. Rates of CO and CO₂ production from dry Smith Roland subbituminous coal vitrain at 650°C, 20% O₂ (SVLA).

Figure 27. Rates of CO and CO₂ production from dry Lower-Wilcox lignite vitrain at 1000°C, 5% O₂ (LVHB).

Figure 28. Rates of CO and CO₂ production from dry Lower-Wilcox lignite vitrain at 1000°C, 20% O₂ (LVHA).

Figure 29. Effect of O_2 concentration on the combustion of dry Pittsburgh #8 vitrain at $650^\circ C$.

4.4.3 Inorganic Constituents

The effect of mineral matter on the combustion of Beulah lignite and its char were examined in the ignition apparatus (see Table 9). The demineralized materials showed dramatically lower mass recoveries, decreased $CO_2:CO$ product and rate ratios, lowered ρ maximum values, decreased total combustion times, and similar ignition delays to those of the untreated materials. The CO/CO_2 production profiles of the demineralized char were similar to those of the demineralized lignite (the profiles of the demineralized lignite are shown in Figure 30). Comparison of this figure with Figure 31 shows that the demineralized material only produced the initial CO_2 peak previously associated with pyrolysis (see Figure 23). The optical microscopy results shown in Table 1C show that the demineralized char did not ignite at $650^\circ C$. At $825^\circ C$ the demineralized material did ignite, but showed a longer ignition delay and combustion duration than the untreated char; these results further demonstrate the lower reactivity of the demineralized char. The fact that the demineralized materials did not ignite under conditions at which rapid combustion of the untreated materials was observed clearly demonstrates that the reactivity of Beulah lignite is greatly promoted by its inorganic constituents.

Figure 30. Rates of CO and CO₂ production from dry demineralized Beulah lignite at 650°C, 5% O₂ (BDLA).

Figure 31. Rates of CO and CO₂ production from dry Beulah lignite vitrain at 650°C, 5% O₂ (BVLE).

TABLE 16

OPTICAL MICROSCOPY RESULTS FROM THE COMBUSTION OF DRY 180-
TO 250- μ m BEULAH LIGNITE (PSOC-1507) AND CHAR PARTICLES

	Temp. (°C)	O ₂ (%)	Ignition Delay (s)		Combustion Duration (s)		Cloud Duration (s)		Shrinkage Duration (s)	
			Avg.	Std. D.	Avg.	Std. D.	Avg.	Std. D.	Avg.	Std. D.
Volatiles and Mineral Matter										
Vitrain	650	20	0.09	0.03	0.70	0.30	0.18	0.05	--	--
Char	650	20	<0.05	--	0.56	0.19	--	--	--	--
Demin. Char	650	20	No ignition		--	--	--	--	12.85	0.383
Vitrain	650	5	0.53	0.16	2.16	0.76	0.59	0.12	--	--
Char	650	5	0.35	0.05	2.69	0.40	--	--	--	--
Demin. Char	650	5	No ignition		--	--	--	--	24.45	6.91
Vitrain	825	20	0.05	0.03	0.51	0.17	--	--	--	--
Char	825	20	<0.05	--	0.51	0.17	--	--	--	--
Demin. Char	825	20	0.10	0.16	1.72	0.31	--	--	--	--
Vitrain	825	5	0.13	0.02	1.05	0.60	--	--	--	--
Char	825	5	0.07	0.01	1.87	0.97	--	--	--	--
Demin. Char	825	5	0.11	0.06	2.00	0.59	--	--	--	--
Vitrain	1000	20	<0.05	--	<0.37	--	--	--	--	--
Char	1000	20	<0.05	--	1.65	0.27	--	--	--	--
Demin. Char	1000	20	<0.05	--	3.59	1.84	--	--	--	--
Vitrain	1000	5	<0.05	--	0.37	0.05	--	--	--	--
Char	1000	5	<0.05	--	3.32	1.55	--	--	--	--

The effects of demineralization on the combustion of Smith Roland subbituminous coal were examined in the ignition apparatus (see Table 11). The demineralized material showed a decreased mass recovery, a decreased $\text{CO}_2:\text{CO}$ product ratio, a similar $\text{CO}_2:\text{CO}$ rate ratio, a slightly higher ρ maximum, a decreased total combustion time, and a slightly smaller ignition delay than that of the untreated material. A comparison of the overall combustion profile of the demineralized material (Figure 32) with the original material (Figure 25) shows that the demineralized material is dramatically reduced in reactivity, producing only the initial pyrolysis peak. The results are similar to those obtained for Beulah lignite. The relatively high ρ maximum observed for this material presumably results from the oxidation of the pyrolysis products; however, ignition of the bulk of this material was not indicated.

The effects of demineralization on the combustion of Lower-Wilcox lignite were examined in the ignition apparatus at 1000°C (see Table 13). Demineralization slightly increased the $\text{CO}_2:\text{CO}$ ratios, decreased the ignition delay and dramatically increased the ρ maximum of this material. The CO/CO_2 production profiles of the demineralized lignite are shown in Figure 33; comparison of this with the original material (Figure 28) clearly shows the enhanced reactivity of the demineralized material. Both the demineralized lignite and demineralized lignite char were examined by optical microscopy (see Table 17). These results also show that the demineralized materials have a higher reactivity, since at low temperatures these particles oxidized while the untreated materials did not react. Under conditions where ignition was observed, only small differences were produced by demineralization, except for the longer ignition delay and shorter combustion duration observed for the demineralized char than the untreated material. These results indicate that the inherent inorganic constituents decrease the reactivity of Lower-Wilcox lignite and/or that physical changes of the material produced during demineralization enhance its reactivity. Ehrburger et al. (36) have shown that the demineralization of a coal through a process similar to the one employed in the present studies significantly increased the porosity of a coal containing 13% ash. Dry Lower-Wilcox lignite contains ~21% ash; therefore, it is likely that demineralization of this lignite greatly enhances its surface area. The enhanced reactivity of this lignite produced by demineralization may be a result of increased surface area.

The effects of demineralization on the combustion of Pittsburgh #8 bituminous coal were examined in the ignition apparatus at 1000°C (see Table 14). The demineralized material had a similar ρ maximum, lower ignition delay and slightly higher $\text{CO}_2:\text{CO}$ ratios than the original material. The overall CO/CO_2 production profiles of the demineralized material are shown in Figure 34. Comparison with the original material (Figure 35) shows demineralization to have little effect on the combustion of this material. Optical microscopy results comparing the char and the demineralized char are shown in Table 18. In general, the demineralized material was more reactive than the untreated. Demineralization of Pittsburgh #8 bituminous coal produced smaller changes in this material's behavior than observed for the other three coals examined. Inorganic constituents are shown to play a minor role in the combustion of this bituminous coal.

Figure 32. Rates of CO and CO₂ production from dry demineralized Smith Roland subbituminous coal vitrain at 650°C, 5% O₂ (SDLA).

Figure 33. Rates of CO and CO₂ production from dry demineralized Lower-Wilcox lignite at 1000°C, 20% O₂ (LDHA).

TABLE 17

OPTICAL MICROSCOPY RESULTS OF DRY 180- to 250- μ m
LOWER-WILCOX LIGNITE (PSOC-1443) PARTICLES

	Temp. °C	O ₂ (%)	Ignition Delay (s)		Combustion Duration (s)		Cloud Duration (s)		Shrinkage Duration (s)	
			Avg.	Std. D	Avg.	Std. D.	Avg.	Std. D.	Avg.	Std. D.
Lithotype										
Attritus	650	20	No Reaction		--	--	--	--	--	--
Vitrain	650	20	No Reaction		--	--	--	--	--	--
Temperature and O ₂ Conc.										
Vitrain	650	20	No Reaction		--	--	--	--	--	--
Vitrain	825	20	0.38	0.08	38.53	5.72	--	--	--	--
Vitrain	1000	20	0.19	0.05	3.81	1.70	--	--	--	--
Vitrain	650	5	No Reaction		--	--	--	--	--	--
Vitrain	825	5	No Reaction		--	--	--	--	103.0	14.59
Vitrain	1000	5	0.13	0.01	4.26	1.50	--	--	--	--
Volatiles and Mineral Matter										
Vitrain	650	20	No Ignition		--	--	--	--	--	--
Char	650	20	No Ignition		--	--	--	--	--	--
Demin. Char	650	20	No Ignition		--	--	--	--	36.95	11.35
Demin. Char	650	20	No Ignition		--	--	--	--	123.6	23.37
Vitrain	650	5	No Ignition		--	--	--	--	--	--
Char	650	5	No Ignition		--	--	--	--	--	--
Demin. Char	650	5	No Ignition		--	--	--	--	96.06	27.14
Demin. Coal	650	5	No Ignition		--	--	--	--	--	--
Vitrain	825	20	0.38	38.53	38.53	5.72	--	--	--	--
Char	825	20	0.27	0.05	116.1	12.41	--	--	--	--
Demin. Char	825	20	0.61	0.08	27.32	1.70	--	--	--	--
Demin. Char	825	20	0.34	0.09	29.57	6.06	--	--	--	--
Vitrain	825	5	No Ignition		--	--	--	--	103.0	14.59
Char	825	5	No Ignition		--	--	--	--	--	--
Demin. Char	825	5	No Ignition		--	--	--	--	82.36	11.55
Demin. Coal	825	5	No Ignition		--	--	--	--	98.74	20.53
Vitrain	1000	20	0.19	0.05	3.81	1.70	--	--	--	--
Char	1000	20	0.21	0.05	27.23	4.03	--	--	--	--

Figure 34. Rates of CO and CO₂ production from dry demineralized Pittsburgh #8 bituminous coal at 1000°C, 20% O₂ (PDHA)

Figure 35. Rates of CO and CO₂ production from dry Pittsburgh #8 bituminous coal at 1000°C, 20% O₂ (PVHB).

TABLE 18

OPTICAL MICROSCOPY RESULTS OF DRY 180- TO 250- μ m PITTSBURGH #8 (PSOC-1451)
BITUMINOUS COAL PARTICLES

	Temp. (°C)	O ₂ (%)	Ignition Delay (s)		Combustion Duration (s)		Cloud Duration (s)		Shrinkage Duration (s)	
Temperature and O ₂ Conc.			Avg.	Std. D.	Avg.	Std. D.	Avg.	Std. D.	Avg.	Std. D.
Vitrain	650	20	No Ignition		--	--	5.37	0.40	16.40	3.35
Vitrain	825	20	No Ignition		--	--	1.29	0.11	10.56	0.98
Vitrain	1000	20	<0.05	--	0.88	0.22	--	--	--	--
Vitrain	650	0	No Ignition		--	--	12.46	2.28	59.95	9.52
Vitrain	825	5	No Ignition		--	--	2.76	0.70	22.19	2.30
Vitrain	1000	5	<0.05	--	9.62	1.17	--	--	--	--
Volatiles and Mineral Matter										
Vitrain	650	20	No Ignition		--	--	5.37	0.40	16.40	3.35
Char	650	20	No Ignition		--	--	--	--	--	--
Demin. Char	650	20	No Ignition		--	--	--	--	29.60	17.95
Vitrain	650	0	No Ignition		--	--	12.46	2.28	59.95	9.52
Char	650	5	No Ignition		--	--	--	--	--	--
Demin. Char	650	5	No Ignition		--	--	--	--	56.69	31.04
Vitrain	825	20	No Ignition		--	--	1.29	0.11	10.56	0.98
Char	825	20	0.08	0.03	0.75	0.20	--	--	2.98	1.08
Demin. Char	825	20	<0.05	--	6.61	1.18	--	--	--	--
Vitrain	825	5	No Ignition		--	--	2.76	0.70	22.19	2.30
Char	825	5	No Ignition		--	--	--	--	--	--
Demin. Char	825	5	0.03	0.01	10.63	2.61	--	--	--	--
Vitrain	1000	20	<0.05	--	0.88	0.22	--	--	--	--
Char	1000	20	<0.05	--	1.00	0.19	--	--	--	--
Demin. Char	1000	20	<0.05	--	2.70	0.48	--	--	--	--
Vitrain	1000	5	<0.05	--	9.62	1.17	--	--	--	--
Char	1000	5	<0.05	--	9.50	4.23	--	--	--	--
Demin. Char	1000	5	<0.05	--	8.81	1.79	--	--	--	--

The four demineralized coals behaved more uniformly than the original materials; however, significant differences were still apparent in their combustion behavior. The most significant differences between the two demineralized materials observed during combustion were the dramatically higher $\text{CO}_2:\text{CO}$ ratios observed for the Lower-Wilcox lignite than the Pittsburgh #8 bituminous coal (compare Tables 17 and 18). This result shows that a parameter other than inorganic composition dictates the oxidation products of these materials.

In order to further characterize the effects of inorganic constituents on the ignition and combustion of coals, and to help ascertain whether the observed effects of demineralization were a result of physical changes in the materials or actual removal of the inorganic constituents, the demineralized materials were reloaded with calcium. Calcium was selected over sodium or potassium since it has shown larger promotional effects than these other elements (37), and because it is easily ion-exchanged into the coals, producing a material containing calcium in a form similar to its original.

The cation concentrations of the original, demineralized and calcium-reloaded materials are shown in Table 7. The initial concentrations of calcium were highest in the Beulah lignite and the Smith Roland subbituminous coal. As a result, demineralization of these materials produced much larger changes in these concentrations than in the other two materials. The calcium-reloaded samples contained calcium concentrations proportional to their initial concentrations.

The ignition and combustion characteristics of the calcium-reloaded Beulah lignite was examined in the ignition apparatus (see Table 9). The $\text{CO}_2:\text{CO}$ ratios and mass recoveries of the reloaded material were similar to those of the original material. Comparison of the ρ maximum values suggests that the demineralized material is more reactive than the calcium-reloaded material, but this comparison is deceptive and is a result of the demineralized material containing the initial volatiles-release peak even though the bulk of the particles did not ignite. Comparison of the CO/CO_2 production profiles of the reloaded material (Figure 36) with those of the original (Figure 31) and the demineralized lignite (Figure 30) clearly demonstrates the intermediate reactivity of the calcium-reloaded lignite. The lower reactivity of the calcium-reloaded material than the original lignite is consistent with the lower calcium concentration in the reloaded material than in the original lignite.

Calcium, while having little effect on volatiles release, promotes the char combustion of Beulah lignite. In fact, its presence or absence dictates whether the char combustion stage occurs. Since the form of calcium has been shown to remain constant during the initial heating of coal (38), calcium must be promoting heterogeneous reactions. Because the ignition of the bulk of the lignite particle is dependent on the presence of calcium, it is apparent that heterogeneous reactions are more important to the ignition of this material than homogeneous ones at the employed conditions.

Figure 36. Rates of CO and CO₂ production from dry, calcium-reloaded Beulah lignite at 650°C, 5% O₂ (BRLA).

The effects of reloading demineralized Smith Roland subbituminous coal with calcium are shown in Table 11. Due to the complexity of the reaction, comparison of the CO/CO₂ production profile (Figure 37) with those of the original coal (Figure 25) and the demineralized coal (Figure 32) is more beneficial than a comparison of the tabulated data. This comparison shows that the char combustion stage, while nonexistent in the demineralized coal, did occur in the calcium-reloaded coal but at a lower rate than that observed for the original coal. The promotional effects of calcium were not as great as those observed for Beulah lignite. The lower calcium concentration in the Smith Roland calcium-reloaded sample is consistent with this result. Again, it appears that the ignition of the bulk of this coal is more dependent on heterogeneous than homogeneous reactions.

The initial stage of CO/CO₂ production from Smith Roland subbituminous coal was also altered by inorganic constituents. The initial period of reactivity for the calcium-reloaded material was significantly lower than that observed for the demineralized material, as seen by comparison of Figures 32 and 37. Calcium and other inorganic constituents have been shown to decrease the rate of volatiles production from coals (39,40). Inhibition of the initial stage of combustion usually associated with volatiles release and enhanced char reactivity is produced by the inorganic constituents of Smith Roland subbituminous coal, with calcium indicated as a major contributor to these effects.

Figure 37. Rates of CO and CO₂ production from dry calcium-reloaded Smith Roland subbituminous coal at 650°C, 5% O₂ (SRLA).

The effects of reloading demineralized Lower-Wilcox lignite with calcium are shown in Table 13. The CO/CO₂ production profiles are shown in Figure 38. The major differences between the calcium-reloaded material and the demineralized material are the increased CO₂:CO ratios produced by calcium-reloading. A small increase in ρ_{max} was also observed, as was an increase in the ignition delay, but these differences were not large in comparison to the particle-to-particle variations observed. Calcium apparently promotes the production of CO₂ during the oxidation of this material. The relatively small effects of calcium-reloading in comparison to those observed for Beulah lignite are consistent with the smaller concentration of calcium reloaded onto the Lower-Wilcox lignite.

In order to discern whether the dramatically higher reactivity of demineralized Lower-Wilcox lignite (as compared to the original material) is due to physical changes in the coal resulting from the demineralization process or to inhibitory effects of mineral matter, it would be necessary to check the effects of all minerals present in the initial sample. However, the fact that one of the inorganic constituents, i.e., calcium, did not inhibit this material's combustion rate is consistent with promotion being induced by physical changes in the material that occur during demineralization.

Figure 38. Rates of CO and CO₂ production from dry, calcium reloaded-Lower-Wilcox demineralized lignite at 1000°C, 20% O₂ (LRHA).

The effects of reloading demineralized Pittsburgh #8 bituminous coal with calcium are shown in Table 14. The CO/CO₂ production profiles are shown in Figure 39. The only significant difference between the demineralized material and the calcium-reloaded material was the lower ρ_{max} observed for the calcium-reloaded material. This result is inconsistent with the results obtained from the other three coals. Since demineralization produced little effect on this material's behavior, and the amount of calcium reloaded into the demineralized material was small, the decreased rate produced by calcium-reloading is most likely produced by other changes in this material due to the reloading procedure, besides the addition of calcium.

4.4.4 Volatile Matter

In order to characterize the effects of volatile matter on the combustion of the four selected coals, chars of these materials were prepared and examined in the ignition apparatus and by optical microscopy. A comparison of the results obtained at 500° and 650°C for Beulah lignite and its char in the ignition apparatus is shown in Table 9. Beulah lignite char behaved similarly to the vitrain at 500°C, except that less resolution between the two oxidation steps was observed for the char. The average CO/CO₂ combustion profiles of the lignite and its char at 500°C are shown in Figures 40 and 41, respectively. The behavior of the char particles varied greatly at this condition; some ignited readily and burned in a single combustion stage, while others produced CO/CO₂ production profiles similar to those observed for the vitrain. In general, however, the major oxidation peak of the char occurred sooner than that of the lignite, indicating that the presence of volatiles increases the ignition delay of the bulk of the lignite particles.

Figure 39. Rates of CO and CO₂ production from dry, calcium-reloaded Pittsburgh #8 demineralized coal at 1000°C, 20% O₂ (PRHA).

Figure 40. Rates of CO and CO₂ production from dry Beulah lignite vitrain at 500°C, 20% O₂ (BV5A).

Figure 41. Rates of CO and CO₂ production from Beulah lignite char at 500°C, 20% O₂ (BC5A).

The results obtained at 650°C in the ignition apparatus (see Table 9) show that the lignite had a higher ρ maximum and burned in two stages while the char only exhibited single-stage oxidation. The onset of CO₂ release, i.e., the ignition delay, was similar for the two materials. The CO/CO₂ production profiles of the lignite and the char at this condition are shown in Figures 31 and 42, respectively. The previously noted observations are pictured in these figures.

Both Beulah lignite and its char were also observed by optical microscopy and the results are shown in Table 16. Under most conditions the combustion duration of the char was longer than the lignite, showing a slower overall reaction rate. For all conditions studied the char emitted light, i.e., ignited more readily than the lignite. This fact indicates that the initial CO₂ release peak observed for the lignite is due to pyrolysis and not ignition. This same conclusion was reached from the oxygen concentration studies on Beulah lignite. Apparently, the presence of volatile matter inhibits the ignition of Beulah lignite; however, it promotes the reactivity of the bulk of the particle, once ignited.

The delay of the onset of heterogeneous combustion by the presence of volatile matter has been reported by Huang et al. (29). These workers observed homogeneous ignition to precede the surface oxidation of a subbituminous coal and rapid heterogeneous ignition of its char. The surface reaction of the coal occurred much later than the surface reaction of the char; the heterogeneous combustion of the coal was delayed by the presence of volatile matter. This result is due to the endothermic nature of the devolatilization process and/or a depletion of oxygen at the particle surface.

Figure 42. Rates of CO and CO₂ production from Beulah lignite char at 650°C, 5% O₂ (BCLB).

A comparison between Smith Roland subbituminous coal and its char is made in Table 11. The most significant difference between these materials is the single-staged oxidation of the char as compared to the two-staged oxidation of the coal. A comparison of the CO/CO₂ production profiles of the coal and its char also shows this result (see Figures 25 and 43). This is an expected result of the removal of volatile matter by the charring process. The onset of CO₂ production was not inhibited by the removal of volatiles, indicating that for this material, homogeneous reactions are not of major importance to the ignition process. The ρ maximum for the char was slightly higher than that of the coal, this may be a result of the large deviation in the char measurements.

A comparison between Lower-Wilcox lignite and its char is made in Table 13. A higher reactivity of the char, as indicated by its larger ρ maximum and shorter combustion duration, was observed. This result is also seen by a comparison of the CO/CO₂ production profiles (Figures 28 and 44). In contrast, a longer combustion duration was observed for the original lignite than the char in the optical microscopy studies (see Table 17). This latter result is attributed to difficulties in clearly distinguishing the combustion duration by optical microscopy at this condition. The char of Lower-Wilcox lignite appears to be slightly more reactive than the original material.

Figure 43. Rates of CO and CO₂ production from dry Smith Roland subbituminous coal char at 650°C, 5% O₂ (SCLA).

Figure 44. Rates of CO and CO₂ production from dry Lower-Wilcox lignite char at 1000°C, 20% O₂ (LCHA).

A comparison of Pittsburgh #8 bituminous coal and its char is made in Table 14. The char showed a lower ρ maximum than the coal and higher $\text{CO}_2:\text{CO}$ ratios. The optical microscopy studies showed the char to ignite at lower temperatures than the coal; however, under conditions where both materials ignited, no significant differences in the ignition delays or combustion durations were observed. It was noted during the particle sizing of the bituminous coal char that it was comprised mostly of highly porous cenospheres; therefore, the surface area of this material was much greater than that of the original coal. The tendency of this coal to form a low density material upon charring is also shown by the density measurements of Table 7. As a result, it is unclear whether the observed differences between this coal and its char are a result of variations in volatile matter concentration or changes in surface area. However, it is indicated that the char requires less severe ignition conditions than the coal, regardless of the char characteristic to which this property is ascribed.

Conti and Hertzberg (19) have reported the auto ignition temperatures (AITs) of various coal clouds. The AITs decreased in the order of Pittsburgh #8 bituminous coal > Wyoming subbituminous coal > Beulah lignite. The amount of volatile matter in these materials decreased in the same order; however, the differences in the volatile matter concentrations were small. The chars of these materials were not examined. This study emphasized the promotional effect of volatile matter on the ignition.

Beulah lignite was found to ignite at lower temperatures than Pittsburgh #8 bituminous coal in the present studies as well. Volatile matter, however, was not found to promote the ignition of any of the presently studied coals. In fact, the cases for which the most accurate data was obtained, i.e., Beulah lignite and Smith Roland subbituminous coal, volatile matter inhibited the ignition of the bulk of the coal particles. It is likely that the different parameters measured in the two experiments, i.e., cloud ignition as opposed to single particle ignition, are sensitive to different coal properties. However, it has also been indicated that the relative effects of heterogeneous reactions during the initial stages of combustion are more significant for low- rather than high-rank materials (8,16). Therefore, it appears that volatile matter is more likely to promote the ignition of higher- rather than lower-rank materials. As a result, the rapid ignition observed for Beulah lignite is thought to be a result of the rapid onset of heterogeneous ignition.

4.4.5 Moisture

The effects of moisture on ignition and combustion were only examined for Beulah lignite. This material was selected because it naturally contains the highest moisture content. The results obtained in the ignition apparatus are shown in Table 10. Only at the least severe conditions, i.e., 650°C at 5% O_2 , were significant differences observed between the dry and moist lignite. At these conditions no difference in the onset of CO_2 release was noted; however, ρ maximum was lower and the combustion duration longer for the moist material. A comparison of the CO/CO_2 production profiles of the moist and dry lignite, Figures 45 and 31, respectively, also shows the difference in combustion rate. The optical microscopy results (see Table 15) show the moist lignite to have a shorter ignition delay and longer combustion duration than

Figure 45. Rates of CO and CO₂ production from moist Beulah lignite vitrain at 650°C, 5% O₂ (BVLF).

the dry material. The latter observation is consistent with the ignition apparatus results. The former result is not understood and is perhaps the result of the relatively high particle-to-particle variation observed in both sets of data.

Moisture does not affect the ignition and combustion of Beulah lignite except under mild conditions. The maximum combustion rate is affected more dramatically than the ignition delay, indicating either that ignition occurs prior to the vaporization of a significant amount of the initially contained moisture, or that if the release of moisture occurs rapidly, this process deactivates the remaining char.

Conti and Hertzberg (19) have examined the effects of moisture on the auto ignition temperatures (AITs) of Beulah lignite and Wyoming subbituminous coal. The AITs of these materials decreased by 15°-25°C upon drying. Either the differences noted by Conti and Hertzberg are outside the sensitivity of the present experiments, or the AITs and single particle ignition delays are sensitive to different properties of the coal. It may be significant that the AITs show the same trends exhibited by the presently measured ρ maximum as opposed to the ignition delays.

4.4.6 Gas Temperature

The effects of gas temperature on the ignition and combustion of Beulah lignite, Lower-Wilcox lignite and Pittsburgh #8 bituminous coal were characterized. The results obtained from the ignition apparatus are shown in Tables 10, 12, and 14, respectively. The optical microscopy results are shown in Tables 15, 17, and 18. As expected, the ignition delays decreased and the combustion rates increased with increased gas temperature. The temperature at which ignition occurred was a function of material type. The ignition temperatures increased in the order Beulah lignite $\leq$ Smith Roland subbituminous coal $<$ Lower-Wilcox lignite $<$ Pittsburgh #8 bituminous coal. At increased gas temperatures the combustion behavior of Beulah lignite and Pittsburgh #8 bituminous coal became similar, as can be seen from a comparison of Figures 46 and 35.

Figure 46. Rates of CO and CO₂ production from dry Beulah lignite vitrain at 1000°C, 20% O₂ (BVHA).

For the combustion of Beulah lignite, the $\text{CO}_2:\text{CO}$ ratios decreased upon increasing the temperature from 500° to 650°C and increased upon increasing the temperature from 650° to 1000°C (see Table 10). This is a result of the interplay produced by CO_2 being the favored surface product at low particle temperatures and CO oxidation occurring in the boundary layer at high particle temperatures. At low gas temperatures both the particle and boundary temperatures are low; therefore, CO_2 is the predominant surface product and the rate of CO oxidation in the boundary layer is negligible. At the intermediate gas temperature of 650°C , the particle temperature is slightly higher, shifting the surface products towards CO, decreasing the $\text{CO}_2:\text{CO}$ ratio, and keeping the boundary layer oxidation rate low. At 1000°C , CO becomes the favored surface product; however, the boundary layer is now hot enough to produce significant CO oxidation, resulting in a net increase in CO_2 production.

Lower-Wilcox lignite and Pittsburgh #8 bituminous coal failed to ignite at the lower gas temperatures and therefore, a similar discussion of these materials is not presented.

4.4.7 Lithotype

The effects of lithotype on the ignition and combustion of Beulah and Lower-Wilcox lignite and Smith Roland subbituminous coal were examined. The ignition apparatus results are shown in Tables 10, 12, and 11, respectively. The optical microscopy results from Beulah and Lower-Wilcox lignite are shown in Tables 15 and 17. The fusain lithotype of Beulah lignite ignited the most readily. This result is consistent with the results obtained from Beulah lignite char, since the fusain lithotype is similar to char. The attritus lithotype of Beulah lignite was slightly less reactive than the other two lithotypes, as indicated by the longer combustion duration observed by optical microscopy. The attritus lithotype of the Lower-Wilcox lignite and Smith Roland subbituminous coal also showed lower reactivities than the vitrain, as demonstrated by the lower ρ maximum values of the attritus measured in the ignition apparatus (Tables 12 and 11). The differences observed between lithotypes of the same coal were small compared to the differences observed between coals.

4.4.8 Material Rank

Large differences were observed in the ignition and combustion behaviors of the four coals studied. These differences were not highly correlated with material rank. The differences between the two lignites studied were as large or larger than any difference observed between either of the lignites and the bituminous coal. Most of these differences have been presented and discussed in earlier sections. The order of ignition temperatures were Beulah lignite $\leq$ Smith Roland subbituminous coal $<$ Lower-Wilcox lignite $<$ Pittsburgh #8 bituminous coal. The order of ρ maximum values was Beulah lignite $\geq$ Smith Roland subbituminous coal $>$ Pittsburgh #8 bituminous coal $>$ Lower-Wilcox lignite.

The $\text{CO}_2:\text{CO}$ ratios observed at 1000°C decreased in the order Pittsburgh #8 bituminous coal > Beulah lignite > Lower-Wilcox lignite. Since CO production is favored at higher particle temperatures produced by higher rates (higher ρ maximum values), it would be expected that Lower-Wilcox would yield the lowest percentage of CO. Since this is not the case, it is apparent that the surface products are not being measured when a gas temperature of 1000°C is employed. This conclusion was also reached from the comparison of the effects of gas temperature on the $\text{CO}_2:\text{CO}$ ratios produced from Beulah lignite. Since significant conversion of CO to CO_2 in the boundary layer of the particles occurs at this gas temperature, higher combustion rates (as observed for Pittsburgh #8 and Beulah lignite) and more CO production at the surface will also enhance boundary layer oxidation of the CO produced. As a result, it is postulated that the higher percentage of CO leaving the boundary layer during the combustion of Lower-Wilcox is due to slower oxidation of CO in the boundary layer.

The large differences observed between the various materials were removed by demineralization. This result indicates that the inorganic content is one of the most significant parameters in determining a material's reactivity. Calcium content was indicated to be responsible for the high reactivities of Beulah lignite and Smith Roland subbituminous coal. For the Lower-Wilcox lignite, the calcium concentration was low and had little effect. It is thought that this material's increase in reactivity upon demineralization is a result of physical changes of this material during the demineralization process; however, little evidence for this speculation is available. If the parameters affecting the combustion of Lower-Wilcox lignite are to be understood, further experiments are necessary. The inorganic content was more highly correlated to the various ignition and combustion trends than material rank.

4.4.9 Modeling

Attempts to correlate the ignition delays obtained with Arrhenius pre-exponential factors and activation energies by simultaneously solving the unsteady-state energy and mass balances were made (40). Difficulties in obtaining unique solutions using this technique have called into question the usefulness of this procedure.

A chemical rate constant for Beulah lignite was estimated to have an activation energy of 11 kcal/mole and a preexponential factor of $0.26 (\text{g C}/\text{cm}^2 \text{ s atm})$. The apparent order of the reaction with respect to oxygen concentration was 0.25. Details of this calculation are available (34).

4.5 Publications

1. Sweeny, P.G., Grow, D.T., and McCollor, D.P. "Studies on Ignition of Coal: The Effects of Rank, Temperature, Volatile Content and Lithotype," Prepr. Am. Chem. Soc., Div. Fuel Chem. 1988, 33(4), 853.
2. Sweeny, P.G., and Grow, D.T. "Ignition and Combustion Characteristics of a Lignite," Energy and Fuels, submitted.

4.6 Future Work

Future experiments will include measuring NO_x and/or SO_2 release from single particles, or establishing the feasibility of measuring total light emission and subsequently using optical pyrometry to monitor the combustion of particles in the ignition apparatus. This work will be performed by an AWU fellow.

5.0 REFERENCES

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U.S. DEPARTMENT OF ENERGY
FEDERAL ASSISTANCE MANAGEMENT SUMMARY REPORT

Page ____ of ____

1. Program/Project Identification No DE-FC21-86MC10637	2. Program/Project Title Coal/Char Reactivity	3. Reporting Period 4/01/88 through 6/30/89
4. Name and Address University of North Dakota Energy and Mineral Research Center Box 8213, University Station, Grand Forks, ND 58202		5. Program/Project Start Date 4/01/86
		6. Completion Date 3/31/92

11. Major Milestone Status	Units Planned	
	Units Complete	
a. Assessment of Mineral and Structural Effects	P	1 ▼ 2 ▼
	C	
	P	
	C	
b. Bulk Diffusion	P	1 ▼
	C	
	P	
	C	
c. Ignition Phenomenon of Coal Particles	P	1 ▼
	C	
	P	
	C	
	P	
	C	
	P	
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	P	
	C	
	P	
	C	
	P	
	C	
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	C	
	P	
	C	
	P	
	C	

12. Remarks

13. Signature of Recipient and Date	14. Signature of DOE Reviewing Representative and Date
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		6. Completion Date 3-31-92

Milestone ID No.	Description	Planned Completion Date	Actual Completion Date	Comments
a.1	Systematically examine the influence of levels of Ca, K, and Na on burning rate with emphasis on Ca.	8/31/88	8/31/88	
a.2	Determine particle burning rates for coal chars. Relate reactivity data to other PETC projects.	12/31/88	12/31/88	
b.1	Screening experiments to explore the limits of bulk diffusion.	2/28/89	2/28/89	
c.1	Examine the mechanisms of coal/char ignition.	2/28/89	2/28/89	

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b.1	Screening experiments to explore the limits of bulk diffusion.	2/28/89	2/28/89	
c.1	Examine the mechanisms of coal/char ignition.	2/28/89	2/28/89	
d.1	Char combustion -- Examine the effects of other divalent cations on the burning rates of chars.	6/30/89	6/30/89	
e.1	Coal/char ignition -- Connect an NO _x analyzer to the ignition apparatus. This increases the sensitivity to determine ignition delays as well as information on nitrogen release.	6/30/89	6/30/89	Inconsistent results-- cost/benefit ratio of instrument repair deemed too high for continued work.

3.4 Liquefaction Reactivity of Low-Rank Coals

LIQUEFACTION REACTIVITY OF LOW RANK COAL

Final Technical Progress Report for the period April 1, 1988 -
June 30, 1989, Including the Quarterly Technical Progress Report
for the Period April through June 1989

by

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October, 1989

Contracting Officer's Technical Representative: Nand K. Narain

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1.0 EXECUTIVE SUMMARY

Further development of new catalysts for the hydrotreating of low-severity liquefaction products was continued in this quarter. Work on the hydrodesulfurization capabilities of the new solid acid catalysts was essentially and successfully completed. Conversions of model organosulfur compounds were very high with clay-, pillared clay-, and silica gel-based acid catalysts. The culmination of the effort was the total removal of organic sulfur from the Wyodak low-severity product in a single-stage hydrogenation with the SZC catalyst. Gas chromatographic analysis of the distillate with very sulfur-sensitive helium afterglow discharge atomic emission detection showed that no organosulfur compounds were present. Elemental analysis of the vacuum bottoms showed that no sulfur was present.

Catalytic studies were completed with diphenyl ether and bibenzyl as models for hydrodeoxygenation and hydrocracking activity in the clay-based strong acid catalysts. Sodium montmorillonite and acid washed montmorillonite were tested as well as chromia-pillared clay with both low and high chromium content. The major problem with these catalysts is that they induce condensation to give oligomeric forms; however, no coking was observed.

Molybdenum- and bimetal-loaded chromia-pillared clays were prepared, and silica-pillared clay was prepared as a support for metal and acid catalysts. Testing of these catalysts is in progress.

2.0 GOALS AND OBJECTIVES

The efficient production of environmentally acceptable distillate fuels requires catalysts for hydrogenation and cleavage of the coal macromolecules and removal of oxygen, nitrogen, and sulfur heteroatoms. Currently, two-stage processes for coal conversion are under development. The first stage converts coal to a soluble form with minimal cracking and hydrogenation. This processing presently involves no catalyst other than the coal mineral matter present and addition of a promoter, hydrogen sulfide, which may have a catalytic effect. The second stage involves hydrogenation upgrading of the first-stage product to distillates with fixed- or ebullated-bed catalysts.

The catalysts currently used in the second stage of coal liquefaction for hydrotreating the first stage product are the same as those used in conventional petroleum refining; however, this application has not been very successful. Improvements in upgrading efficiency could be obtained if catalysts with longer life and better activity and selectivity were available. Rapid deactivation of the conventional Co-Mo and Ni-Mo catalysts on an alumina support have been attributed to coke formation (1), metals deposition (2), and inhibition of active center by chemisorbed compounds (3).

The objectives of this research project are to develop and test novel heterogeneous catalysts for hydrotreatment upgrading of first-stage coal liquefaction products. The new hydrogenation catalysts are based on pillared clays and hydrotalcites, which have very large micropore dimensions that can accommodate the coal macromolecules, but yet do not possess strong acidities that lead to coking at high temperatures.

A second objective is to develop a solid acid catalyst for depolymerization of coal macromolecules. The acid catalysis process for coal liquefaction is believed to operate by ionic mechanisms. Some molten acids have successfully depolymerized coal, but the poor efficiencies of catalyst recovery and the corrosive nature of the catalyst make the process uneconomical. Stable solid acid catalysts will be developed which will avoid these difficulties. These catalysts are also based on pillared clays as well as a silica bases.

3.0 ACCOMPLISHMENTS

3.1 Introduction

The development of new heterogeneous catalysts for hydrotreating was initiated. The synthesis of several new catalysts was accomplished. The new catalysts are basically of two types: sulfided metal hydrogenation catalysts, and solid acid ionic hydrogenation catalysts. These are discussed separately below.

3.1.1 Metal hydrogenation catalysts on pillared smectite support

Acid smectite clays are used as catalysts in petroleum-cracking and various other reactions. Unfortunately they dehydrate and collapse at temperatures above 200°C. Acid zeolites are more stable at high temperatures; however their pores are too narrow to be useful for coal macromolecules, and they are not effective in upgrading as compared with conventional Ni-Mo or Co-Mo catalysts. In the pillared clays, intercalation of hydroxylated or complexed metal cations maintains the clay layer structure after loss of water and generates large pore sizes. These structures are stable up to 450 and 500°C. The alumina cluster pillared clays are effective catalysts for petroleum catalysis. Chromia-pillared clays with even larger pore spacings have considerable potential for upgrading. A selection of pillared clays with and without incorporated hydrogenation catalysts are being prepared and tested with first-stage coal liquefaction products as well as model compounds and polymers. The catalysis of C-O, C-N, and C-S bond breakage as well as alkyl-aryl bond breakage and arene hydrogenation have been investigated.

3.1.2 Solid acid-catalyzed hydrocracking

Acid-catalyzed coal conversion has been thoroughly investigated; however, the efficiencies of catalyst recovery are not high enough or the catalyst is consumed, resulting in high cost. Another disadvantage is the corrosive nature of the catalyst. A stable solid acid catalyst may have more potential in recovery schemes. Acid zeolites can be used at high temperatures but have pore sizes too small for the large coal macromolecules. Thermally stable pillared clay catalysts with large interlayer pores are more attractive for acid-catalyzed depolymerization of the coal macromolecules. Chromium and aluminum cluster pillared smectites are being tested both in the Bronstead acid and Lewis acid form, the latter being formed from reactions with metal chlorides. The reactions with these pillared catalysts will be compared with reactions with other solid acids such as the Drago aluminum chloride-silica complex and similar zinc chloride complexes.

3.2 EXPERIMENTAL

Catalyst Preparation:

Preparation of silica-gel-zinc chloride and chromia-pillared clay catalysts has been reported in our previous quarterly report.

Preparation of acid-washed montmorillonite:

Sodium-exchanged montmorillonite (5.0 g) was suspended in 200 ml of 1N HCl and stirred for 2 hours. Acid-washed clay was separated by centrifugation, and washed with deionized water until free of acid, and air dried. Final drying was accomplished by heating in vacuum at 110°C overnight.

Preparation of silica-pillared clay.

Smectite clay was purified as described in an earlier quarterly report. A solution of 4.8 g of 2-(2-silyethyl) pyridine in 35 ml of methanol was placed in a round-bottomed flask, and 2.1 ml of water was slowly added. The mixture was stirred for one hour. At this stage, 7.5 g of sodium montmorillonite suspended in 90 ml of deionized water was added. After the addition of the clay, the suspension was stirred for 2 hours at room temperature. The pH was adjusted from 0 to 6 with concentrated ammonium hydroxide. At the end of the pillaring reaction, the pillared clay was separated by centrifugation. The residue was repeatedly washed with deionized water, and air dried. Air-dried pillared clay was calcined at 650°C for 2 hours in synthetic air and stored in a vacuum dessicator.

Preparation of molybdenum catalyst supported on chromia-pillared clay:

a. Preparation of molybdenum (II) allyl dimer:

Molybdenum (II) allyl dimer was prepared by modifying the method of Cotton and Pipal (1,2). All operations were performed under nitrogen in a vacuum atmosphere glove bag. Allylmagnesium bromide (1N, 60 ml, 0.06 mol) was placed in a 250-ml two-necked round-bottomed flask fitted with a dropping funnel, a reflux condenser, and a stirbar. Molybdenum pentachloride (3.0 g, 0.01 mol) dissolved in 100 ml of benzene was slowly added to the ether solution to give a green solution and a gray precipitate. The mixture was stirred overnight, filtered, and evaporated to give a dark green residue. The residue was dissolved in a minimum amount of hexane, filtered, and the solution evaporated to give the product.

b. Preparation of molybdenum supported on chromia-pillared clay:

All operations were performed under dry nitrogen in a glove bag. Chromia-pillared clay (1.00 g) and 10 ml of hexane were placed in a round-bottomed flask fitted with a dropping funnel and stirbar. Molybdenum allyl dimer (0.1 g) dissolved in 10 ml of hexane was slowly added to the stirred slurry of chromia-pillared clay in hexane. The reaction mixture was stirred overnight at

room temperature. The resulting green solid was separated by filtration and air dried. The product was then slowly heated to 200°C in a mixture of 10% H₂S/H₂ over a one-hour period, and left at 200°C for 12 hours.

Preparation of bimetallic metal supported clay catalysts:

Bimetallic metal-supported silica-pillared and chromia-pillared clay catalysts were prepared by incorporating nickel and molybdenum into high chromium chromia-pillared clay and silica-pillared clay.

In a typical reaction ammonium molybdate tetrahydrate (0.21 g) and nickel nitrate hexahydrate (0.13 g) were dissolved in 20 ml of water. The desired pillared clay (1.0 g) was added to the metal salt solution and stirred for 24 hours. The water was then evaporated from the mixture, and the residue slowly heated to 400°C under flowing air over a 2-hour period. The heating was continued for 12 hours, then the residue was cooled to room temperature. The process was repeated for another 12 hours with a mixture of 10% H₂S/H₂.

Preparation of Zinc (II) chloride-supported clay catalysts:

Zinc (II) chloride-supported silica-pillared clay and acid-washed montmorillonite clay catalysts were prepared by heating the desired clay with zinc (II) chloride.

Anhydrous zinc (II) chloride (3.00 g) and acid-washed montmorillonite suspended in 50 ml of dry carbon tetrachloride were placed in a 100-ml round-bottomed flask fitted with nitrogen inlet and nitrogen outlet tubes, and stir bar. The mixture was refluxed in a steady stream of nitrogen until the evolution of hydrogen chloride gas ceased. At the end of the reaction (72 hours), the reaction mixture was cooled to room temperature. The solid was separated by filtration, washed with carbon tetrachloride, and air dried. The final drying was accomplished by heating overnight in a vacuum oven at 110°C.

For the reaction of silica-pillared clay, 0.25 g of anhydrous zinc (II) chloride was used for 1 g of the clay used.

Detailed characterization of the chromia- and alumina-pillared clays, and supported clay catalysts by IR, elemental analysis, and XRD is in progress and will be reported in our next quarterly.

Reductive cleavage of hydrocarbon and ether:

Cleavage Reactions: The catalyst activity of chromia-pillared clay, acid-washed clay, silica-pillared clay and supported clay catalysts were tested by reacting with model organic compounds. Model compounds tested were bibenzyl and diphenyl ether. These reactions were carried out under different conditions of temperature, hydrogen pressure, solvent, and reaction time (Table 1).

TABLE 1

Reductive Cleavage reactions of Model Organic Compounds							
Reactants (g)				React. Cond.		Products	% Conv.
Substr	Cataly.	Solv.	Hydrogen (psi)	Temp. °C	Time hr		
BBE 1.00	AM 1.00	None	1000	350	3	Benzene	75.0
BBE 0.51	H-CPC 0.25	None	1000	350	3	Benzene Ethylbenzene*	63.5
BBE 0.52	SPC 0.25	None	1000	350	3	Benzene Ethylbenzene*	38.3
DPE 1.01	AM 0.50	None	1000	350	3	Benzene* Phenol	29.0
DPE 0.52	HCPC 0.25	None	1000	350	3	Benzene* Phenol	35.3
DPE 1.00	SPC 0.50	None	1000	350	3	Benzene* Phenol	9.5
DPE 0.52	SPCZC 0.25	None	1000	350	3	Benzene Phenol	19.5

BBE = Bibenzyl

DPE = Diphenyl ether

AM = Acid-exchanged sodium montmorillonite

SPC = Silica-pillared clay

SPCZC = Zinc(II) chloride-supported silica-pillared clay

HSPC = High chromium chromia-pillared clay

* = Minor product

In a typical run, 1.0 g of the test compound, and 1.0 g of the desired catalyst and 2.0 g of the desired solvent (if needed) were placed in a microreactor (tubing bomb). The microreactor was evacuated and pressurized with 1000 psi of hydrogen, and placed in a rocking autoclave heated to 350°C for 3 hours. At the end of the reaction period, the microreactor was cooled to room temperature, degassed, and opened. The desired amount of the internal standard was added to the product slurry, and the product slurry was transferred into a centrifugation tube by washing with methylene chloride, and solid catalyst removed by centrifugation. The liquid sample was analyzed by GC FID and GC/MS/HeAD, and GC/FTIR/MS. Carbon and sulfur atomic absorption spectroscopy (GC/MS/HeAD) were used for the qualitative analyses of the reaction

products. Quantitative carbon and sulfur atomic absorption spectroscopy (GC/HeAD) is in progress and will be reported in our upcoming quarterly Technical Progress Reports.

3.3 RESULTS AND DISCUSSION

3.3.1 Synthesis of new catalysts

The synthesis of molybdenum catalyst supported on the chromia-pillared clay was accomplished by reaction of diallylmolybdenum (II) dimer with chromia-pillared clay in hexane. The catalyst was activated by heating over hydrogen sulfide and hydrogen at 200°C.

A bimetallic catalyst was prepared by stirring aqueous ammonium molybdate and nickel nitrate with the chromia-pillared clay. Sulfidation was carried out by the same procedure. Both molybdenum-loaded pillared clays are being characterized and tested with model compounds and low-severity liquefaction products. Results will be reported in future quarterly reports.

Silica-pillared clay was prepared by hydrolysis of 2-[2-(trichlorosilyl)-ethyl] pyridine in methanol followed by exchange of the siloxane cluster into sodium montmorillonite. The zinc chloride complex of the silica-pillared clay was then synthesized. A new batch of chromia-pillared clay was prepared with a higher content of chromium than the original batch. Tests with these and other clay catalysts are reported below.

3.3.2 Hydrocracking and hydrodeoxygenation activity of solid acid catalysts

The reaction of bibenzyl (BBE) with high chromium chromia-pillared clay catalyst in the presence of 1000 psi of molecular hydrogen at 350°C for 3 hours gave 63.5% conversion, which in turn is lower than that obtained with low chromium chromia-pillared clay (99%). Furthermore, a significant amount of the product (ca. 34%) was found to be polybenzyls, such as tri-, tetra-, pentabenzyls, etc. Most of the other product was benzene with ethyl benzene as the minor product. When the same reaction was carried out using silica-pillared clay, conversion of bibenzyl dropped significantly (38%), and benzene was the major and ethylbenzene was the minor reaction product. Also, a significant fraction (20%) of the reaction product was found to be polybenzyls as described before.

In order to demonstrate that Bronsted acidity was responsible for the reductive cleavages of arylmethylen bonds, reaction of bibenzyl with acid-washed montmorillonite at 350°C for 3 hours in the presence of 1000 psi of hydrogen was also investigated. This reaction gave a conversion of 75% with benzene as the major product. The minor components were ethylbenzene, toluene, o-xylene, etc. Almost 40% of the substrate was converted into polymeric material, mainly polybenzyls.

The reaction of diphenyl ether with acid-exchanged sodium montmorillonite, under the conditions described above for bibenzyl, gave 29% conversion (Table 1). Major products were phenol and benzene with the molar ratio of 57:1. Reaction with high chromium chromia-pillared clay gave a

conversion of 35.3%. The major products of this reaction were the same as those described above, and the phenol-to-benzene molar ratio was 5:1. Earlier results with the low chromium pillared clay gave 30 and 38% conversions. The highest conversion for the hydrodeoxygenation of diphenyl ether was with silica gel-zinc chloride (60%).

When silica-pillared clay was used as the catalyst, the conversion dropped significantly (9.5%). Phenol and benzene were the major reaction products, with a phenol-to-benzene molar ratio of 3:1. Reaction of diphenyl ether was also studied using zinc (II) chloride supported on silica-pillared clay. This reaction gave somewhat higher conversion (19.5%) compared to silica-pillared clay alone. The phenol-to-benzene ratio was ca. 1.4:1.

3.3.3 Hydrodesulfurization Activity of Solid Acid Catalyst

Reactions of diphenyl sulfide were carried out with silica gel zinc chloride, chromia-pillared clay, silica gel, sodium-exchanged montmorillonite, acid-exchanged montmorillonite, and spent silica gel-zinc chloride catalysts in hydrogen with and without solvent at 300° or 400°C for 3 hours. Reactions were also carried out in the absence of any catalyst at these two temperatures. Reaction products were mixed with internal standard (octadecane) and analyzed by GC/FID, GC/FTIR/MS and GC/MS/HeAD. Percent conversion, which is a measure of the carbon sulfur bond cleavage was calculated on the basis of starting material (organosulfur substrate) that disappeared during the reaction. Percent conversion was used to determine the effect of catalyst, solvent, and reaction temperature on the cleavages of carbon-sulfur bonds in organosulfur compounds. The objective of these studies is to develop catalysts and search for reaction conditions (temperature, contact time, hydrogen pressure, solvent, etc.) most suitable for the removal of organic sulfur from coal, coal liquids, and crude petroleum.

3.3.3.1 Pillared Clay Catalysts

Hydrodesulfurization of diphenyl sulfide was extensively investigated in order to understand the effects of various catalysts and reaction parameters. Relevant physical and analytical data are given in Table 2. Hydrogenation of diphenylsulfide was carried out in the absence of catalyst to demonstrate the unreactivity of the substrate under noncatalytic conditions. The blank reaction of diphenyl sulfide at 300°C for 3 hours in the presence of 1000 psi of molecular hydrogen resulted in the conversion of only 1%, and benzene was the only product observed. Upon increasing the reaction temperature to 400°C, the conversion increased to 9.6%, and benzene was once again the major product along with a trace amount of thiophenol. It should be mentioned here that the mechanism of this noncatalytic reaction may not be the same as the acid-catalyzed hydrogenation reaction described below.

The catalytic activity of sodium-exchanged montmorillonite was then tested by reacting diphenyl sulfide at 300°C for 3 hours in the presence of 1000 psi of molecular hydrogen. Under these conditions the conversion of diphenyl sulfide was only 10%. Both benzene and thiophenol were formed (molar ratio 6.9:1). This small conversion could be due to the residual acid sites present in the sodium-exchanged montmorillonite. The exchanged clay contains sodium ions in the interlayer space and possesses some acidity due to polarization of the water of hydration of the cations, or to residual hydroxyl

TABLE 2

Reductive Cleavage Reactions of Diphenyl Sulfide.							
Reactants (g)				React. Cond.		Product	%Conv.
Substr	Cataly.	Solv.	Hydrogen (psi)	Temp. °C	Time hr		
DPS 1.00	None	None	1000	300	3	Benzene Thiophenol	1.0
DPS 1.00	None	None	1000	400	3	Benzene Thiophenol	9.6
DPS 1.02	Silica 0.50	None	1000	300	3	Benzene	2.0
DPS 1.01	NM 0.50	None	1000	300	3	Benzene Thiophenol	10.8
DPS 1.02	AM 0.50	None	1000	300	3	Benzene Thiophenol	99.5
DPS 0.52	SZC 0.25	CB 1.00	1000	300	3	Benzene Thiophenol*	28.4
DPS 1.09	SZC 0.50	None	1000	400	3	Benzene Thiophenol*	94.3
DPS 0.58	SSZC 0.25	None	1000	300	3	Benzene Thiophenol	15.9
DPS 0.50	CPC 0.25	None	1000	300	3	Benzene Thiophenol*	93.3
DPS 0.50	CPC 0.25	CB 1.00	1000	300	3	Benzene Thiophenol*	88.6

DPS = Diphenyl sulfide

CB = Chlorobenzene

HCPC = High chromium chromia-pillard clay

SZC = Silica zinc chloride

SSZC = Spent silica zinc chloride

NM = Sodium-exchanged montmorillonite

ANM = Acid-exchanged montmorillonite

* = Minor product

groups of the clay layers. At higher temperatures, dehydration of interstitial water causes the layers to collapse and limit access of substrates to the interstitial sites (3). However, when the reaction was carried out using acid exchanged (HCl) montmorillonite, a 99.5% conversion of diphenyl sulfide was observed. The major products from this reaction were benzene-and-thiophenol in the molar ratio of 9.3:1. The relatively high benzene to thiophenol ratio shows that the catalyst is effective in cleaving both carbon-sulfur bonds of diphenyl sulfide; that is, the thiophenol intermediate is further converted to benzene and hydrogen sulfide. The excellent conversion obtained might be attributed to the strong acidity of the catalyst and perhaps an ability of the anionic catalyst surface layer to stabilize intermediate cations prior to a hydrogenation step. It should be pointed out that the high acidity of the catalysts may not actually be an advantage to coal processing because of the tendency of the highly acidic surfaces to catalyze condensation (coking) reactions.

Our studies were extended to the pillared clay catalysts with the expectation that they would be able to accommodate larger coal molecules in the interlayer space during coal liquid hydrotreating. This type of catalyst was obtained by exchanging the sodium cations with polyoxochromium using a large excess of hydroxy chromium cations. Hydrogenation of diphenyl sulfide with high chromium chromia-pillared clay resulted in the 93.3% conversion of diphenyl sulfide. The products of this reaction were benzene and thiophenol in the molar ratio of 12:1. When the same reaction was carried using low chromium chromia-pillared clay, conversion of 94.5% was observed; however, the ratio of benzene to thiophenol was ca. 1:1 (previous quarterly). Thus, the final step of the reaction, which involves hydrogenolysis of thiophenol, proceeded much more completely with the high chromium pillared clay catalyst. The catalyst sites are probably on the polyoxochromium cation pillars, since they retain some hydroxyl functionality (4). Dithiaphenanthrene was observed as the minor product with both catalysts; that is, high and low chromium chromia-pillared clay. Since this product has been previously observed in the reaction of diphenyl sulfide with aluminum chloride (5), it may be regarded as a product typical of strong-acid catalyzed sulfur cleavage. Cyclohexane, methyl cyclohexane, toluene, biphenyl, and ethyl- and propylbenzenes were some of the minor products of these cleavage reactions.

Since o-dichlorobenzene, a solvent previously investigated for the hydrotreatment of diphenyl sulfide, was found to react under the reaction conditions employed, alternative solvents were explored during this quarter. Chlorobenzene was one such solvent investigated. Reaction of diphenyl sulfide, 1000 psi of hydrogen and high chromium chromia-pillared clay at 300°C for 3 hours in chlorobenzene as solvent resulted in high conversion (89%) of diphenyl sulfide. The major product was benzene with a trace of thiophenol. Dithiaphenanthrene was the minor product of this reaction. Most importantly, chlorobenzene, unlike dichlorobenzene, was exceptionally stable under these conditions. The explanation for the solvent effect may be that the polar chlorobenzene solvent molecules may bind to the catalyst surface by dipolar forces; however, the chlorobenzenes are much less basic than the diphenyl sulfide, and may not form a protonated aromatic intermediate.

3.3.3.2 Silica gel-zinc chloride catalyst

Hydrotreating of diphenyl sulfide with silica-zinc chloride at 1000 psi of hydrogen and 300°C for 3 hours gave an 85% conversion (previous quarterly). The conversion using silica gel without metal halide catalyst was only 2%, with benzene as the only product. Although the conversion using silica-zinc chloride catalyst was good, the large amount of thiophenol in the products seemed to indicate that the catalyst was being deactivated. To demonstrate this hypothesis, catalyst was recovered from the reaction product. The reaction of diphenyl sulfide with this recovered catalyst was carried out at 300°C for 3 hours in the presence of 1000 psi of molecular hydrogen. This reaction gave a conversion of 16%, which suggests that the silica-zinc chloride catalyst is deactivated during the reaction.

The hydrotreating was also carried out at a higher temperature to determine if the deactivation could be prevented. The conversion for a reaction conducted at 400°C improved considerably to 94%. The molar ratio of benzene to thiophenol also increased to 28:1.

The effect of solvent on the conversion and the product distribution was also investigated with this catalyst. Conversion of diphenyl sulfide in chlorobenzene at 300°C for 3 hours in the presence of 1000 psi of hydrogen was 28.4%.

The dichloromethane-insoluble and soluble fractions were characterized to identify the products of these reactions.

Dichloromethane-soluble fraction was found to be mainly catalyst. Quantitative amounts of the catalyst were recovered at the end of each reaction. The absence of any organic residue in the insoluble fraction indicates that no retrograde reaction occurred. Detailed characterization of the spent catalyst to evaluate the efficiency of the catalyst is in progress and will be reported in our next quarterly report.

The dichloromethane-soluble fraction was analyzed both qualitatively and quantitatively by GC/FID, GC/FTIR/MS, and GC/MS/HeAD. Qualitative analysis was performed by carbon and sulfur absorption spectroscopy using GC/HeAD. Quantitative analysis by sulfur and carbon atomic absorption spectroscopy using newly developed GC/HeAD is in progress and will be reported in future quarterlies.

On the basis of the preliminary investigations, we found that acid catalysts and clays pillared with polyoxymetal cations may be useful in removing organic sulfur from coal, coal liquids or petroleum crudes.

3.3.4 Low severity liquefaction of Wyodak subbituminous coal

The objective of this task is to provide a low severity liquefaction stage as a part of the two-stage process for converting low rank coals to liquid product. The presumption is that the first-stage product will be high molecular weight material with a high oxygen content. The elimination of carbon dioxide from decarboxylation of the carboxylic acid groups in the low rank coals should occur in the first stage to avoid consumption of the hydrogen in the second stage via the water/gas shift reaction. Solubilization of the coal in a hot solvent should be effected in the first stage. Good

contact of the coal macromolecules with the heterogeneous catalyst employed in the second stage is essential, so that the catalytic hydrotreatment will be effective in depolymerization, oxygen or heteroatom removal, and perhaps most importantly, prevention of retrograde reactions which can lead to coking. Radicals formed by the homolytic cleavage of the bridging groups must be capped by hydrogen abstraction from solvent or catalyst with which it is in intimate contact.

3.3.4.1 Reaction

In a 2-gallon reactor, a slurry consisting of 904.5 g of Wyodak coal (as received) and 1254.9 g of solvent (tetralin) were placed and the reactor was sealed. The reactor was evacuated and charged with a mixture of 900 psi of carbon monoxide and 100 psi of hydrogen sulfide. The reactor was slowly heated to 384°C, and left at this temperature for one hour. At the end of the reaction the reactor was cooled to room temperature and the gases collected in a gas bag. These gases were analyzed, and the results are given in Table 3.

Table 3

Gas Analysis of Low-severity Reaction Product	
Component	mole percent
Helium	0.00
Hydrogen	6.55
Carbon dioxide	69.62
Propane	0.00
Propylene	0.04
iso-Butane	0.09
Carbonyl sulfide	0.02
n-Butane	0.02
Hydrogen sulfide	2.26
1-Butene	0.00
t-2-Butene	0.00
iso-Pentane	0.00
cis-2-Butene	0.00
n-Pentane	0.00
Ethylene	0.00
Ethane	0.69
Oxygen	2.24
Nitrogen	9.09
Methane	2.51
Carbon monoxide	6.87
Calculated Heating Value, BTU/SCF	
	Saturated 98.5
	Dry 100.2
Calculated Specific Gravity	1.295
Calculated Average Molecular Weight	37.43

3.3.4.2 Low -severity product yield data and initial analysis

Two schemes were used for the work-up of the low severity product to obtain the yield data.

Scheme 1: In this scheme raw product (low-severity product plus tetralin solvent) slurry (10.21 g) was diluted with 200 ml of tetrahydrofuran and stirred for one hour. The solution was then centrifuged to remove insoluble material, and the solid was washed with tetrahydrofuran until the supernatant liquid was free of yellow color. The tetrahydrofuran-insoluble fraction was dried in vacuo at 110°C overnight and weighed. The conversion (86%) was calculated as the percent of the coal (maf) that did not appear in this THF-insoluble fraction. The THF-insoluble fraction was analysed by FTIR and solid state ^{13}C NMR spectroscopy. Infrared spectra of this fraction showed substantial loss of alkyl groups. Also, this fraction was found to be less decarboxylated than the fraction that dissolved in THF. Infrared and NMR spectra of this THF-insoluble fraction showed a substantial increase in the aromatic carbon-to-aliphatic carbon ratio as compared with the original coal. These data confirm the generalization that the portion of the coal which is more easily mobilized under thermal conditions is more aliphatic.

The THF-soluble fraction was added to a large excess of hexane (400 ml) and stirred for one hour. The brown solid was separated by centrifugation and washed with hexane until free of yellow color. The resulting hexane-insoluble material was dried in a vacuum oven at 110°C overnight. Hexane-insoluble material was analyzed by FTIR. Infrared data for this fraction indicated substantial decarboxylation of the carboxylic acids and carboxylate groups, and also an increase in the aliphatic contents as compared with the parent coal.

In Scheme 2, the raw product (low-severity product plus tetralin solvent) slurry (3.1584 g) was distilled directly from a tubing bomb into a series of three traps at 25°C and at liquid nitrogen temperature. The tubing bomb was slowly heated (3°C/min) in vacuo to 250°C until distillation stopped. Distillate was dissolved in 100 ml of methylene chloride. A 20-ml portion of this solution was mixed with 1 ml of internal standard (deuterium-enriched) solution and analysed by GC/MS/HeAD. The majority of the distillate was found to be either solvent or solvent-derived. Although a large number of peaks which may be due to coal-derived material were found, the phenol amount was large enough to be quantitatively analyzed. From the amount of coal (maf) in the THF-soluble and insoluble fractions, a small amount (5%) of the coal-derived material is expected to be present in the distillate. The undistilled residue was dissolved in THF and separated into THF-insoluble and THF-soluble fractions. The THF-insoluble fraction accounted for 23% of the product slurry; thus the conversion to THF soluble products from this scheme was 89% (maf) and corresponds closely to that found by direct solvent precipitation (Scheme 1).

3.3.4.3 Preparation of solvent-free low severity product for second-stage hydrotreatment

For the testing of the new catalysts, a large batch of low severity product which was free of solvent was desired. The THF-soluble fraction from

the first-stage liquefaction was distilled to remove THF and most of the tetralin solvent. The residue, which was a viscous oil that solidified upon cooling to room temperature, was used for the second-stage high severity hydrotreatment reactions. This fraction was analysed by elemental analysis, and the results are given in Table 4. Elemental analysis indicated an increase in the carbon and hydrogen contents compared with the parent coal (maf basis). Sulfur and nitrogen contents were the same as in the parent coal. It may thus be possible that under low severity conditions, desulfurization and denitrogenation did not occur. Oxygen content, (8.34%) was significantly less than that in the starting coal (22.3% maf). GC analysis of the product indicated a very small amount of tetralin and naphthalene remained.

Further analysis of solvent-free low severity product:

Since the distillate obtained after hydrotreating contained small amounts of tetralin, naphthalene and other volatile materials which were originally present in the low severity material, it was essential to distill some of the starting "solvent-free" low severity material for a base-line volatile matter comparison. A sample of the oil bottoms material (2.00 g) from which most of the solvent had been distilled was redistilled under vacuum, giving 18% distillate, 79% THF-soluble bottoms, and 4% of THF-insoluble bottoms.

Both THF-insoluble and THF-soluble fractions were analysed by FTIR. Infrared data for the THF-insoluble fraction indicated this fraction to be more aromatic than the THF-soluble fraction.

On the basis of the GC/MS data, 18% of the distillate was found to be the solvent (tetralin) and 12% was naphthalene. Naphthalene could have come from solvent or coal or both. The remainder of the distillate was a complex mixture of alkanes, substituted naphthalenes, etc.; however a detailed qualitative and quantitative analysis is in progress.

3.3.5 Second-Stage Reaction (catalytic hydrotreatment)

Second-stage catalytic hydrotreatment was carried out on the THF-soluble product from the low severity reaction of Wyodak coal.

In a typical run, 1.0 g of the low severity product, 0.5 g of the zinc chloride-silica gel and 2.0 g of the desired solvent (if needed) were placed in a microreactor (tubing bomb). The microreactor was evacuated and pressurized with 1000 psi of hydrogen, and placed in a rocking autoclave heated to 400°C for 3 hours. At the end of the reaction period, the microreactor was cooled to room temperature, degassed, and opened. The raw product slurry was directly distilled from the tubing bomb, and separated into three fractions distillate, THF-solubles and THF-insolubles as described in Scheme 2. An accurate mass balance was obtained and is given in Table 5.

The THF-insoluble fraction was 11.79%. An infrared spectrum of the THF-insoluble fraction showed enhanced aromatic content, which could either have been formed by loss of alkyl groups or condensation reactions.

The THF-soluble fraction was 54 wt% of the total product. Elemental analysis showed that the fraction contained absolutely no sulfur. The hydrogen-to-carbon ratio increased to 1.46. Because of the presence of small amounts of colloidal silica gel, an exact ultimate analysis was not

obtained. The infrared spectral data indicated this fraction to be more aliphatic than the THF-soluble fraction obtained from the low severity liquefaction of Wyodak coal. This could be due to further cleavage of alkyl groups and hydrogenation of polynuclear aromatics during second-stage catalytic hydrotreatment. Heteroatom removal during catalytic hydrotreatment will be studied by elemental analysis.

The distillate was 35 wt% of the starting material. Since 17.65 wt% of the distillate was already present in the THF-soluble low severity product used for catalytic upgrading, only 17.35 wt% of the distillate was actually formed during the second stage of the reaction. The distillate was diluted to 50 ml with methylene chloride. An aliquot (10 ml) of this solution was mixed with 1 ml of internal standard (n-octadecane in methylene chloride). Another aliquot (10 ml) of this solution was also mixed with 1 ml of internal standard (a mixture of deuterium-labelled organic compounds in methylene chloride). Both these solutions were analyzed by GC/MS/HeAD for the quantitative analyses of the distillate fraction. The most striking aspect of the distillate is a complete absence of sulfur-containing organic compounds, as determined by very sulfur-sensitive helium afterglow discharge atomic emission detection. Removal of nitrogen and oxygen will also be investigated.

Table 4

Elemental Analysis of coal and liquefaction products									
Sample	Proximate Analysis (maf)			Ultimate Analysis (maf)					
	Moist.	Vol. (%)	Fixed	Ash	H	C	N (%)	S	O
	Mat.		C						
Wyodak		48.18	51.81		5.20	70.9	0.92	0.60	22.3
Coal	11.5	39.1	42.0	7.41	5.50	57.5	0.75	0.49	28.3
LSW					6.94	82.9	1.07	0.71	8.34
									7.41*

* As determined values

LSW is THF-soluble fraction obtained from low severity Wyodak by removing most of the tetralin solvent

Table 5

Liquefaction Reaction of Wyodak Coal									
Sample	Reactants (g)			React. Cond.		Products (g)			Conv (%)
	Cat.	Solv.	Hydro. (psi)	Temp (°C)	Time (Hr)	THFI	THFS /HexI	Dist. /HexS	
LSW ^a (10.21) RPS				0.75	1.26 ^c	8.20 ^d	86.0		
LSW ^b (3.1584) RPS				0.22	0.84	2.40	89.5		
LSW THFS (2.0)				0.08	1.60	0.35			
LSW (1.0)	SZC	1000	400	3	0.62	0.54 ^e	0.37		

a = Scheme 1 (Solvent partitioning)

b = Scheme 2 (Vacuum distillation)

c = Hexane insolubles

d = Hexane soluble

e = Includes 0.5046 g of SZC catalyst

RPS = Raw product slurry

Scheme 1

Scheme 2

1. Program/Project Identification No.	2. Program/Project Title Liquefaction Reactivity of Low-Rank Coals	3. Reporting Period 01/01/89 through 03/31/89
4. Name and Address University of North Dakota Energy & Mineral Research Coal Box 8213, University Station, Grand Forks, ND 58202		5. Program/Project Start Date 4/1/86
		6. Completion Date 3/31/92

11. Major Milestone Status	Units Planned	Units Complete
a. Development of characterization methods	P	1 2 3 4 5
	C	
	P	
	C	
b. Low-severity processing	P	1
	C	
	P	
	C	
c. Cleavage reactions	P	1
	C	
	P	
	C	
d. Reactivity of product	P	1
	C	
	P	
	C	
e. Lignite hydroaromatics	P	1
	C	
	P	
	C	
f. L.S. hydroaromatics	P	1
	C	
	P	
	C	
	P	
	C	
	P	
	C	
	P	
	C	

12. Remarks	
13. Signature of Recipient and Date	Signature of DOE Reviewing Representative and Date

1. Program/Project Identification No.	2. Program/Project Title	3. Reporting Period
	Liquefaction Reactivity of Low-Rank Coals	01/01/89 through 03/31/89
4. Name and Address		5. Program/Project Start Date
University of North Dakota Energy & Mineral Research Center Box 8213, University Station, Grand Forks, ND 58202		4/1/86
		6. Completion Date
		3/31/92

Milestone ID. No.	Description	Planned Completion Date	Actual Completion Date	Comments
a.	Development of characterization methods	03-89	03-89	
b.	Low-severity processing	06-88	06-88	
c.	Cleavage reactions	10-88	10-88	
d.	Reactivity of product	11-88	11-88	
e.	Lignite hydroaromatics	11-88	11-88	
f.	L.S. hydroaromatics	12-88	12-88	
g.	Test pillared clay catalyst (MO)	12-89	12-89	
h.	Test pillared clay catalyst (ZN)	12-89	12-89	

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3.5 Gasification Ash and Slag Characterization

GASIFICATION ASH AND SLAG CHARACTERIZATION

**Final Technical Progress Report for the Period April 1, 1988 - June 30, 1989
Including the Quarterly Technical Progress Report
for the Period April - June 1989**

by

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TABLE OF CONTENTS

	<u>Page</u>
LIST OF FIGURES.....	iii
LIST OF TABLES.....	v
PROJECT SUMMARY.....	1
1.0 BACKGROUND STATEMENT/OBJECTIVES.....	1
1.1 Task A -- Mineral Transformations.....	3
1.1.1 Task A -- Objectives.....	3
1.2 Task B -- Volatilization Studies.....	3
1.2.1 Task B -- Objectives.....	4
1.3 Task C -- Physical Properties.....	4
1.3.1 Task C -- Objectives.....	7
2.0 EXPERIMENTAL.....	8
2.1 Task A -- Mineral Transformations.....	8
2.2 Task B -- Volatilization Studies.....	8
2.3 Task C -- Physical Properties.....	10
2.3.1 Viscosity.....	10
2.3.2 Surface Tension.....	12
2.3.3 Sintering Behavior.....	12
3.0 CHARACTERIZATION OF ASHES AND AGGLOMERATES FROM PILOT-SCALE GASIFICATION SYSTEMS.....	14
4.0 PROJECT STATUS/RESULTS AND ACCOMPLISHMENTS.....	17
4.1 Task A -- Mineral Transformations.....	17
4.2 Task B -- Volatilization Studies.....	17
4.2.1 SEMPC Results.....	18
4.2.1.1 Indian Head Coal.....	18
4.2.1.2 Martin Lake Coal.....	18
4.2.1.3 Velve Coal.....	31
4.2.1.4 Wyodak Coal.....	31
4.2.2 CCSEM Results.....	31
4.2.2.1 Martin Lake Char CCSEM Data.....	31
4.2.3 Base-to-Acid Ratio.....	33
4.2.4 Summary.....	35
4.3 Task C -- Physical Properties.....	36
4.3.1 Discussion/Descriptive Models.....	36
4.3.1.1 Sintering.....	43
4.3.2 Conclusion: Application to Gasification Systems.....	47
4.3.3 Future Work.....	48
4.3.4 Model Verification of Sintering, Crystallization, and Mechanical Properties of Selected Coal Ashes.....	48
4.3.4.1 Results and Discussions.....	51

TABLE OF CONTENTS

	<u>Page</u>
4.3.5 Viscous Sintering by the Shrinkage of Large Pores and the Diffusion of Liquid Phase Constituents.....	54
4.3.5.1 Conclusions.....	61
5.0 REFERENCES.....	62

LIST OF FIGURES

<u>Figure</u>	<u>Page</u>
1 Schematic diagram of the pressure pyrolysis unit.....	9
2 Schematic of high-temperature rotating bob viscometer.....	11
3 UNDEMRC surface tension apparatus.....	13
4 Schematic of surface tension bead.....	13
5A PPU Velva chars -- viscosity distribution at 1000°C.....	37
5B PPU Velva chars -- base-to-acid distribution.....	37
6A PPU Pittsburgh #8 chars -- viscosity distribution at 1000°C.....	38
6B PPU Pittsburgh #8 chars -- base-to-acid distribution.....	38
7A PPU Wyodak chars -- viscosity distribution at 1000°C.....	39
7B PPU Wyodak chars -- base-to-acid distribution.....	39
8A PPU Illinois #6 chars -- viscosity distribution at 1000°C.....	40
8B PPU Illinois #6 chars -- base-to-acid distribution.....	40
9A PPU Indian Head chars -- viscosity distribution at 1000°C.....	41
9B PPU Indian Head chars -- base-to-acid distribution.....	41
10 Descriptive model of inorganic behavior.....	42
11 Sintering model -- key to processes involving inorganics.....	44
12 Development of strength through sintering (viscous flow).....	46
13 Particle size distribution of coal ashes used in sintering tests..	50
14 Dependence of density upon sintering temperature for amorphous and crystallized Beulah coal ash, measured in air and CO/CO ₂ atmospheres.....	51
15 Microstructure of Beulah coal ash observed after first minutes of sintering in air.....	52

LIST OF FIGURES (CONT.)

<u>Figure</u>	<u>Page</u>
16 Microstructures of Beulah (a) and Illinois #6 (b) coal ashes sintered at 1200°C for 2 hours in air and CO/CO ₂ , respectively. Magnification 500x.....	53
17 The relationship between the ln of surface tension/viscosity ratio and temperature for Beulah, Pittsburgh #8, and Illinois #6 coal ashes determined in air (a) and CO/CO ₂ (b) atmospheres.....	56
18 The relationship between the ln of relative density and sintering temperature for Beulah, Pittsburgh #8, and Illinois #6 coal ashes sintered in air (a) and CO/CO ₂ (b) atmospheres.....	57
19 Schematic for the three steps in the sintering of coal ashes.....	58
20 The effects of sintering temperature and atmosphere on strength in Beulah, Pittsburgh #8, and Illinois #6 coal ashes (with the defined demineralogical composition at 1000°C) sintered under air (a) and CO/CO ₂ (b).....	59
21 The effects of sintering atmospheres (curve A) and crystallization in air (curve B) on the strength of amorphous Beulah coal ash.....	60
22 Variation of strength with time for amorphous Beulah sintered at 900° and 1100°C in air.....	60
23 Schematic representation of closed pores opening during phase transformation.....	61

LIST OF TABLES

<u>Table</u>	<u>Page</u>
1 Gasification Ash and Slag Project Tasks.....	2
2 Test Matrix: Pressure Pyrolysis.....	9
3 Phase Analysis of H ₂ Production Agglomerates.....	16
4A Wyodak Char and Coal Samples.....	19
4B Wyodak Ash and Char Analysis.....	20
4C Wyodak Char XRD Analysis.....	20
5A Velva Char and Coal Samples.....	21
5B Velva Ash and Char Analysis.....	22
5C Velva Char XRD Analysis.....	22
6A Indian Head Char and Coal Samples.....	23
6B Indian Head Ash and Char Analysis... ..	24
6C Indian Head Char XRD Analysis.....	24
7A Martin Lake Char and Coal Samples.....	25
7B Martin Lake Ash and Char Analysis.....	26
7C Martin Lake Char XRD Analysis.....	26
8A Illinois #6 (Old Ben) Coal and Char Samples.....	27
8B Illinois #6 (Old Ben) Ash and Char Analysis.....	28
9A Pittsburgh #8 Char and Coal Samples.....	29
9B Pittsburgh #8 Ash and Char Analysis.....	30
9C Pittsburgh #8 Char XRD Analysis.....	30
10 CCSEM Data: Martin Lake Char.....	32
11 Chemical Composition of Chars (From SEMPC).....	34
12 Composition of Coal Ashes.....	50
13 Mineralogical Composition of Crystallized Coal Ashes.....	53

GASIFICATION ASH AND SLAG CHARACTERIZATION

PROJECT SUMMARY

The formation, behavior, and fate of the inorganic constituents in coal gasification systems are critical to the successful design and operation of a gasifier. The behavior of the ash has to be considered in order to decide whether a given coal is suitable for utilization in a given gasification system. The overall objective of the Gasification Ash and Slag Characterization Project is to obtain laboratory- and bench-scale data on the formation, flow, and sticking behavior of coal ash and slag under gasification conditions. With this data, the project aims to develop the techniques and methods required to establish the behavior of inorganic constituents of a given coal ash under gasification conditions. In order to accomplish these goals, the project has undertaken detailed experimental and modeling studies. An important aspect of these studies has been the application of the results and models developed to the behavior of ash in pilot-scale and full-scale coal gasification systems. This step has helped to both verify and develop the models as well as to indicate further areas of needed research.

The eventual outcome of the Gasification Ash and Slag Project will be a unified picture of the behavior of inorganic species within a gasifier. The unified picture will include a set of theoretical and empirical models with which the behavior of an ash can be adequately predicted. These models will be invaluable to the designers and gasifier operators in assessing coal feed material for utilization in gasification systems.

1.0 BACKGROUND STATEMENT/OBJECTIVES

The coal gasification industry presently relies on qualitative empirical methods developed for combustion systems to predict the suitability of a coal and critical operating parameters with respect to ash behavior for a given gasification system. The methods developed for combustion tend to be inaccurate and sometimes produce erroneous predictions of ash behavior for gasification systems. The gasification industry requires better methods to determine the behavior of ash in a gasifier. New methods must be more accurate and rigorous than the methods used at present, in addition to being easily utilized by both operators and designers of gasification systems.

The behavior of ash in coal gasification systems is not well understood. Unlike coal combustion systems, where well-defined analytical tests can be used to evaluate a given coal ash in terms of the effect of the ash on combustor performance, there are no similar techniques specific to coal gasification. Indeed, while it is acknowledged that there are significant differences between the environment in a gasifier and that in a coal combustor, gasifier operators and designers still use predictive techniques of ash behavior developed for combustors. While the major ash-related problem in a combustor is the formation of fireside deposits on heat transfer surfaces, the operation of a gasifier is directly related to the formation and behavior of the ash. This is because the gasifier, be it a dry or a slagging type,

requires the removal of ash material in order to maintain production. Therefore, it is essential to establish which characteristics of coal ash formed in a gasifier affect the actual operation and gas production.

The approach used in this study has been to follow the inorganic constituents of the coal from the original feedstock through the various chemical and physical processes that occur in gasification. The processes selected for study include mineral transformations and ash formation under both air and reducing atmospheres, in addition to char formation, mineral transformations, and loss of inorganics during pressure pyrolysis. Associated with these experiments have been the determination of physical properties including viscosity, surface tension, and sintering behavior of molten slags formed from the coal ashes. Table 1 lists the various tasks of the project. The modeling efforts associated with this project have been quite extensive in the areas of viscosity, surface tension, sintering, and prediction of ash phases and constituents using thermochemical equilibrium techniques at high temperatures and atmospheric pressure.

The project is divided into four tasks.

TABLE 1
GASIFICATION ASH AND SLAG PROJECT TASKS

Tasks	Objectives
A. Mineral Transformations	To determine the mineral transformations that occur between coal minerals under controlled temperature and atmosphere.
B. Pressure Pyrolysis	To determine and model the change in chemistry/mineralogy of inorganic coal constituents under various pressure and temperature conditions.
C. Physical Properties	To determine and model the surface tension and viscosity of liquid phases present in coal ash systems.
D. Sintering Phenomena	To determine and model the causes and characteristics of sintering behavior.

1.1 Task A -- Mineral Transformations

Coal is a relatively dirty fuel compared to oil. It contains a complex mixture of inorganic mineral matter as well as (particularly for western coals) organically associated inorganic elements. The mode of occurrence, specific chemical and crystalline structure, and the spatial distribution of these minerals can all have an effect on the ash species produced as the residue of coal gasification. Usually the chemical composition of the ash produced from a sample of the feed coal under oxidizing conditions is the only analytical data used to characterize this ash. However, the bulk chemical composition does not provide sufficient insight into the behavior of the coal ash within the gasifier.

Experimental studies of the mineral transformations of a suite of coal ashes and various model mixtures have been completed (1). The results have shown that mineral transformations and changes in chemical composition are quite complex. Detailed correlation and analysis of the data are required in order to determine the mechanisms responsible for mineral transformations during coal gasification. In particular, the various coal characteristics, as well as gasification conditions, will be expected to have direct effects on the mechanisms of mineral transformation.

1.1.1 Task A -- Objectives

The first task involved the characterization and identification of mechanisms responsible for the complex mineral transformations that coal minerals exhibit in gasification systems. This involved the generation of ash and slag samples in bench-scale units simulating gasification environments using both high- and low-rank coals. In addition, model mixtures of minerals common to coal, acetic acid salts of various alkali and alkaline earth elements, and iron oxalate were studied under simulated gasification atmospheres in the laboratory. The use of model mineral mixtures gave baseline data on mineral transformations under well-controlled conditions. The inclusion of mineral mixtures with addition of acetic acid salts permitted study of the effects of organically bound metals on mineral transformations. It must be remembered that for western coals, some elements are present within the organic matrix of the coal. The effect of the behavior of these elements, usually Na, Mg, and Ca, on the mineral transformations must be understood in order to be able to properly predict the formation and behavior of ash in a gasifier and how the ash may affect gasifier performance. Model mineral mixtures with additions of potassium acetate were also studied. This is important, as potassium has been identified as an element that has catalytic activity during coal gasification. Therefore, the effect of potassium on mineral transformation and its characteristics within the product may have a bearing on the behavior of the element as a gasification catalyst. The mineral transformation data was reported in the 1988 Gasification Ash and Slag Characterization Final Report (1).

1.2 Task B -- Volatilization Studies

A major aspect of the operation of a coal gasification system is predicting the chemical composition of the ash formed in the gasifier. Normal laboratory ashing techniques do not necessarily produce ash that is comparable to that formed in a gasifier. A particular concern is the loss of species

from the ash matrix due to volatilization. This will have a direct effect on the bulk chemical composition of the ash and may have an effect on the catalytic activity of certain elements during gasification. Of course, the loss of species due to volatilization will depend on the distribution and origin of the species as well as gasification conditions. Therefore, it is important to understand chemical as well as mineralogical transformations that occur within coal during gasification. In order to establish the degree of volatilization, detailed laboratory experiments have to be performed under high-pressure and high-temperature conditions. The complex nature of volatilization requires detailed modeling studies. This modeling is best accomplished using thermochemical techniques. We are developing a program called PHOEBE to replace SOLGASMIX, and a data base for volatilization studies of coal ash. Detailed evaluation of the program and how it relates to gasification systems is a crucial aspect to the development of a model of inorganic volatilization during gasification.

1.2.1 Task B -- Objectives

The second task involves the study of vaporization of inorganic constituents during gasification processes. This included the use of a computer simulation model of solid-gas-liquid phase equilibria in high-temperature (1000-2000 K) systems. Relevant experimental data was provided by the preparation of coal chars in a pressure pyrolysis unit under controlled conditions. In addition, the chemical composition data from samples studied in the first task will provide data on the loss of inorganics during preparation of ash and slag samples.

1.3 Task C -- Physical Properties

Ash in gasification systems is removed either as a granular or powdered material or as molten slag. For a given gasifier operation, it is necessary for the ash to be in the correct form in order to remove the material during normal operation. That is, for dry-bottom gasifiers, the ash has to remain granular or in powder form, and for wet-bottom or slagging gasifiers the ash has to form a molten slag of sufficiently low viscosity that the material will flow at the slag exit temperature. The extent to which ash melts and agglomerates to form granular or molten slag material is dependent on the chemical and mineralogical nature of the ash, and the various temperatures, residence time, and atmospheric conditions experienced by the ash. However, insight into the behavior can be derived from coal ash deposition studies in combustion systems. These studies have identified a mechanism of sintering by viscous flow as that responsible for the formation and growth of ash deposits. This relation has been described by Raask (2) and is given by:

$$\frac{ds}{dt} = \frac{3\gamma k}{2r\eta} \quad [1]$$

where ds/dt represents the rate of increase in strength, k is a constant, r is the radius of the particles, and γ and η are the surface tension and viscosity of the liquid phase, respectively. Note that the relation is given for a system at constant temperature.

For a given ash system, the viscosity of the liquid phase tends to be the major parameter for the sintering process. The higher the viscosity, the lower the rate of sintering, and vice versa. Therefore, the degree of sintering is dependent on the viscosity and relative amount of the liquid phase. For slagging systems, the bulk of the ash melt flows through a slag tap. In this case, the viscosity of the bulk material is a controlling factor. The bulk viscosity will be dependent on the chemical composition and the temperature. In some cases, crystallization occurs within the melt. This has two effects. First, it reduces the amount of liquid phase; and second, it alters the chemical composition of the melt. Both of these effects can alter the bulk flow properties. In dry-bottom systems, sintering occurs to a lesser extent than in the slagging gasifier. Here the ash species may form a liquid phase with a very different composition than the bulk composition. In this case, the degree of sintering at a given temperature will be dependent on the amount of liquid phase formed, the chemical composition, and the viscosity, as well as the surface tension. The greater the amount of liquid phase formed and the lower the viscosity of the liquid, the greater the degree of sintering. In the dry-bottom system, it is important to limit the degree of sintering to prevent excessive clinking (formation of large agglomerates). This can only be achieved by the reduction of the amount of liquid phase and/or the viscosity of the liquid phase involved in the sintering. Crystallization can also occur in the ash samples within the dry-bottom gasifier. This will tend to reduce the amount of liquid phase and alter the chemical composition, and hence viscosity, of the component liquid phase.

Therefore, the determination and the modeling of the viscous flow behavior of coal ashes, as well as possible component liquid phases, is important to the understanding of the behavior of a given ash under gasification conditions. Various models of coal ash viscosity have been developed. However, these tend to be rank-dependent and empirically based. Furthermore, they give relatively limited insight into the viscous flow behavior of component liquid phases formed under less extreme conditions. Another factor is that the models have been developed for coal combustion systems and the models use coal ash as the basis of predicting behavior. Schobert et al. (3) have compared the measured viscosity under reducing conditions of a range of molten low-rank coal ashes with the various models available. They found that the empirical models of Watt and Fereday (4) and Reid and Cohen (5) did not fit the measured data well. The explanation was that the methods were based on bituminous coal ashes and include only the concentrations of SiO_2 , Al_2O_3 , Fe_2O_3 , CaO , and MgO . The study showed that the computational method of Urbain gave the best results. The Urbain method has a number of features that make it very attractive to the study of ash behavior. First, it includes all components; second, it is based on the viscosity behavior of silicate melts because it was developed for metallurgical slags; third, it uses mole fraction of components; and fourth, it uses the Frenkel relationship (6) as opposed to the Arrhenius relationship. The use of all components ensures that the method is not constrained by a compositional range. The method is also enhanced because the basis of the technique is the flow properties of silicate melts and not specifically those of coal ashes. Certainly, the component liquid phases within an ash are silicate based but may be far removed, in a chemical sense, from coal ashes. Silicate viscosity models use a structure that defines a component oxide as network former, network modifier, or amphoteric. In general, the higher the

level of network former, the greater the degree of polymerization within the melt and the higher the viscosity at a given temperature. Network modifiers tend to reduce the degree of polymerization and, hence, reduce viscosity. Amphoteric components can act both as network former or modifier, depending on their relative concentrations. In the case of coal ashes, the classification of the component oxides are:

Network former:	SiO ₂ , TiO ₂
Network modifier:	CaO, MgO, Na ₂ O, K ₂ O, FeO
Amphoteric:	Al ₂ O ₃ , Fe ₂ O ₃

The role of SO₃ is not defined in this model.

The use of mole fractions is a direct consequence of the use of this model. That is, the effect or role of a component oxide will depend on the relative amount of molecules available and not on relative weight percent. The use of the Frenkel (6) model:

$$\text{viscosity} = A \exp(E/RT) \quad [2]$$

has been found to give better results than the Arrhenius relationship:

$$\text{viscosity} = A \exp(E/RT). \quad [3]$$

Schobert (3) used the Urbain model as the basis of a modified Urbain viscosity calculation. However, as the focus was on the bulk flow properties of low-rank coal ash slags from a slagging gasifier, the method developed was rank dependent and gave very little insight into the flow properties of component liquid phases.

For the Ash and Slag study, the original Urbain method was used as the basis of a modeling effort. Unique features of this project were the use of model mixtures and the preparation of a computer data base of the viscosity of silicate melts. The melts included glasses from simple oxide systems. The basis of this study was straightforward. In order to predict the flow properties of a complex aluminosilicate melt (coal ash), it is necessary to model the viscosity of simpler systems. That is, the model should be applicable to both simple oxide melts and complex oxide melts. This has the added benefit of enabling the determination of the viscosity of residual liquid phases and component liquid phases as well as bulk properties. If the crystallization behavior or partitioning of various components is known, then the effect of these processes on the sintering or bulk flow properties can be predicted.

The surface tension is the measure of the relative wetting characteristics of a material on a substrate. In gasification systems, surface tension of the slag or component liquid phase can affect the rate of sintering, formation of slag, or the attack of refractory components. For slagging units, a low interfacial surface tension is required to enhance capture and assimilation within the slag. However, a high surface tension is required between the slag and the refractory to reduce attack or corrosion of the refractory. For dry-bottom systems, a high particle-to-particle surface tension reduces the initial adhesion of contacting particles and hence reduces agglomeration.

Therefore, the surface tension of ash melts and component liquid phases can have an important effect on the operation of a gasifier. It is necessary to be able to model the surface tension of the slags. In order to do this, the surface tension of a number of coal ash slags and model mixtures were measured under reducing conditions. As the substrate in surface tension experiments can have an effect on the surface tension, it was decided to measure the surface tension on an inert substrate. In this study, vitreous carbon was used. The method used to determine the surface tension was the sessile drop method, which involves the determination of the shape of a slag bead on a substrate at elevated temperatures.

The viscosity and surface tension of the molten phases in coal ash systems are very important parameters. Both the viscosity and the surface tension will be dependent on the chemical composition of the molten phase and the operating conditions of the gasifier. The actual behavior of the liquid phase and the bulk flow properties of ash and slag products will be dependent on the combined effects of these parameters.

Knowledge of the physical properties of the molten phases present in ash systems can only be related to bulk ash properties by detailed experimentation. In all cases of ash behavior in gasification systems, the adhesion/cohesion of ash particles, followed by reaction and consolidation, are critical processes. Therefore, a detailed study of these processes and how they are affected by ash composition (chemical and mineralogical), temperature, viscosity, and surface tension is warranted. The process of interest can best be described as sintering. Sintering is a process of consolidation of a granular material of high surface energy to a bulk mass of low surface energy. In the case of fixed-bed gasifiers such as the Lurgi type, sintering of ash, while encouraged, has to be limited so as to ensure that clinkers too large to pass through the grate are not formed. In the case of entrained flow, where a slag is formed, the sintering process has to be fast and complete. This ensures that the slag remains a homogeneous liquid and performs as predicted in terms of bulk flow behavior.

1.3.1 Task C -- Objectives

The third task evaluates slag viscosity behavior under reducing conditions. The task will involve the study of compositional and rheological properties of slag produced from both reduced and oxidized coal ashes and the development of a predictive viscosity model. Of particular importance is the modeling effort to predict the Newtonian flow temperature regime and the effect of crystallization within the slag on bulk flow properties. Viscosities will be determined for coal ashes produced under reducing and oxidizing conditions, model mineral mixtures, and coal ashes with additives. All viscosities are determined under a reducing atmosphere.

Associated with the third task are the determination and subsequent modeling of surface tension of coal ashes. The surface tension of various coal ashes and model mixtures were determined under gasification environments on vitreous carbon substrates. This task also involved determination and modeling of sintering behavior of ashes under a reducing atmosphere.

2.0 EXPERIMENTAL

2.1 Task A -- Mineral Transformations

The chemical compositions and mineral phase compositions of the ashes and slags produced have been reported previously. This task involved using data base computer programs to correlate changes in composition and mineralogy due to the various reaction conditions. The data was compiled in a Lotus spreadsheet. From this data base, facilities of Lotus, as well as SAS and Reflex, were used to determine correlations. SAS is an advanced statistical package used to perform a wide variety of statistical procedures. Reflex is a p.c.-based data base computer program with a wide range of graphing as well as sorting and statistical correlation capabilities.

The coal ashes will be prepared by heating the coal samples at 500°C in air for about 48 hours or until no weight change is noted. The ashes will then be treated under a reducing atmosphere at 1000°C for 8 hours. This last procedure is to ensure that the mineral phase assemblage in the sample prior to sintering is that which would be expected in a gasifier. The mineral phase assemblage of the ashes and pellets will be determined using X-ray diffraction and SEMPC. The sintered pellets will be produced by heating the ash at 1100°, 1200°, and 7300°C for 2, 8, and 16 hours under reducing conditions.

2.2 Task B -- Volatilization Studies

Pressure pyrolysis of coals was used to obtain data on the degree of volatilization of various components under simulated gasification conditions. A schematic of the pressure pyrolysis unit is given in Figure 1. The unit is used to prepare chars from coals at a variety of temperatures and pressures. The coals to be studied and the various conditions used to prepare chars are given in Table 2. Samples of -60 mesh coal are placed in crucibles and placed in the reactor. The temperature and pressure are adjusted to run conditions and are held constant for 2 hours. Samples of the coal and the low-temperature ashes of the chars are submitted for detailed computer-controlled scanning electron microscope analysis with a technique called SEMPC. The technique gives both amount and composition of the mineral phases as well as a composition of the ash based on the composite compositions of the mineral phases.

The data, i.e., the change in chemical composition and mineral transformation, will be integrated using modeling techniques based on thermochemical principles. These models, such as SOLGASMIX (7) and PACKAGE (8), were developed to determine or predict phases in hostile environments. For example, SOLGASMIX has been applied to the analysis of the behavior of potassium within the plasma of MHD systems for temperatures of over 2000 K. PACKAGE was developed at Aerodyne for use with the NASA CEC code for the study of rocket flames and emissions. With respect to coal utilization systems, SOLGASMIX and its derivatives appear to have been used more often by researchers than PACKAGE. A version of SOLGASMIX has been part of the PCGC-2 modeling effort at Brigham Young University, and researchers at Argonne, MIT, PSI, and NBS use thermochemical models based on SOLGASMIX. PACKAGE is used by researchers at Morgantown Energy Technology Center (METC) and at Aerodyne Research Corporation. Recently, Southern Research Institute has developed a code based on thermochemical techniques to model volatilization of trace elements during coal gasification.

Figure 1. Schematic diagram of the pressure pyrolysis unit.

TABLE 2

TEST MATRIX: PRESSURE PYROLYSIS
Run Time = 2 hours; Atmosphere = 10% H₂-90% N₂

Coal	Char 1 650°C Ambient	Char 2 850°C Ambient	Char 3 850°C 200 psi	Char 4 850°C 400 psi	Char 5 650°C 200 psi	Char 6 650°C 400 psi
Martin Lake	X	X	X	X	X	X
Indian Head	X	X	X	X	X	X
Velva	X	X	X	X	-	-
Wyodak	X	X	X	X	X	X
Pittsburgh #8	X	X	X	X	X	X
Illinois #6	X	X	X	X	-	-

Both programs were made available to UNDEMRC. A mainframe version of SOLGASMIX was supplied by Dr. Bonnel of NBS. PACKAGE was supplied by Dr. Nagarajan, formerly of the University of West Virginia. Due to previous experience with SOLGASMIX, it was decided to initially use SOLGASMIX for thermochemical predictions and modeling of phase equilibria in gasification systems.

2.3 Task C -- Physical Properties

2.3.1 Viscosity

The viscosity of coal ashes and model mineral mixtures was determined using a rotating bob viscometer. A schematic of the viscometer apparatus is given in Figure 2. The gas flow through the viscometer was controlled to produce an atmosphere of 8% hydrogen and 92% nitrogen. Viscosities in the range of 1 to 3000 poise (0.1 to 300 Pa·s) could be measured. Both oxidized and reduced HTA (High Temperature Ash) from Task A were used as the starting material for the viscosity studies of coal ashes. Reduced HTA was used for the mineral mixtures. In some cases, slag was prepared from the HTA (oxidized and reduced) of the coals in a separate furnace. This was done to prevent excessive frothing of the sample in the viscometer. After determination of the viscosity/temperature relationship of the sample during the cooling cycle, the furnace was cooled and the sample removed. The samples were then subjected to X-ray fluorescence, X-ray diffraction, and scanning electron microscopy analysis. The scanning electron microscopy analysis involved the use of a technique developed at UNDEMRC called scanning electron microscopy point count (SEMP). This technique is used to determine the relative concentration of the phases in a sample and their chemical composition. For the viscometer samples, the analysis was focused on verifying that the sample was homogeneous. Work also focused on the composition and relative amount of the crystalline phases. An advantage of the SEMPC technique is that it is able to determine the chemical composition, using microprobe data, of both amorphous and crystalline phases in a sample. Details of the technique can be found elsewhere. The results of these analyses are required to:

1. Model the crystallization behavior of slags, and
2. Relate the crystallization behavior to bulk flow properties.

The viscosity data from this task is part of an extensive data base of viscosity/temperature data. This data base will be used to develop a model to predict flow properties both in the Newtonian and non-Newtonian regimes. Unlike other attempts to model ash viscosity, for example Watt and Fereday (4), and Sage and McIlroy (9), the data base includes, in addition to results from this task, viscosity data from all ranks of coal, simple oxide glasses, and geological samples. As discussed in a previous report (10), the model to be used will be that of Urbain (11), which has a number of advantages over other models. These advantages include the incorporation of all components and a theoretical model of the structure of silicate melts. The model will not be restricted to a specific range of ash compositions, as is the case with most empirical models of viscosity of component liquid phases of coal ash. The study involves the compilation of viscosity, chemical composition, and temperature data and associated analyses including statistical correlations.

Figure 2. Schematic of high-temperature rotating bob viscometer.

A key aspect is the prediction of the crystallization behavior of coal ash melts. This is important, as the crystallization directly affects the composition of the component liquid phases. Indeed, the relative amount of crystalline phases can have a direct influence on the sintering or even bulk flow properties of slags. While most models of viscosity cover the Newtonian range, there is a need to understand the bulk flow properties of slags after the onset of crystallization. This requires the modeling of the crystallization behavior of slags. Studies by Kalmanovitch and Williamson (12) have shown the applicability of equilibrium phase diagrams to crystallization in coal ash systems. These diagrams will be used in conjunction with a thermochemical equilibrium program, PHOEBE, and crystallization data from the viscosity tests in the development of a model of crystallization behavior of slags. This model, combined with the model to predict Newtonian flow behavior of slags, will be used to develop an overall model of bulk flow properties of slags. The final model will also have direct applicability to the understanding of ash sintering behavior in dry-bottom gasifiers.

In order to model the crystallization behavior, detailed information on the phases present must be obtained. This requires the use of SEMPC to determine both the relative amount of phases and the composition of the phases present in the slag samples.

2.3.2 Surface Tension

The surface tension of a liquid or melt is the measure of the degree of "wetting" exhibited by the phase on an adjacent (usually solid) surface. A high surface tension results in a non-wetting liquid material. In this case, the liquid will form a spherical bead on the surface of the substrate. A low-surface tension results in wetting of the substrate with the liquid covering a large area of the substrate. The surface tension is important to the study of ash behavior in gasification systems. It affects the interaction of molten slag with gasifier surfaces, as well as the fundamental sintering process. In the latter, the surface tension of the liquid phase on the surface of an ash particle affects the initial adhesion of particles. After adhesion, the surface tension forces pull the liquid phase to the neck region, enhancing the sintering process. In the first case, the low surface tension enhances adhesion between contacting particles. However, sintering is enhanced by high surface tension.

The technique used in the study for the determination of surface tension was the sessile drop technique. This involves the melting of a previously prepared slag (completely molten sample) that was cooled, then ground and pressed into a pellet of known dimensions. The pellet is mounted on a vitreous carbon inert substrate and heated in a horizontal furnace under controlled atmospheric conditions. The change in shape as the pellet melts and tries to form a symmetrical bead on the carbon is recorded using a camera. The photograph of the symmetrical bead is then analyzed to determine the dimensions of the bead. From these dimensions, the surface tension can be calculated. The temperature at which the sample formed the bead is also recorded. A schematic of the apparatus used and the bead dimensions measured are shown in Figures 3 and 4, respectively. In this study, the surface tension is determined under a reducing atmosphere simulating gasifier conditions. The surface tension will be measured for all the coal ashes and model mineral mixtures in Task A (Mineral Transformations). Analysis of the samples will include X-ray diffraction and scanning electron microscopy with electron microprobe. Specific interest will be focused on the crystallization effects and the composition of the surface liquid phase.

2.3.3 Sintering Behavior

Sintering is the process of consolidation of a solid substance of high surface area (for example, a powder) to a solid mass. In this process the density of a given mass of sample will decrease compared to the initial sample. The sintering process is very important, as it is responsible, at least in part, for the formation of agglomerates, clinkers, and slags in coal gasification systems.

The sintering process requires mass transfer to occur. In the case of ash systems, the predominant mass transfer process is via viscous flow of liquid phase between adjacent particles. The relation of viscosity and surface tension to the sintering process has been discussed above. However, it is necessary to establish the rate at which the sintering occurs and the effect of viscosity and surface tension on the rate of sintering.

Figure 3. UNDEMRC surface tension apparatus.

Figure 4. Schematic of surface tension bead.

In the sintering experiments, ash from a series of coals will be produced under reducing conditions (CO/CO_2) and sintered at various temperatures (1000° , 1100° , 1200° , and 1300°C) for various times. The density of the sintered masses will be determined using a pycnometer. Furthermore, the samples will be analyzed using X-ray diffraction, scanning electron microscopy, electron microprobe, and SEMPC. The detailed analysis will establish the various phases present and their relation to the sintering process. In particular, the SEMPC analysis will be used to establish the chemical composition of the component liquid phases responsible for sintering. The chemical composition will be used to predict the viscosity and surface tension of the component liquid phases.

The objectives for this year were to:

1. Complete analysis of chars from a suite of coals prepared using the pressure pyrolysis unit.
2. Continue development of a computer code (PHOEBE) and associated database for determining high-temperature complex phase equilibria.
3. Compile a surface tension data base for a wide range of alumino silicate slags.
4. Develop techniques to determine sintering behavior of coal ashes.

3.0 CHARACTERIZATION OF ASHES AND AGGLOMERATES FROM PILOT-SCALE GASIFICATION SYSTEMS

A major aspect of this project is to relate the results of the laboratory-scale studies and the modeling efforts to ash-related phenomena in pilot-scale and, in some cases, full-scale coal gasification systems. In conjunction with this project, a program to develop fluidized bed gasification for hydrogen production was undertaken at EMRC. The coals projected for use in the pilot-scale program were part of this project's test series. These coals were Martin Lake, Wyodak, Indian Head, and Velva. The pilot-scale program included the use of various bed and catalytic additives. Bed materials included limestone, sand (quartz), and trona (a sodium carbonate/bicarbonate mineral). The catalytic material used was trona.

During gasification tests with these coals and bed materials, agglomeration was observed. The agglomerates and associated bed material were sampled and analyzed. The focus of the analysis was to determine if the bed material/coal ash/catalytic material combination used was incompatible for fluidized bed gasification under the conditions used. The analysis techniques used included X-ray diffraction and SEMPC analysis. X-ray diffraction was used to determine the crystalline phase assemblage of both the non-agglomerated bed material and the associated agglomerates. Comparison of the phase assemblage indicates which phase transformations the fluidized bed components underwent during gasification and processes that occurred prior to and during the agglomeration process. Further detail of these processes is given by the SEMPC analysis. The technique quantifies the amount of the various phases present as well as indicating the distribution of chemical components. This data can be used to investigate the fundamental processes that cause agglomeration in fluidized bed gasifiers under a variety of conditions.

Various agglomerates and ashes from the hydrogen production gasifier at EMRC were collected and analyzed. Table 3 lists the results of the analysis of five samples taken from the various runs. The analyses included SEMPC and X-ray diffraction analysis. The SEMPC analysis includes the relative proportion of phases and the chemical composition of the region analyzed.

Sample 1 had a high level of unclassified points (70%). The other phases present included akermanite ($\text{Ca}_2\text{MgSi}_2\text{O}_7$ - a melilite phase), albite ($\text{NaAlSi}_3\text{O}_8$), wollastonite (calcium silicate), illite (potassium-rich aluminosilicate), iron oxide, kaolinite-derived material, periclase (MgO), montmorillonite (a calcium-rich aluminosilicate), nepheline (NaAlSiO_4), and quartz. The chemical analysis shows the sample to be rich in SiO_2 , Al_2O_3 , Fe_2O_3 , CaO , MgO , and Na_2O . More detailed study of the unclassified points showed that there was significant reaction between the silica sand particles and the sodium derived from the trona. The presence of phases such as akermanite, nepheline, and albite are consistent with low-temperature eutectic formation. The corresponding eutectic for the formation of albite is about 732°C (based on the $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ equilibrium phase diagram). This is below the nominal operating temperature of the gasifier and, hence, significant amounts of a sodium-rich liquid phase of low viscosity would be formed, which would cause the formation of troublesome agglomerates.

Sample 2 contained significant levels of albite, montmorillonite, and quartz. Only 39.7% of the points were unclassified. Examination of the montmorillonite-classified points showed that the material was also sodium-rich. As no X-ray diffraction pattern could be obtained for this phase, it was assumed to be amorphous. The chemical composition of the sample indicated that it was SiO_2 -rich. The presence of albite in the sample suggests the formation of a low-temperature eutectic below the operating temperature of the gasifier, which caused the observed agglomeration.

Sample 3 contained some akermanite, albite, hercynite (FeAl_2O_4), iron oxide, montmorillonite, and quartz. The amount of unclassified points was quite high at 78.1%. The montmorillonite, on closer examination, was observed to be sodium-rich. Once again there was no crystalline phase observed in the sample by X-ray diffraction that corresponded to the chemical composition of the montmorillonite. Hence, it can be classified as an amorphous phase. The chemical composition of the sample showed that it was SiO_2 -rich and relatively Fe_2O_3 -rich compared to Samples 1 and 2.

Sample 4 contained a very high level of unclassified points (91.9%). The only other phases observed were akermanite, albite, iron oxide, kaolinite-derived, montmorillonite, and quartz. The phase assemblage is very similar to that observed for Sample 3 and suggests that, with the exception of montmorillonite (amorphous phase), the samples were the same. This is confirmed by comparison of the chemical composition of the two samples. The chemical compositions were very similar except for the low Na_2O content of Sample 4.

Sample 5 had a different phase assemblage than the other four samples. The sample was very rich in quartz, with dicalcium silicate, wollastonite, iron oxide, kaolinite-derived, and spurrite (sodium calcium silicate carbonate). The chemical composition of the sample showed that it was very high in SiO_2 . Excluding SiO_2 , the major components are Fe_2O_3 , CaO , and Na_2O . There was very little Al_2O_3 present. The analysis suggests that the glue material

TABLE 3
PHASE ANALYSIS OF H₂ PRODUCTION AGGLOMERATES

Phase ^a	Sample				
	1	2	3	4	5
Akermanite (Ca ₂ MgSi ₂ O ₇)	4.5	0.0	0.4	0.5	0.0
Alumina (Al ₂ O ₃)	0.0	0.0	0.0	0.0	0.0
Albite (NaAlSi ₃ O ₈)	7.4	17.2	2.1	0.5	0.0
Anhydrite (CaSO ₄)	0.4	0.0	0.0	0.0	0.0
Anorthite (CaAl ₂ Si ₂ O ₈)	0.0	0.0	0.0	0.0	0.0
Ca ₂ SiO ₄	0.0	0.0	0.0	0.0	2.1
Calcite (CaCO ₃ /CaO)	0.0	0.0	0.0	0.0	0.0
Wollastonite (CaSiO ₃)	4.1	0.0	0.0	0.0	1.2
Hercynite (FeAl ₂ O ₄)	0.0	0.0	0.4	0.0	0.0
Illite	0.4	0.0	0.0	0.0	0.0
Iron Oxide	1.6	1.7	3.3	1.4	0.4
Kaolinite-Derived	1.2	0.0	0.0	0.9	1.2
Kaolinite (Al ₂ O ₃ (SiO ₂) ₂)	0.0	0.0	0.0	0.0	0.0
Melilite (Ca ₂ Al ₂ SiO ₂)	0.0	0.0	0.0	0.0	0.0
Periclase (MgO)	0.4	0.0	0.0	0.0	0.0
Montmorillonite	5.3	22.4	14.0	2.7	0.0
Nepheline (NaAlSiO ₄)	0.4	0.0	0.0	0.0	0.0
Quartz	2.1	19.0	1.7	1.4	41.7
Spurrite	0.0	0.0	0.0	0.0	0.4
Unclassified	70.0	39.7	78.1	91.9	52.9
Chemical Composition:					
SiO ₂	49.6	66.8	53.0	51.1	87.1
Al ₂ O ₃	12.1	13.9	15.5	14.1	1.1
Fe ₂ O ₃	8.3	4.7	11.3	14.2	4.2
TiO ₂	1.4	0.7	1.4	2.3	0.1
P ₂ O ₅	0.0	0.0	0.0	0.0	0.0
CaO	13.1	6.2	8.5	9.5	3.5
MgO	6.0	2.7	5.4	6.1	0.1
Na ₂ O	7.7	4.2	4.1	1.6	3.7
K ₂ O	1.0	0.8	0.8	1.2	0.2
SO ₃	0.6	0.1	0.1	0.0	0.1

^a Quantity of phase reported as weight percent.

responsible for the agglomeration was rich in sodium, calcium and silica. By removing the quartz-classified points from the SEMPC analysis, a chemical composition of the matrix can be ascertained. This showed that the matrix was rich in calcium, sodium, and silica. Reference to the appropriate phase diagram shows that the matrix material has a very low eutectic. The presence of spurrite is also interesting. This phase is associated with troublesome clinker formation in cement kilns (based on calcium silicate formation). The phase has also been observed in agglomerates formed at the Great Plains Gasification Project during a recent test with limestone addition.

4.0 PROJECT STATUS/RESULTS AND ACCOMPLISHMENTS

4.1 Task A --- Mineral Transformations

The results of the mineral transformation of ashes and model mineral mixtures have been compiled in a Lotus spreadsheet. These data were used to determine the relationship between original coal mineral contents and chemical composition with the mineral contents and chemical composition of the ashes produced under both oxidizing and reducing conditions. The relationship between ash mineral and chemical composition with the composition of slags produced under reducing conditions were also investigated. To date, there are no relationships to report.

4.2 Task B -- Volatilization Studies

The pressure pyrolysis unit was used in the experiments to produce char under simulated gasification conditions. The chars produced are analyzed by two detailed analytical techniques: computer-controlled scanning electron microscopy (CCSEM) and scanning electron microscopy point count (SEMPC).

CCSEM is used to determine the size and mineralogy of grains present in the chars and the raw coal. This technique is based on a method developed by Huffman et al. SEMPC is used to quantify the inorganic phases present in the chars. The SEMPC technique was developed at the Energy and Mineral Research Center to study ash behavior in coal utilization systems. The technique involves the quantitative analysis of about 450 random points over the surface of a suitably prepared sample. The chemical composition data for each point is analyzed by a computer program to classify the composition to 1 of 40 phases. These phases include crystalline and amorphous phases. Full details of the technique can be found elsewhere (13). The computer program also averages the chemical composition of all the points analyzed. This data is used to obtain an average (bulk) composition of the sample in addition to the composition of each individual point. The advantage of this technique over X-ray diffraction and X-ray fluorescence is that the composition and quantity of both the amorphous and crystalline points are determined separately. Furthermore, for each of the chemical compositions classified as amorphous, the program determines the base-to-acid ratio and the viscosity at 1000°C using the model developed by Kalmarovitch and Frank (14). The temperature of 1000°C was chosen since this is a reasonable temperature at which liquid phase sintering proceeds. The base-to-acid ratio is calculated for each amorphous point to obtain a measure of the relative reactivity of each composition. This ratio is widely used in the ceramic and refractory industries to predict material performance at high temperature.

The viscosity and base-to-acid ratio data distributions within each sample are represented using histograms. In the case of the base-to-acid ratio, the distribution clearly shows groups of liquid phases with different reactivity usually seen as a multimodal distribution. The importance of this data is that the area under each peak and the relative difference in base-to-acid ratio between the peaks can be related to the amount and relative reactivity, respectively, of the component liquid phases within the sample.

4.2.1 SEMPC Results

The results obtained from the test series during this reporting period are listed in Tables 4 through 9. The data include the relative amount of phases and the overall chemical composition for each of the samples analyzed by SEMPC. Each table includes data for one of the coals. In the case of the chars produced in the pressure pyrolysis unit, the SEMPC analysis was performed on low-temperature ash. SEMPC analysis was also performed on the raw coal. The data shows that the major mineral phases present are illite (a potassium-bearing aluminosilicate phase), kaolinite (aluminosilicate), quartz, and pyrite. The major chemical components are SiO_2 , Al_2O_3 , Fe_2O_3 , and SO_3 . The chemical compositions are consistent with the chemical compositions of the ashes formed under an oxidizing atmosphere.

4.2.1.1 Indian Head Coal

In the case of Indian Head coal, three chars were produced and analyzed. Char 1 has less illite than Chars 2 and 3. Char 2 had the least number of kaolinite-derived points. Kaolinite-derived points are those that have an Si/Al molar ratio corresponding to that of the kaolinite mineral (i.e., a Si/Al molar ratio of about unity) but contain other components that preclude the designation of the point as kaolinite. Furthermore, the other components are not in sufficient quantity, on a stoichiometric basis, to classify the point as that of a known mineral phase. Therefore, the point is designated as derived from a kaolinite clay particle. For our purposes, we assume that these points are amorphous. Char 1 also had less anhydrite (calcium sulfate) than Char 3, and Char 2 showed almost none. Other phases present, such as quartz, iron oxide, and montmorillonite (a calcium/sodium-rich aluminosilicate clay mineral) were present in similar concentrations in both samples. In terms of chemical composition, the two chars had very similar levels of all components on both SO_3 -inclusive and SO_3 -free bases.

4.2.1.2 Martin Lake Coal

Chars 1, 2, and 3 have been analyzed for the Martin Lake coal. The SEMPC analysis shows that the major phase was unclassified (amorphous). Kaolinite-derived points were the most dominant of the classified points. Anhydrite and quartz were also present. Only Char 3 showed illite, while only Char 1 showed spurrite. The calcium-derived points detected by this technique are predominantly calcium oxide (the presence of oxygen is assumed in this technique) with some sulfur present. The points include partially sulfated to fully sulfated lime particles. The classification of calcium-derived, therefore, includes anhydrite (calcium sulfate) but excludes calcite. This classification is useful, since for fluidized bed systems, limestone is used as a sulfur sorbent where a measure of the degree of sulfation is required. For Martin Lake coal, the chemical composition of the char samples is consistent with the chemical composition of the coal.

TABLE 4A
WYODAK CHAR AND COAL SAMPLES (SEMP)

Phase ^a	Coal	Char 1	Char 2	Char 3
Alumina	0.0	0.0	0.0	0.0
Periclase	0.0	0.0	0.0	0.0
Pyroxene	0.0	0.0	0.0	0.0
Calcite	0.0	0.4	0.0	0.4
Montmorillonite	28.6	2.5	0.7	1.2
CaSiO ₃	0.0	0.0	0.0	0.0
Mullite	0.0	0.0	0.0	0.0
Illite	0.0	0.0	0.0	0.4
Iron Oxide	0.0	10.7	8.8	0.0
Kaolinite-derived	9.5	0.8	0.7	9.0
Anhydrite	0.0	0.0	0.0	0.0
Anorthite	0.0	1.6	1.5	0.0
Albite	0.0	0.0	0.0	0.0
Quartz	33.3	3.7	3.7	7.4
Akermanite	0.0	0.0	0.0	0.0
Melilite	0.0	0.4	0.7	1.6
Nepheline	0.0	0.0	0.0	0.0
Apatite	0.0	0.0	0.0	0.0
Pyrrhotite	0.0	0.4	0.0	0.0
Spurrite	0.0	0.0	0.0	0.0
Na ₂ CaSiO ₄	0.0	0.0	0.0	0.0
Ca ₁₂ Al ₁₄ O ₃₃	0.0	0.0	0.0	0.0
Ca ₂ SiO ₄	0.0	0.0	0.0	0.0
Pyrite	0.0	0.0	0.0	0.0
Hercynite	0.0	0.0	0.0	0.0
Kaolinite (Pure)	0.0	0.0	0.0	0.0
Calcium-derived	0.0	1.2	0.7	1.6
Merwinite	0.0	0.0	0.0	0.0
Sodium Calcium Sulfate	0.0	0.0	0.0	0.0
Sodium Sulfate	0.0	0.0	0.0	0.0
Dolomite	0.0	0.0	0.0	0.0
Sulfated Dolomite	0.0	0.0	0.0	0.0
Unclassified	14.3	80.7	83.8	77.0

Chemical Composition

SiO ₂	73.5	23.5	25.8	24.3
Al ₂ O ₃	15.7	13.0	13.7	12.0
Fe ₂ O ₃	1.5	6.0	4.8	5.8
TiO ₂	0.8	1.7	1.6	1.8
P ₂ O ₅	0.8	0.9	1.0	1.3
CaO	1.6	38.4	37.0	38.2
MgO	0.8	3.4	3.5	3.4
Na ₂ O	0.2	0.1	0.1	0.1
K ₂ O	1.2	0.5	0.4	0.5
SO ₃	3.9	12.5	12.2	12.3

^a Quantity of phase reported as percent basis.

TABLE 4B
WYODAK ASH & CHAR ANALYSIS (SO₃--FREE)

	<u>Oxid. Ash</u>	<u>Red. Ash</u>	<u>Coal</u>	<u>Char 1</u>	<u>Char 2</u>	<u>Char 3</u>
SiO ₂	33.1	40.2	76.5	26.9	29.4	27.7
Al ₂ O ₃	21.3	18.3	16.3	24.9	15.6	13.7
Fe ₂ O ₃	4.4	4.2	1.6	6.9	5.5	6.6
TiO ₂	2.2	2.0	0.8	1.9	1.8	2.0
P ₂ O ₅	1.9	1.3	0.8	1.0	1.1	1.5
CaO	27.1	26.4	1.7	43.9	42.2	43.6
MgO	8.4	6.1	0.8	3.9	4.0	3.9
Na ₂ O	1.1	1.0	0.2	0.1	0.1	0.1
K ₂ O	0.3	0.3	1.3	0.6	0.5	0.6
Si/Al	1.32	1.87	3.99	1.08	1.88	2.02

TABLE 4C
WYODAK CHAR XRD ANALYSIS

<u>1</u>	<u>2</u>	<u>3</u>
Quartz (SiO ₂)M	Quartz (SiO ₂)M	Quartz (SiO ₂)M
Calcite (CaCO ₃)t	Calcite (CaCO ₃)m	Anhydrite (CaSO ₄)t
	Albite (NaAlSi ₃ O ₈)t	Calcite (CaCO ₃)t
		Unknown t

M = Major
m = Minor
t = Trace

TABLE 5A
VELVA CHAR AND COAL SAMPLES (SEMPG)

Phase ^a	Coal	Char 1	Char 2	Char 3	Char 4
Alumina	0.0	0.0	0.0	0.4	0.0
Periclase	0.0	0.5	0.4	0.9	0.0
Hauyne	0.0	0.0	0.0	0.0	0.0
Pyroxene	0.0	0.0	0.0	0.0	0.0
Calcite	5.3	17.2	0.9	2.2	1.3
Montmorillonite	0.0	1.5	0.0	0.0	10.0
CaSiO ₃	0.0	0.0	0.0	0.0	0.0
Mullite	0.0	0.0	0.0	0.0	0.0
Illite	0.0	0.5	0.0	0.0	12.2
Iron Oxide	0.0	0.5	0.0	0.4	0.0
Kaolinite-derived	0.0	3.9	11.5	7.0	3.0
Anhydrite	0.0	1.5	0.0	0.0	3.0
Analcime	0.0	0.0	0.0	0.0	0.0
Anorthite	0.0	1.5	0.0	0.0	0.0
Albite	0.0	0.0	0.0	1.7	0.0
Quartz	42.1	2.5	0.9	0.0	3.5
Akermanite	0.0	0.0	0.0	0.0	0.0
Melilite	0.0	0.0	0.0	0.0	0.0
Nepheline	0.0	0.0	0.0	0.0	0.0
Apatite	0.0	0.0	0.0	0.0	0.0
Pyrrhotite	0.0	0.0	0.0	0.0	4.3
Spurrite	0.0	0.0	0.0	0.0	0.0
Na ₂ CaSiO ₄	0.0	0.0	0.0	0.0	0.0
Ca ₁₂ Al ₁₄ O ₃₃	0.0	0.0	0.0	0.0	0.0
Ca ₂ SiO ₆	0.0	0.0	0.0	0.0	0.0
Pyrite	42.1	0.0	0.0	0.0	1.3
Hercynite	0.0	0.0	0.0	0.0	0.0
Kaolinite (Pure)	0.0	0.0	0.0	0.0	0.0
Calcium-derived	0.0	2.5	0.9	1.3	1.3
Merwinite	0.0	0.0	0.0	0.0	0.0
Sodium Calcium Sulfate	0.0	0.0	0.0	0.0	0.0
Dolomite	0.0	0.0	0.0	0.0	0.0
Sulfated Dolomite	0.0	0.0	0.0	0.0	0.0
Unclassified	10.5	71.5	85.9	87.0	63.5
Chemical Composition					
SiO ₂	36.0	15.9	14.6	16.3	31.3
Al ₂ O ₃	0.9	8.7	8.5	8.4	13.3
Fe ₂ O ₃	18.6	8.9	8.4	8.6	21.4
TiO ₂	0.1	0.4	0.5	0.5	1.1
P ₂ O ₅	0.1	0.4	0.2	0.7	0.2
CaO	2.8	49.3	52.0	49.0	4.0
MgO	0.2	5.1	5.32	5.5	0.0
Na ₂ O	0.2	0.1	0.1	0.2	0.0
K ₂ O	0.1	0.7	0.6	0.8	1.7
SO ₃	40.9	10.3	9.6	10.8	26.7

^a Phase quantity reported as weight percent.

TABLE 5B
VELVA ASH & CHAR ANALYSIS (SO₃-Free)

	<u>Oxid. Ash</u>	<u>Red. Ash</u>	<u>Coal</u>	<u>Char 1</u>	<u>Char 2</u>	<u>Char 3</u>	<u>Char 4</u>
SiO ₂	25.6	32.3	60.9	17.7	16.2	18.1	42.6
Al ₂ O ₃	12.8	13.3	1.5	9.7	9.4	9.3	18.1
Fe ₂ O ₃	7.8	7.5	31.5	9.9	9.3	9.6	29.1
TiO ₂	1.0	1.5	0.2	0.4	0.6	0.6	1.5
P ₂ O ₅	0.6	0.0	0.2	0.4	0.2	0.8	0.3
CaO	40.1	35.4	4.7	55.0	57.5	54.4	5.4
MgO	9.9	8.3	0.3	5.7	5.9	6.1	0.0
Na ₂ O	1.9	1.1	0.3	0.1	0.1	0.2	0.0
K ₂ O	0.3	0.6	0.2	0.8	0.7	0.9	2.3
Si/Al	1.70	2.06	40.6	1.55	1.46	1.65	2.00

TABLE 5C
VELVA CHAR XRD ANALYSIS

<u>1</u>	<u>2</u>	<u>3</u>
Quartz (SiO ₂)M	Quartz (SiO ₂)M	Quartz (SiO ₂)M
Calcite (CaCO ₃)m	Calcite (CaCO ₃)M	Calcite (CaCO ₃)M
	Gehlenite (Ca ₂ Al ₂ SiO ₇)t	
	Unknown t	

M = Major
m = Minor
t = Trace

TABLE 6A
INDIAN HEAD CHAR AND COAL SAMPLES (SEMPG)

Phase ^a	Coal ^b	Char 1	Char 2	Char 3
Alumina	0.0	0.0	0.0	0.0
Periclase	0.0	0.0	0.0	0.0
Pyroxene	0.0	0.0	0.0	0.0
Calcite	0.5	0.0	0.0	0.0
Montmorillonite	2.0	1.7	0.4	1.9
CaSiO ₃	0.0	0.0	0.0	0.0
Mullite	0.0	0.0	0.0	0.0
Illite	2.0	1.7	2.1	3.8
Iron Oxide	0.5	1.2	1.2	1.0
Kaolinite-derived	0.5	18.6	11.1	23.8
Anhydrite	8.4	3.3	0.4	5.7
Analcime	0.0	0.0	0.0	0.0
Albite	0.0	0.0	0.0	0.0
Quartz	4.9	2.5	1.2	2.9
Akermanite	0.0	0.0	0.0	0.0
Melilite	0.0	0.0	0.0	0.0
Nepheline	0.0	0.0	0.0	0.0
Apatite	0.0	0.0	0.0	0.0
Pyrrhotite	0.0	0.0	0.0	0.0
Spurrite	0.0	0.0	0.0	0.0
Na ₂ CaSiO ₄	0.0	0.0	0.0	0.0
Ca ₁₂ Al ₁₄	0.0	0.0	0.0	0.0
Ca ₂ SiO ₄	0.5	0.0	0.0	0.0
Pyrite	0.0	0.0	0.0	0.0
Hercynite	0.0	0.0	0.0	0.0
Kaolinite (Pure)	0.0	0.0	0.0	0.0
Calcium-derived	3.0	2.9	1.2	1.9
Merwinite	0.0	0.0	0.0	0.0
Sodium Calcium Sulfate	0.0	0.0	0.0	0.0
Sodium Sulfate	0.0	0.0	0.0	0.0
Dolomite	0.0	0.0	0.0	0.0
Sulfated Dolomite	0.0	0.0	0.0	1.9
Unclassified	80.3	70.7	82.3	62.9
Chemical Composition				
SiO ₂	29.4	25.4	22.4	27.0
Al ₂ O ₃	13.8	11.7	9.9	13.2
Fe ₂ O ₃	6.4	9.2	12.3	9.3
TiO ₂	0.5	0.7	0.6	0.8
P ₂ O ₅	0.1	0.0	0.0	0.0
CaO	20.4	28.3	32.1	27.7
MgO	6.0	3.6	2.5	4.0
Na ₂ O	2.5	0.5	0.1	0.6
K ₂ O	2.5	1.2	1.2	1.2
SO ₃	18.2	19.1	18.6	16.3

^a Quantity of phase reported on percent basis.

TABLE 6B
INDIAN HEAD ASH & CHAR ANALYSIS (SO₃-FREE)

	<u>Oxid. Ash</u>	<u>Red. Ash</u>	<u>Coal</u>	<u>Char 1</u>	<u>Char 2</u>	<u>Char 3</u>
SiO ₂	31.9	36.0	35.9	31.1	27.6	32.3
Al ₂ O ₃	14.7	15.3	16.9	14.3	12.2	15.8
Fe ₂ O ₃	10.5	10.7	7.8	11.3	15.1	11.1
TiO ₂	1.0	0.9	0.6	0.9	0.7	1.0
P ₂ O ₅	0.5	0.1	0.1	0.0	0.0	0.0
CaO	30.2	23.7	24.9	34.7	39.5	33.1
MgO	7.7	6.8	7.3	4.4	3.1	4.8
Na ₂ O	2.7	3.3	3.1	0.6	0.1	0.7
K ₂ O	0.8	1.2	3.1	1.5	1.5	1.4
Si/Al	1.84	2.00	2.09	1.84	1.92	1.73

TABLE 6C
INDIAN HEAD CHAR XRD ANALYSIS

<u>1</u>	<u>2^a</u>	<u>3</u>	<u>4^a</u>
Quartz (SiO ₂)M		Quartz (SiO ₂)M	
Calcite (CaCO ₃)m		Calcite (CaCO ₃)m	
Anhydrite (CaSO ₄)t		Unknown t	

^a Not available.

M = Major

m = Minor

t = Trace

TABLE 7A
MARTIN LAKE CHAR AND COAL SAMPLES (SEMP)

Phase ^a	Coal ^b	Char 1	Char 2	Char 3
Alumina		0.0	0.0	0.0
Periclase		0.0	0.0	0.0
Pyroxene		0.0	0.0	0.0
Calcite		0.0	0.0	0.0
Montmorillonite		0.0	0.0	0.0
CaSiO ₃		0.0	0.0	0.0
Mullite		0.0	0.0	0.0
Illite		0.0	0.0	1.1
Iron Oxide		1.3	1.4	0.0
Kaolinite-derived		13.3	12.2	18.7
Anhydrite		2.7	1.4	3.3
Analcime		0.0	0.0	0.0
Albite		0.0	2.0	0.0
Quartz		0.0	0.0	0.0
Akermanite		2.0	2.0	2.2
Melilite		0.0	1.4	0.0
Nepheline		0.0	0.0	0.0
Apatite		0.0	0.0	0.0
Pyrrhotite		0.0	0.0	0.0
Spurrite		1.3	0.0	0.0
Na ₂ CaSiO ₄		0.0	0.0	0.0
Ca ₁₂ Al ₁₄		0.0	0.0	0.0
Ca ₂ SiO ₄		0.0	0.0	0.0
Pyrite		0.0	0.0	0.0
Hercynite		0.0	0.0	0.0
Kaolinite (Pure)		0.0	0.0	0.0
Calcium-derived		0.0	0.0	0.0
Merwinite		2.0	0.0	4.4
Sodium Calcium Sulfate		0.0	0.0	0.0
Sodium Sulfate		0.0	0.0	0.0
Dolomite		0.0	0.0	0.0
Sulfated Dolomite		0.0	0.0	0.0
Unclassified		78.0	82.4	70.3
Chemical Composition				
SiO ₂		15.8	19.2	14.0
Al ₂ O ₃		10.0	11.0	10.0
Fe ₂ O ₃		12.5	9.9	7.6
TiO ₂		1.2	0.9	0.9
CaO		34.7	33.5	36.3
MgO		3.1	3.9	4.3
Na ₂ O		0.0	0.1	0.1
K ₂		0.2	0.2	0.2
SO ₃		22.2	---	---

^a Quantity of phase reported as weight percent.

TABLE 7B
MARTIN LAKE ASH & CHAR ANALYSIS (SO₃-FREE)

	<u>Oxid. Ash</u>	<u>Red. Ash</u>	<u>Coal</u> ^a	<u>Char 1</u>	<u>Char 2</u>	<u>Char 3</u>
SiO ₂	38.7	29.0		20.3	24.3	19.1
Al ₂ O ₃	15.3	17.7		12.9	13.9	13.6
Fe ₂ O ₃	10.7	6.7		16.1	12.5	10.4
TiO ₂	1.0	1.6		1.5	1.2	1.2
P ₂ O ₅	0.0	1.0		0.0	0.3	0.0
CaO	24.0	31.5		44.6	42.4	49.5
MgO	6.8	9.2		4.0	4.9	5.9
Na ₂ O	2.6	1.1		0.0	0.1	0.1
K ₂ O	0.8	0.1		0.3	0.3	0.3
Si/Al	2.15	1.39		1.57	1.75	1.40

TABLE 7C
MARTIN LAKE CHAR XRD ANALYSIS

<u>1</u>	<u>2</u> ^a	<u>3</u>
Quartz (SiO ₂)M		Quartz (SiO ₂)M
Calcite (CaCO ₃)m		Calcite (CaCO ₃)m
Bassinite (Ca ₂ (SO ₄) ₂ H ₂ O)m		Gehlenite (Ca ₂ Al ₂ SiO ₇)t
		Bassinite (Ca ₂ (SO ₄) ₂ H ₂ O)t

M = Major
m = Minor
t = Trace

TABLE 8A

ILLINOIS NO. 6 (OLD BEN) COAL AND CHAR SAMPLES (SEMPG)

Phase ^a	Coal	1	2	3
Alumina	0.0	0.0	0.0	0.0
Periclase	0.0	0.0	0.0	0.0
Pyroxene	0.0	0.0	0.0	0.0
Calcite	1.8	1.0	0.0	0.0
Montmorillonite	0.8	11.5	14.4	9.3
CaSiO ₃	1.8	0.0	0.0	0.0
Mullite	0.0	0.0	0.0	0.0
Illite	29.8	16.7	18.3	2.2
Iron Oxide	1.8	1.0	3.3	3.1
Kaolinite-derived	7.0	1.0	0.0	0.0
Anhydrite	1.8	16.7	7.2	9.7
Analcime	0.0	0.0	0.0	0.0
Anorthite	0.0	0.0	0.0	0.0
Albite	1.8	0.0	0.0	0.0
Quartz	21.1	12.5	7.8	4.8
Akermanite	0.0	0.0	0.0	0.0
Melilite	0.0	0.0	0.0	0.0
Nepheline	0.0	0.0	0.0	0.0
Apatite	0.0	0.0	0.0	0.0
Pyrrhotite	0.0	3.1	3.3	0.9
Spurrite	0.0	0.0	0.0	0.0
Na ₂ CaSiO ₄	0.0	0.0	0.0	0.0
Ca ₁₂ Al ₁₄ O ₃₃	0.0	0.0	0.0	0.0
Ca ₂ SiO ₄	0.0	0.0	0.0	0.0
Pyrite	7.0	0.0	0.0	0.0
Hercynite	0.0	0.0	0.0	0.0
Kaolinite (Pure)	3.5	0.0	0.0	0.0
Calcium-derived	3.5	5.2	3.9	0.0
Merwinite	0.0	0.0	0.0	0.0
Sodium Calcium Sulfate	0.0	0.0	0.0	0.0
Sodium Sulfate	0.0	0.0	0.0	0.0
Dolomite	0.0	0.0	0.0	0.0
Sulfated Dolomite	0.0	0.0	0.0	0.0
Unclassified	21.1	49.0	46.7	70.9
Chemical Composition				
SiO ₂	48.8	49.2	43.3	44.1
Al ₂ O ₃	14.8	15.2	14.3	12.2
Fe ₂ O ₃	10.8	11.5	14.9	15.3
TiO ₂	0.2	0.6	1.4	1.4
P ₂ O ₅	0.3	0.0	0.1	0.5
CaO	2.9	5.4	6.9	5.2
MgO	1.0	0.1	0.1	0.6
Na ₂ O	1.0	0.2	0.1	0.1
K ₂ O	2.9	4.0	3.5	5.6
SO ₃	17.3	13.9	15.2	14.7

^a Quantity of phase reported as weight percent.

TABLE 8B

ILLINOIS NO. 6 (OLD BEN) ASH & CHAR ANALYSIS (SO₃-Free Basis)

	<u>Oxid. Ash</u>	<u>Red. Ash</u>	<u>Coal</u>	<u>Char 1</u>	<u>Char 2</u>	<u>Char 3</u>
SiO ₂	50.8	53.4	59.0	57.1	51.1	51.7
Al ₂ O ₃	20.1	20.1	17.9	17.6	16.9	14.3
Fe ₂ O ₃	17.3	14.1	13.1	13.3	17.6	17.9
TiO ₂	1.2	1.2	0.2	0.7	1.6	1.6
P ₂ O ₅	0.3	0.3	0.4	0.0	0.1	0.6
CaO	5.4	5.3	3.5	6.3	8.1	6.1
MgO	1.2	1.5	1.2	0.1	0.1	0.7
Na ₂ O	0.6	0.7	1.2	0.2	0.1	0.1
K ₂ O	3.1	3.4	3.5	4.6	4.1	6.6
Si/Al	2.26	2.66	3.30	3.24	3.02	3.62

^a Not available.

TABLE 9A
PITTSBURGH #8 CHAR AND COAL SAMPLES (SEMPG)

Phase ^a	Coal	Char 1	Char 2	Char 3	Char 4
Alumina	0.0	0.0	0.0	0.0	0.0
Periclase	0.0	0.0	0.0	0.0	0.0
Pyroxene	0.0	0.0	0.0	0.0	0.0
Calcite	0.8	0.0	0.0	0.4	0.0
Montmorillonite	7.0	20.2	22.7	28.0	26.9
CaSiO ₃	0.0	0.0	0.0	0.0	0.0
Mullite	0.0	0.0	0.0	0.0	0.0
Illite	6.2	24.7	20.1	27.6	25.0
Iron Oxide	0.0	0.4	1.5	1.2	1.4
Kaolinite-derived	0.0	0.8	1.0	0.4	1.9
Anhydrite	8.3	10.7	9.8	18.5	12.7
Anorthite	0.0	0.0	0.0	0.0	0.0
Albite	0.0	0.0	0.0	0.0	0.0
Quartz	14.9	7.8	7.2	3.7	4.2
Akermanite	0.0	0.0	0.0	0.0	0.0
Melilite	0.0	0.0	0.0	0.0	0.0
Nepheline	0.0	0.0	0.0	0.0	0.0
Apatite	0.4	0.0	0.0	0.0	0.0
Pyrrhotite	0.0	0.8	3.6	2.1	2.4
Spurrite	0.0	0.0	0.0	0.0	0.0
Na ₂ CaSiO ₄	0.0	0.0	0.0	0.0	0.0
Ca ₁₂ Al ₁₄ O ₃₃	0.0	0.0	0.0	0.0	0.0
Ca ₂ SiO ₄	0.0	0.0	0.0	0.0	0.0
Pyrite	0.0	0.0	0.0	0.0	0.0
Hercynite	0.0	0.0	0.0	0.0	0.0
Kaolinite (Pure)	0.0	0.0	0.0	0.0	0.0
Calcium-derived	0.0	0.8	0.6	0.4	0.9
Merwinite	0.0	0.0	0.0	0.0	0.0
Sodium Calcium Sulfate	0.0	0.0	0.0	0.0	0.0
Sodium Sulfate	0.0	0.0	0.0	0.0	0.0
Dolomite	0.0	0.0	0.0	0.0	0.0
Sulfated Dolomite	0.0	0.0	0.0	0.0	0.0
Unclassified	61.6	44.9	31.4	35.0	40.1
Chemical Composition					
SiO ₂	50.2	49.8	45.6	45.4	41.3
Al ₂ O ₃	12.3	18.7	17.2	18.9	17.1
Fe ₂ O ₃	10.2	9.5	11.9	13.6	15.3
TiO ₂	1.34	1.2	1.4	1.3	1.4
P ₂ O ₅	0.54	0.1	0.1	0.0	0.1
CaO	6.05	4.3	5.4	4.7	5.4
MgO	0.34	0.0	0.1	0.0	0.0
Na ₂ O	0.05	0.0	0.0	0.0	0.0
K ₂ O	5.17	3.3	2.9	3.2	3.2
SO ₃	13.6	13.0	15.3	12.6	16.0

^a Quantity of phase reported as weight percent.

TABLE 9B
PITTSBURGH #8 ASH & CHAR ANALYSIS (SO₃-FREE BASIS)

	<u>Oxid. Ash</u>	<u>Red. Ash</u>	<u>Coal</u>	<u>Char 1</u>	<u>Char 2</u>	<u>Char 3</u>	<u>Char 4</u>
SiO ₂	51.1	51.3	58.2	58.8	53.8	51.8	49.1
Al ₂ O ₃	22.0	20.4	14.3	22.1	20.3	21.9	20.3
Fe ₂ O ₃	17.1	17.7	11.8	11.2	14.1	15.5	18.2
TiO ₂	1.1	1.2	1.6	1.4	1.6	1.5	1.7
P ₂ O ₅	0.4	0.3	0.6	0.1	0.1	0.0	0.1
CaO	4.3	5.3	7.0	5.1	6.4	5.4	6.4
MgO	1.5	1.3	0.4	0.0	0.1	0.0	0.0
Na ₂ O	0.0	0.0	0.1	0.0	0.0	0.0	0.0
K ₂ O	2.5	2.5	6.0	3.9	3.4	3.6	3.8
Si/Al	1.97	2.14	4.07	2.26	2.25	2.01	2.06

^a Phases reported as weight percent.

TABLE 9C
PITTSBURGH #8 CHAR XRD ANALYSIS

<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>
Quartz (SiO ₂)M	Quartz (SiO ₂)M	Quartz (SiO ₂)M	Quartz (SiO ₂)
Pyrite (FeS ₂)†		Anhydrite (CaSO ₄)†	Anhydrite (CaSO ₄)†
Melilite (Ca ₂ Al ₂ Si ₂ O ₇)†		Gehlenite (Ca ₂ Al ₂ SiO ₇)†	Gehlenite (Ca ₂ Al ₂ SiO ₇)†
	Pyrrhotite (FeS)†	Unknown †	Iron Sulfide (FeS)†
			Unknown †

M = Major
m = Minor
t = Trace

4.2.1.3 Velva Coal

All of the Velva chars have been analyzed by the SEMPC technique. The coal contained quartz, pyrite, and calcite as discernible mineral phases. The amount of unclassified points was relatively small (10.5%). The char, however, had a very high level of unclassified points. Phases detected in the char include calcite, iron oxide, kaolinite-derived, quartz, periclase (MgO), and calcium-derived. With respect of the calcium-derived phases, note that no anhydrite was observed in this sample. Comparison of the chemical composition of the coal with the char shows great discrepancy. The chemical composition of the coal was based on the average analysis of the coal minerals and does not include the organically bound elements such as Ca and Mg. The char contains high levels of CaO and MgO compared to the coal. This indicates that the bulk of these elements were bound in the organic fraction of the coal and reacted with the other ash elements during pyrolysis of the coal.

4.2.1.4 Wyodak Coal

Both the Wyodak coal and Char 3 have been analyzed by SEMPC. The raw coal contained montmorillonite clay (mixed-layer, calcium-bearing clay), kaolinite-derived material (probably impure kaolinite), and quartz. About 14% of the points were unclassified. Char 3, however, contained some montmorillonite, some illite (potassium-rich aluminosilicate), iron oxide, less quartz, and more kaolinite-derived points than the raw coal. Of interest is the presence of anhydrite, pyrrhotite (FeS), and albite ($\text{NaAlSi}_3\text{O}_8$) in the char. The albite is a product of a high-temperature reaction between aluminosilicate, quartz, and sodium. Indeed, the presence of albite is indicative of a melt or glassy phase being present. The char, overall, did not have a very high level of unclassified points compared to the other chars analyzed. With respect to the chemical composition of the coal minerals and the char, both samples had similar Al_2O_3 , K_2O , and MgO contents. The coal had higher SiO_2 than the char; all other components were lower than char. The iron oxide content of the coal was much lower than the char. In terms of chemical composition of the coal and char with respect to the oxidized and reduced ashes, there were marked differences. The laboratory-prepared ashes were low in SiO_2 , K_2O , and Fe_2O_3 compared to the char. The ashes also had higher CaO and MgO contents than the char.

It would be premature to speculate on the effect of pressure pyrolysis of the coal on the chemical and mineral composition of the char. However, major differences have been observed between the laboratory-prepared ashes, the raw coal and the chars. Further analysis of the data will be made when more data is available.

4.2.2 CCSEM Results

4.2.2.1 Martin Lake Char CCSEM Data

The CCSEM results of the two Martin Lake chars are summarized in Table 10. The two chars (Char 2 produced at 850°C-ambient pressure and Char 2 produced at 850°C-200 psi) show that pressure has a major effect on the size and mineralogy of the sample. The results of the CCSEM analysis of Martin Lake Char 2 and Char 3 show that the higher temperature used in the

TABLE 10
CCSEM DATA: MARTIN LAKE CHAR

<u>Distribution of Mineral Phases - Percent</u>		
	<u>Char 2</u>	<u>Char 3</u>
% Quartz	15.1	19.4
% Aluminosilicate	52.4	41.8
% K-Aluminosilicate	0.7	0.4
% Ca-Aluminosilicate	3.3	5.5
% Sodium Aluminosilicate	0.7	1.2
% Iron Aluminosilicate	0.7	2.4
% Iron Oxide	0	1
% Ankerite	0	0.4
% Rutile	0	0
% Calcium Silicate	0.2	1
% Pyrite	5.9	1.6
% Gypsum	5.6	6.7
% Gypsum/Barite	0.1	0
% Aluminosilicate/Gypsum	4.1	5.3
% Unknown	10.7	13.3

<u>Size Distribution (Microns) of Major Minerals in Martin Lake Chars</u>						
% In Each Size Bin:	<u><1.2</u>	<u>1.2-2.1</u>	<u>2.1-4.0</u>	<u>4.0-6.0</u>	<u>6.0-11.0</u>	<u>>11.0</u>
Quartz Char 2	0.0	5.3	32.7	7.3	38.0	15.3
Quartz Char 3	0.9	7.4	35.2	27.0	29.6	0.0
Aluminosilicate Char 2	0.2	4.6	25.2	18.5	28.1	23.5
Aluminosilicate Char 3	1.2	10.4	44.3	15.7	22.4	6.0
Ca Al-Silicate Char 2	0.0	17.6	35.3	17.6	29.4	0.0
Ca Al-Silicate Char 3	2.2	19.6	41.3	0.0	37.0	0.0
Fe Al-Silicate Char 3	3.7	7.4	33.3	18.5	37.0	0.0
Na Al-Silicate Char 3	0.0	11.1	88.9	0.0	0.0	0.0
Pyrite Char 2	0.0	4.9	26.2	18.0	34.4	16.4
Pyrite Char 3	0.0	11.1	61.1	27.8	0.0	0.0

preparation of Char 3 caused a major change in size and chemistry of mineral inclusions. Table 10 compares the mineralogy as a percent of total minerals observed. The major differences were observed with the aluminosilicate and pyrite mineral phases. There was a marked decrease in the percent aluminosilicate observed for Char 3 and a corresponding increase in amount of Ca-, Na-, and Fe-aluminosilicate phases. Char 3 also had much less pyrite. There was also more iron oxide and calcium silicate observed in Char 3 as compared to Char 2.

The CCSEM data also includes the size distribution of the minerals observed. Table 10 compares the size distribution of quartz aluminosilicate phases and pyrite for the two char samples. The data shows that the large grains tend to be absent in Char 3 compared to Char 2. The bulk of the Na-, Ca-, and Fe- tend to be present in the <6.0 micrometers size range. The pyrite in Char 2 tended to be much larger than the pyrite in Char 3. There was no pyrite observed in the size range above 6.0 microns for Char 3, whereas about 50% of the pyrite was present in the size range above 6.0 microns for Char 2.

The presence of smaller mineral grains in Char 3 compared to Char 2 observed for Martin Lake is quite significant in terms of gasifier operation. The data indicates that with the higher temperature smaller ash particles would be formed. This process may lead to a higher proportion of ash to be gas-entrained as well as the facilitation of sintering processes. The rate of sintering is inversely proportional to the radius of the particles.

Table 11 lists the chemical composition of the chars from Pittsburgh #8 and Velva. The table includes both the bulk chemical analysis and the average composition of the amorphous or liquid phases on a sulfate-free basis. The sulfate-free basis is calculated by subtracting the equivalent amount of Ca, Mg, K, or Fe that would be bound to S.

The bulk composition of the Pittsburgh #8 ashes show marked variation with respect to SiO_2 , Al_2O_3 , and Fe_2O_3 . A significant feature is the low K_2O observed for Char 4 and the very high Fe_2O_3 content in Char 4. The average composition of the liquid phases for Chars 1, 2, and 3 are very similar. Char 4 has much higher Fe_2O_3 and lower K_2 than Chars 1-3.

4.2.3 Base-to-Acid Ratio

SEMPC was rerun with improved mineral criteria on Pittsburgh #8 and Velva char samples 1 through 4. The data are quite complex and require some detailed interpretation. Table 9 lists the phase assemblage observed for Pittsburgh #8. Apart from a trace amount of anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$) observed in Char 1, no crystalline silicate, aluminate, or aluminosilicate phase was observed in any of the char samples. Quartz was, however, present in all of the chars. The amount of quartz was about the same for Chars 1 and 2 (7.8% and 8.1%, respectively) and about the same for Chars 3 and 4 (3.7% and 3.5%, respectively). Chars 2 and 3 had somewhat higher iron oxide levels than Chars 1 and 2. Char 4 had significantly more calcium oxide than the other chars.

TABLE 11
CHEMICAL COMPOSITION OF CHARS (FROM SEMPC)

	Chemical Composition, Wt%									
	<u>SiO₂</u>	<u>Al₂O₃</u>	<u>Fe₂O₃</u>	<u>TiO₂</u>	<u>P₂O₅</u>	<u>CaO</u>	<u>MgO</u>	<u>Na₂O</u>	<u>K₂O</u>	<u>SO₃</u>
<u>Pittsburgh #8 (Bulk)</u>										
Coal	48.7	23.0	7.2	2.0	0.0	3.1	0.2	0.7	3.5	11.6
Char 1	49.8	18.7	9.5	1.2	0.1	4.3	0.0	0.0	3.3	13.0
Char 2	45.6	17.2	11.9	1.4	0.1	5.4	0.1	0.0	2.9	15.3
Char 3	45.5	18.9	13.6	1.3	0.0	4.7	0.0	0.0	3.2	12.6
Char 4	31.4	13.3	21.4	1.2	0.2	4.0	0.0	0.0	1.7	26.8
<u>Pittsburgh #8 (Amorphous Phase Sulfate-Free)</u>										
Coal	58.2	27.5	6.8	2.2	0.0	0.0	0.2	0.8	4.3	0.0
Char 1	58.0	25.1	10.0	1.6	0.1	0.6	0.0	0.1	4.4	0.1
Char 2	56.4	24.7	10.9	2.1	0.1	1.4	0.1	0.0	4.2	0.0
Char 3	55.3	24.8	12.5	1.7	0.0	1.3	0.0	0.0	4.2	0.1
Char 4	50.8	23.1	20.0	2.1	0.4	0.5	0.1	0.0	3.0	0.0
<u>Velva (Bulk)</u>										
Coal	36.0	0.9	18.5	0.1	0.1	2.8	0.2	0.2	0.1	40.8
Char 1	15.9	8.6	8.8	0.4	0.4	48.8	5.1	0.1	0.7	10.3
Char 2	14.7	8.5	8.4	0.5	0.2	51.8	5.3	0.1	0.6	9.6
Char 3	16.2	8.4	8.5	0.5	0.7	48.6	5.4	0.2	0.8	9.9
Char 4	20	11.9	7.1	2.1	0.4	35.9	2.3	0.3	2.1	17.7
<u>Velva (Amorphous Phase Sulfate-Free)</u>										
Coal	Not Applicable									
Char 1	33.0	14.8	9.0	0.7	0.1	35.7	4.4	0.3	1.9	0.1
Char 2	25.1	11.5	9.4	0.7	0.0	46.5	5.8	0.2	0.7	0.1
Char 3	26.8	12.0	9.4	0.4	0.1	44.4	5.5	0.4	0.9	0.1
Char 4	34.6	21.5	8.0	3.1	0.3	26.2	2.7	0.6	2.8	0.1

Anhydrite (CaSO₄) was observed in only Chars 2 and 4; however, the level of anhydrite was low. There was marked variation in the amount of pyrite (FeS₂) observed in the samples. Char 1 had only 0.8% pyrite present, and no pyrite was detected in Char 3. Chars 2 and 4, however, had 4% and 8.7% pyrite, respectively. Pyrrhotite (FeS) was observed in Chars 1, 3, and 4. Char 4 had the greatest amount of pyrrhotite from sulfate [Fe₂(SO₄)₃] was observed in Char 4 only.

The last group of phases in Table 9 includes all of the phases unclassified and designated amorphous phases. Indeed, for our analysis, the unclassified phases are treated as amorphous. The unclassified points are those that do not have a chemical composition that corresponds to a crystalline phase common to coal ash systems.

The level of unclassified material was remarkably similar for all four char samples. Kaolinite was observed in all samples. Illite, a potassium-rich aluminosilicate phase was observed in all samples. However, there was significant variation in the levels of illite, with Char 4 having the least (2.2%) and Char 3 having the greatest (9.9%).

The SEMPC results for the Velva chars are summarized in Table 5. The data is very different than that observed for Pittsburgh #8 chars. Significant amounts of aluminosilicate phases were observed in all chars. However, marked differences were observed in the levels of the aluminosilicate and silicate phases. Char 4 showed the greatest difference with anorthite, pyroxene $[(Ca,Mg,Fe)_2Si_2O_6]$, wollastonite $[(Ca,Mg,Fe)SiO_3]$, and Na_2CaSiO_4 observed.

Quartz was observed in all four chars. Chars 1 and 4 had similar levels (2.5% and 2.9%, respectively), and Chars 2 and 3 also had similar levels (10.9% and 13%, respectively). Iron oxide was observed in only Chars 1 and 3 (0.9% and 0.4%). There was marked variation in the amount of calcium oxide observed in the samples. Char 1 had a significant level of 11.8%, while Chars 2 and 3 had 3.4% and 4.3%, respectively. No calcium oxide was observed in Char 4. Ankerite $(Ca,Mg,Fe)CO_3$ was observed in all the samples, with Char 4 having the greatest level. Char 1 had 0.5% anhydrite present. No other sulfate or sulfide phases were observed in the chars.

There were differences observed in the amount of amorphous material in the char samples. Char 1 had only 82.3% amorphous phases, whereas the other char samples had over 90% amorphous phases.

The SEMPC data is also used to determine the chemical composition of the sample. Furthermore, it is used to obtain the average composition of the amorphous phases in the sample. The composition is calculated on a sulfate-free basis, as we are concerned with the aluminosilicate matrix. The sulfate-free composition is calculated by taking the equivalent amount of calcium, sodium, or potassium that is associated with the sulfur. Table 8 summarizes the chemical composition data for Pittsburgh #8 and Velva coals and chars. The data shows that there are marked differences in the composition of the bulk coal sample compared to the char samples and differences in the chemical composition of both the bulk sample and the amorphous phase with respect to the pressure pyrolysis conditions. The Pittsburgh #8 sample showed differences with respect to the levels of Fe, Ca, and K. Indeed, there is some evidence of loss of potassium during the preparation of Char 4.

The Velva samples also showed major differences in terms of the chemical composition of both the bulk and amorphous phases. The differences were more marked than with Pittsburgh #8, with variation observed in nearly all the major components such as SiO_2 and CaO .

4.2.4 Summary

The CCSEM and SEMPC data given above is a small sample of that obtained for the project to date. The major point to make is that the characterization data obtained from these techniques show that major transformations occur in terms of the size, mineralogy, and chemistry of the coal inorganics under gasification conditions. Careful analysis of the data obtained to date has revealed limited trends in terms of behavior. This precludes the accurate prediction of the characteristics of the ash species formed during gasification at this stage. However, the CCSEM and SEMPC data can be used to obtain insight into the behavior of ash species. Further interpretation of the data is needed to be able to predict the behavior of the coal inorganics in a gasification system.

As mentioned above, the SEMPC data is used to examine the reactivity and viscosity of the amorphous phases in the samples. This data is important in order to relate the transformations that occurred during char formation in the pressure pyrolysis unit (PPU) and the behavior of the ash species formed with respect to sintering. Figures 5A through 9B are histograms of the viscosity and base-to-acid ratios of the amorphous phases present in the char samples from Velva, Pittsburgh #8, Wyodak, Illinois #6, and Indian Head chars, respectively. The observations are as follows:

4.2.4.1 Velva

Chars 1 and 2 have very similar viscosity distributions (calculated at 1000°C). Char 1 appears to have a slightly higher proportion of liquid phases with high viscosities. Char 4, however, shows a marked difference compared to the other chars. The bulk of the liquid phases for Char 4 are above $\log_{10} 6.0$. This indicates that the liquid phases formed under Char 4 conditions would exhibit lower sintering. The base-to-acid distribution, Figure 5B, shows that the three chars had very different potential for liquid phase sintering. Char 1 shows a relatively flat distribution, with values between 1 and 8. Char 2, while showing approximately the same spread of values as Char 1, had a Gaussian distribution, with a peak at about 3.5. Char 4 had a large peak at 1.0, with no significant peaks at other base-to-acid ratios. The results show that the relative reactivity of liquid phases would be in the order

Char 1 > Char 2 >> Char 4

4.2.4.2 Pittsburgh #8

The viscosity and base-to-acid distributions for this coal include data obtained from the SEMPC analysis of LTA from the raw coal. In general, the viscosity distribution (Figure 6A) shows very little difference between the chars. The distributions are Gaussian, with a peak at $\log 9.0$. The coal ash did not have a Gaussian distribution. The base-to-acid distributions (Figure 6B) show no variation with PPU condition. All char samples had peaks at 1.0.

The data indicate that under the PPU conditions used, the liquid phases formed from the Pittsburgh #8 coal do not have characteristics that would facilitate sintering processes.

Figure 5A. PPU Velva chars -- viscosity distribution at 1000°C.

Figure 5B. PPU Velva chars -- base-to-acid distribution.

Figure 6A. PPU Pittsburgh #8 chars -- viscosity distribution at 1000°C.

Figure 6B. PPU Pittsburgh #8 chars -- base-to-acid distribution.

Figure 7A. PPU Wyodak chars -- viscosity distribution at 1000°C.

Figure 7B. PPU Wyodak chars -- base-to-acid distribution.

Figure 8A. PPU Illinois #6 chars -- viscosity distribution at 1000°C.

Figure 8B. PPU Illinois #6 chars -- base-to-acid distribution.

Figure 9A. PPU Indian Head chars -- viscosity distribution at 1000°C.

Figure 9B. PPU Indian Head chars -- base-to-acid distribution.

4.2.4.3 Wyodak

The viscosity distribution for Wyodak is shown in Figure 7A. The distribution includes the chars as well as the coal LTA. The distributions for the chars are all Gaussian, with a peak at log 2.0. There appears to be very little variation of viscosity distribution with PPU conditions. However, the low viscosity would indicate that all the samples would have a high potential for liquid phase sintering.

The base-to-acid ratio distributions for the chars are also very similar. The spread of values are between 1 and 7. There is slight variation in position of the peak value.

The data for the Wyodak chars indicates that gasification processes will for ash particles which will have characteristics amenable to viscous flow sintering. The actual characteristics tend to be insensitive with respect to atmosphere and temperature.

4.2.4.4 Illinois #6

The viscosity distributions of Chars 1, 2, and 4 formed from Illinois #6 are shown in Figure 8A. All the distributions are Gaussian. Chars 1 and 2 have peaks at log 9.0, and Char 4 peaked at log 7.0. Furthermore, Char 4 appears to have a higher level of low viscosity liquid phases.

The base-to-acid distributions (Figure 8B) show that the liquid phases have very similar ratios. About 90% of the liquid phases for each of the chars have base-to-acid ratios of 1.0. There is very little spread of values. Char 4, however, shows a greater spread of values.

The data indicate that the liquid ash species formed from Illinois #6 have characteristics which will not readily participate in viscous flow sintering processes. However, an effect was noted with respect to PPU condition, indicating that the more extreme the gasification condition, the greater will be the propensity for ash to sinter.

4.3 Task C -- Physical Properties

4.3.1 Discussion/Descriptive Models

The behavior of coal inorganic constituents during coal gasification is quite complex. Figure 10 is a simplified schematic of the general behavior of the inorganics during gasification. The partitioning of inorganic components with respect to ash-entrained or gas-entrained species is particularly important. It is critical to the proper operation of the gasifier that the level of gas-entrained inorganic species is kept to a minimum because they can cause serious deposition/corrosion problems in downstream regions of the gasifier. With respect to the ash-entrained species, it is very important that the bulk of the ash be retained in the form required for efficient ash removal. The ash form depends on the design of the gasifier. For example, slagging gasifiers require the formation of a homogeneous melt phase from the ash, while fluidized bed gasifiers require that only limited interaction between ash particles and bed material occurs in order to maintain fluidization.

DESCRIPTIVE MODEL OF INORGANIC BEHAVIOR

- ① Required to form with bulk of ash – limited in size
- ② Required to exhibit limited agglomeration
- ③ Required to capture bulk of ash and to have proper flow characteristics
- ④ Formed from organically bound elements
- ⑤ Formed from fragmentation of minerals or from finely dispensed minerals

Figure 10. Descriptive model of inorganic behavior.

In general, the behavior of the ash-entrained inorganic species and the deposition phenomena associated with the gas-entrained species can be expressed as a function of liquid phase sintering. Slags, for example, are a product of extensive liquid phase sintering. Clinkers formed in Lurgi-type gasifiers have been shown by Kalmanovitch (13) to be formed by the presence and behavior of liquid phases. Because of the importance of liquid phase sintering in ash behavior for coal gasifiers, the development of a model to describe this behavior is required.

4.3.1.1 Sintering

The sintering relationship derived by Frenkel (6) is often used to describe the sintering of coal ash (Raask (2)). Simply stated, for two spherical particles of radius (r), the development of strength (s) with time (t) is given by:

$$ds/dt = (3 \gamma K)/2 \eta r \text{ at constant temperature (T)} \quad [4]$$

where γ and η are the surface tension and viscosity of the liquid phases, respectively, and k is a constant.

While this relationship is useful, it does not provide sufficient insight into the behavior of ash under the dynamic conditions observed in a gasifier. Figure 11 shows the key processes that coal inorganic constituents undergo to form particles that will sinter. The first stage involves transformations of coal minerals and inorganic constituents to form ash precursors that are still associated with the char particles. After char burnout, the ash particle formed is a product of the original mineral grain, local inorganic constituents, and local atmospheric and temperature conditions. For simplicity, it has been assumed in the schematic that the ash forms a molten surface phase. It must be stressed that the composition of the liquid phase may not necessarily have the same composition as the solid material.

In order for sintering to occur, adjacent particles must come into contact with each other and remain in contact for a sufficient time. For two particles, A and B, surrounded by liquid phases A1 and B1, respectively, the probability of adhesion occurring is a function of the reciprocal surface tension of the liquid phases. Of course, other factors, such as the particle trajectory, momentum, and amount of liquid phase present, also contribute to the sintering process. Nevertheless, without the "sticky" nature of a liquid phase on the surfaces of the particles, there would be no adhesion.

Once the particles have adhered, sintering proceeds by viscous flow mechanisms. This involves the flow of liquid from convex surfaces to concave surfaces, causing the formation of a "neck" between the two particles. The formation of the neck is facilitated by high surface tension and low viscosity of the liquid phase. This is, in effect, the sintering model according to Frenkel. The driving force for the sintering process is the lower surface energy of a consolidated mass compared to that of a powder. For complex heterogeneous systems, such as coal ash, other factors must be considered. These factors include the difference between the amount and chemistry of the

DEVELOPMENT OF STRENGTH THROUGH SINTERING (VISCOUS FLOW)

Three Types of Driving Force

$\Delta G_{S,A}$ = Lowering of total surface area

$\Delta G_{A,B}$ = Reaction between liquids A & B

$\Delta G_{M,A,B}$ = Free energy of mixing

$$\Delta G_{A,B} \gg \Delta G_{M,A,B} > \Delta G_{S,A}$$

AB_l and A_l will tend to react with B_l and B_s (and vice versa)

→ More melting

→ More Liquid phase

→ More sintering

Figure 11. Sintering model -- key to processes involving inorganics.

liquid phases present and the surfaces of particles. Two liquids, if miscible, will have a lower free energy when combined than as individual components due to the release of the free energy of mixing. The lower free energy of the combined liquids facilitates the movement of the liquid phases during sintering, provided that the viscosities and diffusion coefficients are suitable. The degree to which the free energy is lowered will depend on the chemical composition and the amount of the liquid phases present. Liquid phases that react to form a new liquid phase have a greater effect on the sintering than those that mix with no chemical reaction. The energy released during the sintering process is much greater in the case of reacting liquids than those that are simply miscible. Driving forces for the sintering process are shown in Figure 12. The presence of reactive liquid phases also has other effects. The product liquid phase AB1 will tend to be more reactive to the solid in particles A and B than the liquid phases A1 and B1. The reaction between the liquid phase AB1 and the solid particles will increase the amount of liquid phase present, which will further facilitate the sintering process. The relative reactivity of the liquid phases is, of course, a function of their chemical composition.

Thus the following parameters must be considered in order to gain sufficient insight into the sintering behavior of coal ash:

- 1) the amount of liquid phases
- 2) the surface tension of the liquid phases
- 3) the viscosity of the liquid phases
- 4) the chemical composition of the liquid phases
- 5) the relative reactivity of the liquid phases
- 6) the size of the sintering particles

It should be stressed that to study these parameters, more detailed techniques are required because the necessary data cannot be obtained by bulk analytical techniques such as X-ray diffraction and X-ray fluorescence.

Therefore, based on the description of the various processes involving coal inorganics during gasification, the main objective of the project is to determine the effects of the distribution of inorganic constituents in coal feedstocks (and the effects of gasification conditions) on the partitioning of inorganic species, and other physical factors that affect the sintering behavior of the ash species formed and the subsequent operation of a gasifier. This goal will be accomplished by the measurement of physical properties and the detailed characterization of chars prepared under simulated gasification conditions.

4.3.2 Conclusion: Application to Gasification Systems

The most important goal of this study is to apply the results and models developed to full-scale gasifier systems. Because of the complexity of the results obtained by measurement of physical properties and detailed characterization of chars produced in simulated gasification environments, it is clear that initiating the development of a numerical model describing coal ash behavior in gasifiers at this time would be premature.

SINTERING MODEL

KEY TO PROCESSES INVOLVING INORGANICS

Figure 12. Development of strength through sintering (viscous flow).

However, there is sufficient data to develop and use a combination of both descriptive models and well-chosen experiments to give insight into coal ash behavior in gasifiers. The descriptive models of ash behavior in a gasifier directly use the data from detailed characterization (using CCSEM and SEMPC) of both the feedstock and the ash and char material formed under the experimental conditions. The models developed to date have focused on the change in chemical composition, mineralogy, and size of the inorganic constituents of coal, char, and ash as a function of atmospheric and temperature conditions. A particular emphasis has been placed on the sintering of ash species formed and the effect of gasifier conditions on the sintering behavior. Other studies have focused on the partitioning of inorganic species into the gas phase. This has been observed to be a cause of deposition and other ash-related problems in full-scale gasifiers.

In the case of applying the results to full-scale gasifiers, the following data are considered necessary:

1. temperature
2. atmospheric conditions
3. size and mineralogical distribution of coal minerals
4. distribution of organically bound inorganics
5. characteristics of ash species formed

The temperature and atmospheric conditions are known from the design of the system. However, the size and mineralogical distribution of coal feed material can be a major variable. In order to obtain this data, sampling from a gasifier is an after-the-fact operation. It is important to have a predictive method. The EMRC has developed a method that involves performing a small-scale experiment under simulated gasification conditions, and characterizing the original coal, char, and ash produced using CCSEM and SEMPC. This is a major change in direction from the use of bulk analytical techniques, which, if useful, are not sufficient for the purpose of understanding the impact of the inorganic constituents on gasifier operation. Also, we have shown that standard laboratory ash is not representative of the ash formed in gasification systems, which necessitates performing a different experiment. This process is needed to determine the state of the inorganics. Furthermore, for coals that have organically bound inorganic species, the determination of the amount of organically bound elements by chemical fractionation is important. The organically bound inorganics can have a major impact on the gasification process as well as the nature of the ash species formed. We consider all of this data necessary for input into descriptive models for ash behavior in gasification systems. This technique is akin to performing an ash fusion experiment and using the results to characterize the performance of a fuel in a combustion system.

4.3.3 Future Work

The Gasification Ash and Slag Project has resulted in the compilation of a large data base of surface tension, viscosity, sintering, and quantitative chemical analysis of many coal ash, slag, and char samples, and begun development of preliminary descriptive models for prediction of ash behavior in gasification systems. Future work will consist of further interpretation of this data, its application to model development, and final verification of descriptive models in pilot- and full-scale gasification systems.

4.3.4 Model Verification of Sintering, Crystallization, and Mechanical Properties of Selected Coal Ashes

Sintering, crystallization and mechanical properties of three coal ashes are being studied to obtain an understanding of ash deposit and agglomerate formation in combustion and gasification systems. Results show that viscous sintering is accomplished by the shrinkage of closed pores and/or by the diffusion of slag constituents in a liquid film along the grain surfaces. These processes are dependent on temperature, atmosphere, and ash composition. In addition, studies show that the strength of sintered pellets produced from crystallized Beulah lignite ash are weaker than those produced from the amorphous form of the ash. Further, the amorphous form sintered in a CO/CO₂ atmosphere is not as strong as the amorphous form sintered in air.

An understanding of ash agglomerate and deposit growth and strength development requires basic knowledge of the chemical reactions in solid-solid, solid-liquid, and solid-gas systems; mineral transformations; and mechanical properties at elevated temperatures. The early work on viscous sintering originates from Frenkel (2). He assumed that mass transfer takes place under the influence of a surface tension gradient. The Frenkel model provides a satisfactory description of the early stage of sintering when the shrinkage, $\Delta L/L_0$, is less than 10% (15), where $\Delta L = L - L_0$ (L_0 is the initial length of the pellet and L is the length at time t). Two other models were derived by Mackenzie and Shuttleworth (16) and Scherer (15). The Mackenzie and Shuttleworth model is concerned with the shrinkage of isolated closed pores and is able to predict densification kinetics in the late stage of sintering. Scherer analyzed a particular cubic array of cylindrical particles, and his model can be applied to all stages that occur in the sintering body.

The mechanism of viscous sintering of coal ashes involves one or several stages. When a thin liquid layer is formed between particles, the meniscus tends to pull them together (17). The result is the rearrangement of particles by sliding and the formation of closed pores and voids. Consequently, viscous sintering may be imposed by the shrinkage of pores (15). If the quantity of liquid phase present is relatively large, the driving force for sintering may arise from the Ostwald ripening mechanism (18) and plastic flow (19). In a system that contains a wide range of particles of various sizes, it is likely that the smallest particles would enhance the initial densification rate (20).

Surface crystallization or devitrification may reduce the amount of amorphous phase and change sintering behavior. Generally, crystallization and devitrification are initiated by the presence of: external surfaces, active nucleating heterogeneities, stable immiscibility, absorbed OH species, network defects that distort the Si-O bond lengths, and by the local variation of glass composition (21,22). Surface crystallization or devitrification, performed at temperatures below $T(g)$, usually results in the weakening of soda-lime silicate glasses because it introduces tensile stresses. At temperatures above $T(g)$, strength increases markedly due to a healing effect of surface flaws (23).

The objective of this work is to describe the processes involved in the development of strength in deposits and agglomeration in gasification systems. So far, coal fly ashes have been used in fundamental studies of sintering processes, strength development, and sticking coefficients (24). Coal fly ashes contain a mixture of crystalline and amorphous components that behave differently during the sintering process. In order to alleviate this problem, coal ashes were produced with defined mineralogical compositions and amorphous forms to examine sintering processes and strength development.

The coals used (Beulah, Pittsburgh #8, and Illinois #6) were pulverized to -150 mesh and burned in air under ASTM ashing conditions. The resulting ashes were ground to -150 mesh and (before sizing) were dried at 100°C for 1 hour. The particle size distributions of the ashes are shown in Figure 13. The compositions of the ashes on a sulfur-free basis are listed in Table 12. In addition, Beulah was melted at 1500°C, homogenized at that temperature for 3 hours, and quenched at room temperature to produce a homogenous glass. The glass was ground to -150 mesh. The particle size distribution was similar to that shown in Figure 13. The amorphous Beulah glass was crystallized at 1000°C for 1 hour, ground to -150 mesh, and a 1:2 mixture of amorphous:crystallized was prepared.

The slag bulk viscosity was measured using a rotating bob viscometer (described elsewhere (25,26)) in air and reducing CO/CO₂ (60%/40%) atmospheres. Slag surface tension was determined by the sessile drop technique (27) both in air and reducing atmospheres.

Figure 13. Particle size distribution of coal ashes used in sintering tests.

TABLE 12
COMPOSITION OF COAL ASHES
(WT% EXPRESSED AS EQUIVALENT OXIDE)

Coal Ash	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	CaO	MgO	Na ₂ O	K ₂ O	P ₂ O ₅
Beulah	27.5	14.2	9.9	2.8	27.4	5.9	10.8	1.0	0.4
Pittsburgh #8	50.8	20.2	17.5	1.3	5.2	1.3	0.0	2.5	0.2
Illinois #6	48.6	23.1	14.3	1.2	5.6	1.6	0.5	3.1	0.3

Beulah, Pittsburgh #8, and Illinois #6 coal ashes with defined mineralogical composition, and amorphous Beulah were used in the sintering experiments in air and reducing [CO/CO₂ (60/40)] atmospheres. The sintering tests were conducted for 2 hours as a function of temperature. Sintered samples were analyzed to determine their crystalline phases, densities, and mechanical strengths. Five cylindrical specimens (1.52 cm in diameter and 1.90 cm long) formed in a hand press were sintered at appropriate temperatures and times, cooled slowly in the furnace and crushed, and their average compressive strengths were computed and plotted. Fractured surfaces were observed with SEM.

Densities were determined from the displacement of anhydrous methanol at room temperature using a pycnometric method (28,29) with an accuracy of ± 0.02 g/cm³. Duplicate samples were used in the sintering experiments, and average values are presented.

4.3.4.1 Results and Discussion

Densification is a pore filling process. Analytical results indicate that as sintering proceeds, the density of the coal ash passes through a minimum and then increases, as shown in Figure 14. Figure 14 illustrates the changes in density for amorphous and crystallized Beulah coal ash sintered at various temperatures under air and CO/CO₂ atmospheres. The sintering time at temperature, T, was 2 hours, since only small changes in density with times longer than 2 hours were observed. During sintering, open and closed pores are usually formed. The minimum density responds to the maximum volume of sample expressed by the volume of both ash particles and closed pores. The position of the deep minimum is related to the amount of liquid phase, liquid phase viscosity and surface tension gradients, and particle size and shape. Figure 13 shows 50 wt% of particles with sizes below 38 μ m; this indicates the possibility of "pseudo-neck" formation in the first step of the sintering process, as illustrated in Figure 15. The important point is that the minimum in density obtained for amorphous Beulah ash is displaced to a higher temperature if the amorphous ash is crystallized or sintered in a CO/CO₂ atmosphere.

Figure 14. Dependence of density upon sintering temperature for amorphous and crystallized Beulah coal ash, measured in air and CO/CO₂ atmospheres.

Figure 15. Microstructure of Beulah coal ash observed after first minutes of sintering in air.

The crystalline phases produced in the amorphous coal ashes in air and CO/CO₂ atmospheres at 800°-1100°C are listed in Table 13.

TABLE 13
MINERALOGICAL COMPOSITION OF CRYSTALLIZED COAL ASHES

Coal Ash	Treatment in Air	Major Phases
Beulah	700°C/120 min	Amorphous
	800°C/10 min	Nepheline, Sodium Calcium Silicate
	900°C/10 min	Nepheline, Sodium Calcium Silicate
	900°C/180 min	Nepheline, Gehlenite
	1000°C/10 min	Gehlenite
	1100°C/10 min	Gehlenite
	1100°C/15 hr	Gehlenite, Hauyne
Pittsburgh #8	1000°C/60 min	Anorthite, Quartz, Hematite
	1100°C/15 hr	Anorthite, Quartz, Hematite
Illinois #6	1000°C/60 min	Anorthite, Quartz, Hematite
	1100°C/15 hr	Anorthite, Quartz, Hematite

Treatment in CO/CO ₂		
Beulah	800°C/10 min	Gehlenite, trace Na ₂ CO ₃ and CaCO ₃
Pittsburgh #8	1000°C/60 min	Quartz, FeAl ₂ O ₄
Illinois #6	1000°C/60 min	Anorthite, Quartz, Hematite

Gehlenite is formed from amorphous Beulah coal ash at ~800°C in the CO/CO₂ atmosphere, and at 900°C in air with a longer annealing time. It is relatively stable, but after annealing at 1100°C for 15 hours, additional peaks are also observed on the X-ray powder diffraction pattern that indicate formation of a new phase potentially attributable to hauyne. The mineralogical compositions of Pittsburgh #8 and Illinois #6 coal ashes were stable at the temperatures and annealing times tested.

Figure 16 shows the marked differences in the microstructure of pores formed in the sintered Beulah and Illinois #6 coal ashes at 1200°C. In Beulah, the pores are irregular in shape (Figure 16a), and in Illinois #6 (Figure 16b), large spherical pores are formed. The irregular shape of closed pores indicates that the diffusion of gas out of the pores is faster than the transport of liquid slag during pore shrinkage (30).

Figure 16. Microstructures of Beulah (a) and Illinois #6 (b) coal ashes sintered at 1200°C for 2 hours in air and CO/CO₂, respectively. Magnification 500x.

4.3.5 Viscous Sintering by the Shrinkage of Large Pores and the Diffusion of Liquid Phase Constituents

The viscous sintering of coal ashes containing large closed pores proceeding at temperatures above the minimum of density may arise from inward-acting stresses caused by surface and grain-boundary tensions (15,31). The resultant elastic strain can be analyzed by the viscoelastic deformation of materials. For the sake of simplicity we have assumed spherical pores with radius "r" (cm) are formed. They are subjected to a compressive stress (σ) given by the equation:

$$\sigma = - 2 \gamma / r \quad [5]$$

where γ is the surface energy (surface tension).

For the viscoelastic solid, the densification strain rate is related to the pore shrinkage rate, $\dot{\epsilon}$, by

$$\dot{\epsilon} = \dot{\epsilon}_f + \sigma (1-2\nu)/3\eta \quad [6]$$

where $\dot{\epsilon}_f$ is the thermal strain rate, ν is the Poisson ratio, and η is the viscosity.

From Equations 5 and 6

$$\dot{\epsilon} = \dot{\epsilon}_f - 2/3 (\gamma/\eta)(1-2\nu)/r \quad [7]$$

Equation 7 implies that the strain rate depends on the large pore radius and the ratio of (γ/η) . A rapid increase in the densification strain rate is expected to occur when pore size equals grain size (31). For densification measurements it is convenient to use the relation between the strain rate and the relative densification rate of material, $\dot{\rho}$:

$$\dot{\rho} = - 3\rho (\dot{\epsilon} - \dot{\epsilon}_f) \quad [8]$$

where $\rho = d/d_0$ and d_0 is the density of powder before sintering.

By applying Laplace transform procedures, the variation of relative density as a function of time, t , can be expressed by;

$$\ln \rho(t) = C (\ln A) At \quad [9]$$

where $A = 2 (\gamma/\eta)(1-2\nu)/r$ and C is a correlation coefficient. The variation of density with temperature is expressed by the relation of viscosity versus temperature. Since, for coal ashes, surface tension is slightly changed with temperature, we have assumed that $\gamma = \text{const}$.

In practice, viscosity is expressed by Poise (dyne sec/cm²) and surface tension by dyne/cm; thus, the ratio of these gives units of cm/sec. It is postulated that $(\gamma/\eta)L$, represents the atoms and/or ions and defect mobilities in the slag that may be assigned to the diffusion coefficient of species in the slag, so:

$$D(\text{slag}) = (\gamma/\eta)L \quad [10]$$

where L (cm) is the jump length of atom(s) and/or ion(s) or defect(s) from one liquid cluster to another during the cooperative rearrangements between complexes in the melts. A cluster is defined as a short-lived complex of atoms/ions and point defects formed in a liquid slag with a strong interaction between them (32). The critical size of the cluster may be related to the configurational entropy. In a recent theory on the viscosity of SiO₂, Mott (33,34) proposed that the viscosity of vitreous silicon dioxide must be related to the motion of intrinsic defects. The flow takes place through the step-by-step transfer of oxygen between three-dimensional SiO₂ tetrahedrons.

Since the diffusion coefficient fits the Arrhenius-type equation:

$$D = D(o) \exp(-E/kT) \quad [11]$$

where E is an activation energy of a liquid slag and $D(o)$ is a temperature-independent coefficient:

$$\ln (\gamma/\eta) = \ln D(o)/L - E/kT \quad [12]$$

Experimental data are shown in Figures 17 and 18 that represent $\ln (\gamma/\eta)$ versus temperature and $\ln \rho$ versus temperature, respectively. The $\ln \rho$ results were generated with crystallized samples. The negative values of the $\ln (\gamma/\eta)$ and $\ln \rho$ imply that the sintering of coal ashes should proceed by a different mechanism than that for the positive values of $\ln (\gamma/\eta)$ and $\ln \rho$. The negative values of $\ln \rho$, above the minimum, most likely resulted from the shrinkage of large closed pores, and the positive ones by the diffusion of all species in the continuous liquid slag film formed on the particle surfaces without significant formation of large pores. The latter effect is known as surface fluxing. The negative range of $\ln (\gamma/\eta)$ is displaced to lower temperatures if viscosity and surface tension for coal ashes are measured in the reducing atmosphere, CO/CO₂. Thus, $\ln (\gamma/\eta)$ in Equations 10 and 13 provides details about the sintering mechanism proceeding at low and high temperatures.

There are also two different linear relationships of $\ln (\gamma/\eta)$ with T (Figure 17), which implies two different activation energies of liquid slag. Generally, for most glasses the change of viscosity with temperature cannot be represented by the Arrhenius relation, since many exchanges of atoms and ruptures of a variety of bonds are occurring. This brings about changes in activation energy with increasing temperature (35). An interesting point indicated by Figure 17 is that the activation energy for viscous slag measured above 1300°C satisfies the Arrhenius relation and can be attributed to the viscous flow of liquid slag. Below 1300°C, a mixture of viscous liquid and solid clusters and/or high temperature crystalline grains appear to form from existing liquid clusters. The geometrical structure of solid clusters are often very different from the bulk crystal. The energy costs to break the bonds are so high that the cluster would remain stable, because the chemical bonding and electron delocalization are fairly strong (36).

On the basis of our results, we can distinguish three steps in the sintering of pulverized coal ashes:

1. Formation of closed pores at temperatures below the minimum-density temperature.
2. Shrinkage of pores at temperatures above the minimum-density temperature.
3. Diffusion and/or reactive diffusion of melts.

These three steps are schematically shown in Figure 19.

Figure 17. The relationship between the $\ln$ of surface tension/viscosity ratio and temperature for Beulah, Pittsburgh #8, and Illinois #6 coal ashes determined in air (a) and CO/CO_2 (b) atmospheres.

Figure 18. The relationship between the $\ln$ of relative density and sintering temperature for Beulah, Pittsburgh #8, and Illinois #6 coal ashes sintered in air (a) and CO/CO_2 (b) atmospheres.

Figure 19. Schematic for the three steps in the sintering of coal ashes.

To understand mechanisms of ash deposit strength development one must know something about the relevant mechanical properties. The compressive strength of sintered coal ashes depends on annealing temperature, time and surrounding atmosphere (Figures 20-22). The strengthening of the samples with well-defined mineralogical composition (shown in Figure 15) results from the shrinkage of the pores. Generally, the compressive strength measured for pellets sintered in the reducing atmosphere, CO/CO_2 , is larger than that found for pellets sintered in air atmosphere if both are determined at the same temperature. Comparison of mechanical properties with $\ln(\gamma/\eta)$ results imply that more liquid phase is formed in a reducing atmosphere, likely due to an effect of iron (II). For Beulah coal ash, strength is related both to porosity variation and to the instability of its crystalline structure, (Figure 22). The phase transformation, observed in Beulah coal ash, of the type:

occurred in the presence of liquid phase rich in CaO , and allows sharp changes in strength due to the introduction of cracks. In the above reaction, the volume of a unit cell of gehlenite ($V = 300.5 \text{ \AA}^3$) is considerably lower than that of nepheline ($V = 717.3 \text{ \AA}^3$), so phase transformation creates compressive stresses. Generally, compressive stresses increase strength if they are generated on surfaces. If they are large and created in the pore material, they can produce cracks in the necks, but are unable to propagate the cracks through the material. This causes the decrease of strength of the samples with temperature due to the breaking of connections between particles and the opening of closed pores, as shown in Figure 23. As a consequence of this, the liquid medium (methanol) may readily fill the open pores during sample density measurement. This effect is chiefly observed in amorphous Beulah sintered in reducing atmosphere, CO/CO_2 (Figure 14). Alternately, low strength in Beulah coal ash results if its amorphous phase is crystallized at 1000°C (Figure 21). Figure 21 also demonstrates the increase of strength of Beulah coal ash sintered at 1200°C . This effect may be attributed to the healing effect of cracks.

Figure 20. The effects of sintering temperature and atmosphere on strength in Beulah, Pittsburgh #8, and Illinois #6 coal ashes (with the defined mineralogical composition at 1000°C) sintered under air (a) and CO/CO₂ (b).

Figure 21. The effects of sintering atmospheres (curve A) and crystallization in air (curve B) on the strength of amorphous Beulah coal ash.

Figure 22. Variation of strength with time for amorphous Beulah sintered at 900°C and 1100°C in air.

Figure 23. Schematic representation of closed pores opening during phase transformation.

4.3.5.1 Conclusions

Based on the described experimental results, viscous sintering of coal ashes proceeds by the formation of closed pores and their shrinkage, and/or by the diffusion and reactive diffusion of a liquid phase along surface or grain boundaries. Both low strength and low heat transfer capability of a deposit appear to be very dependent on the existence of large pores.

Crystallization may be a highly desirable phenomenon for amorphous fly ashes because the formation of crystallization products decreases concentrations of alkali and alkaline elements in the fly ashes, and displaces the densification process to higher temperatures. This also introduces heterogeneities in the coal ash powders that produce stresses in the surrounding matrix which oppose densification. However, secondary effects related to the phase transformation such as nepheline-gehlenite transformation in the presence of a liquid phase rich in CaO , promotes the strength decrease at higher temperatures. The strength decrease is due to the breaking of some connections in the necks. As a consequence of glass crystallization, fly ash may have lower slagging and agglomeration tendencies. The strength development in Pittsburgh #8 and Illinois #6 coal ashes at temperatures about 1100°C was attributed to the presence of iron that facilitates the sintering processes (mainly in the reducing atmosphere) (24). This phenomenon was observed in our experiments.

5.0 REFERENCES

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4.4 Thermochemical Phase Equilibria: PHOEBE

As more complicated chemical reactions are considered for the synthesis of organic compounds or in the analysis of the performance of complex fuels and propellants, it becomes desirable to develop simpler and more general methods for the calculation of chemical equilibrium. In particular, the equilibrium-phase distribution of the inorganic constituents of coal provides a good starting point for the modeling of ash deposit formation and growth, slagging, and fouling in a combustor. With information regarding the extent and distribution of the various mineralogical phases in the vapor, liquid, and solid phases (provided by equilibrium calculations), a better understanding of not only deposition processes, but also their mitigation may be achieved.

The problem of obtaining the equilibrium values ($x^{*1}, \dots, x^{*NS}$) of NS distinct species at a given temperature, T, and pressure, P, has been extensively addressed in the past, and the utility of obtaining the equilibrium values by minimizing the Gibbs free energy of the system has also been emphasized (1-24). A variety of numerical packages (NASA-CEC, PACKAGE, SOLGASMIX, METC-CEC, etc.) related to this problem has been reported in the literature and their relative merits discussed as well (23,25). While most of these codes are reported to perform adequately, a few instances of misleading or erroneous results also seem to appear (25). In addition, most of these numerical packages require a priori estimates of the phases present at equilibrium, and this introduces further uncertainties in the computed results, especially when the Gibbs free energy is non-convex, as is usually the case when the system is non-ideal (17,18,19,23). Indeed, depending on the initial estimate, convergence to a local minimum, as opposed to the global minimum, is often achieved, and special tests need to be performed to ensure

the globality of the minimum. (Reference 18, for instance, provides "phase-splitting" algorithms for this purpose.) We discuss this aspect of the problem at greater length in a later section.

In the ideal model, the Gibbs free energy of the system is, in general, not differentiable along the boundary $\partial\Omega$ of the feasible set Ω (3,12,24,26). In addition to this geometric obstruction to G being everywhere differentiable, nondifferentiability of G may also arise when the system undergoes a phase transition and some of the system's (macroscopic) parameters become discontinuous or even unbounded (27-29,32,43). Though this physical obstruction is not too important in view of the manner in which the minimization problem is formulated, it nevertheless relates to the problem of phase selection discussed above. Any numerical algorithm designed for obtaining the minimum of G must thus require its differentiability, if needed, only in the interior of the feasible set Ω . To overcome this limitation, and to utilize the elegant Lagrange multiplier formulation for constrained minima, many of the extant algorithms handle the unboundedness of G along $\partial\Omega$ by various ad hoc methods and, as far as we are aware, no rigorous proofs of convergence of these methods have been presented either. It may be noted that Lagrange multiplier formulations of optimization problems for nondifferentiable functions do exist; however, in these formulations, the concept of the derivative is either generalized (e.g., subdifferential) or a completely different methodology adopted (30,31). The PHOEBE algorithm requires the differentiability of G only in the interior of the feasible set Ω , and thus avoids the inherent instabilities induced by abrupt changes or unboundedness of the derivative of G .

The convexity of the ideal Gibbs free energy poses yet another potential problem (4,10,11,12,23,39-42). (Even in the non-ideal case, if the free energy of the system is convex, the same problem may arise.) This problem has to do with the non-uniqueness of the optimal point x_* realizing the minimum of the Gibbs free energy; in fact, the set of Ω_* of optimal points minimizing a convex function is itself convex (see Section 4.4.3 for a precise statement) and thus a continuum of "indifferent" equilibrium states (10,32) may arise. (This situation usually arises along phase boundaries.) The pragmatic solution to this problem is to accept one of the $x_* \in \Omega_*$ and disregard the remainder or, if needed or useful, to accept the entire set Ω_* as the solution set. (A very elegant explanation of such indifferent equilibria states, in terms of center-manifold and integral-manifold theory, is given in (33) where the notion of dormant instabilities are introduced and an explanation of the dynamics of coexisting phases given.)

4.4.1 Mass-Constrained Gibbs Free Energy Minimization

Let S be a closed thermodynamic system at a specified temperature, T , and pressure, P . (As a general guide for notations and terminology, we follow Reference 23.) The system S contains NS chemical species $s_1, \dots, s_{NS}$ which are formed or built from NE elements $a_1, \dots, a_{NE}$. The element abundance vector $b = (b_1, \dots, b_{NE})^t$ (superscript t denotes transpose) specifies the number of moles of each element a_i so that, since the system S is closed, the mass-constraint equations

$$A n = b \quad [1]$$

are to be satisfied by the species abundance vector

$$n = (n_1, \dots, n_{NS})^t \quad [2]$$

where A is the formula matrix whose i^{th} row, j^{th} column matrix element A_{ij} represents the number of moles of element a_i in one mole of species s_j . Additionally, the components of the species abundance vector n are required to satisfy the non-negativity constraints

$$n_i \geq 0, \quad i = 1, \dots, NS, \quad [3]$$

to be physically meaningful. The problem then is to determine

- a) the number of phases $NP_\star$ present at equilibrium.
- b) the equilibrium species abundance vectors

$$n_\star^\alpha = (n_{\star 1}^\alpha, \dots, n_{\star NP(\alpha)}^\alpha)$$

for each equilibrium phase $\alpha = 1, \dots, NP_\star$.

(4) Definition: Let S be the thermodynamic system containing the species $s_1, \dots, s_{NS}$ as defined. A phase in or of S is a subset $P \subseteq S$ such that all the intensive properties of P are translation invariant (over the volume occupied by P).

(5) Definition: Let S be the thermodynamic system described earlier. A phase distribution of S is an indexed, non-empty family $\{P_\alpha | \alpha \in J\}$ of phases of S .

The problem of obtaining the equilibrium values $NP_\star$ and $n_\star$ is then solved in

accordance with the following theorem, which is fundamental to classical thermodynamics (23-24,29,32,43):

(6) Theorem: Let S be the thermodynamic system described above, and r the set of all possible phase distributions on S . If $\{P_\alpha | \alpha \in J\}$ is a phase distribution on S , let G^α denote the Gibbs free energy of phase P_α so that the Gibbs free energy of S is given by^a

$$G = \sum_{\alpha \in J} G^\alpha \quad [7]$$

Let $\{\tilde{n}^\alpha | \alpha \in J\}$ be such that

$$G = \sum_{\alpha \in J} G^\alpha(\tilde{n}^\alpha) = \min_{\{P_\beta | \beta \in K\} \in r} \left\{ \inf \left\{ \sum_{\beta \in K} G^\beta(n^\beta) | A n = b, n \geq 0 \right\} \right\}. \quad [8]$$

Then

a) $NP_\star = |J|$ = cardinality of the index set J

b) $n_\star = \tilde{n}$

^a We assume here that the phases are non-interacting or that the phase-phase interaction energies are negligible.

A few observations regarding the preceding definitions and theorem are in order. First, we wish to point out that the set r containing the totality of possible phase distributions on S is finite. Indeed, since the set S is finite with $|S| = NS$, the cardinality $|r|$ of r is bounded above by (34)

$$|r| \leq 2^{2^{NS}}. \quad [9]$$

Thus the minimization $\min_{\beta \in K} \{P_\beta\}$ over the possible phase distributions is a meaningful operation in Equation 8.

Secondly, in the definition of a phase distribution of S , Definition 5, it appears somewhat surprising that a "covering" type condition of the form

$$\bigcup_{\alpha \in J} P_\alpha \supseteq S$$

is not present. The inclusion of this requirement, though mathematically tempting, will (and usually does) violate real-life systems. For example, in the system $S = \{Al_2O_3(s), Al_2O_3(l), SiO_2(s), SiO_2(l), Al_6Si_2O_{13}(s), Al_6Si_2O_{13}(l)\}$, it is experimentally known (35) that the only phases condensing below the solidus line are $SiO_2(s)$ and $Al_6Si_2O_{13}(s)$; but, of course, $\{SiO_2(s)\} \cup \{Al_6Si_2O_{13}(s)\} \neq S$. The "covering" condition must, therefore, not be included.

Finally, in Equation 8, the existence of the infimum (or minimum) of G over the non-negative species abundance vectors n satisfying $An = b$, has to be established. We take this up in a later section.

4.4.2 Properties of the Formula Matrix A and the Feasible Set Ω .

Let S be the thermodynamic system, as defined earlier, and A the formula matrix for the species in S. From the definition of the formula matrix A, viz., that the i^{th} row j^{th} column element A_{ij} equals the number of moles of element a_i in species s_j it is clear that

(1a) A is a non-negative matrix, i.e., for each i and j, $A_{ij} \geq 0$.

(1b) For each $j = 1, \dots, NS$, there exists an i such that $A_{ij} > 0$.

(1a) is merely an expression of the fact that each species s_j is built from precisely the NE elements $a_1 \dots, a_{NE}$ and, hence, that at least one of its stoichiometric coefficients is positive.

An additional simple result regarding the formula matrix is obtained by making the (almost always true) assumption that the number of elements NE is not greater than the number of species NS, i.e.,

$$NE \leq NS \quad [1c]$$

In this event, the rank, r_A , of the formula matrix A is not greater than the number of elements NE,

$$r_A \leq NE \leq NS \quad [1d]$$

From now on, we will only consider systems for which (1c) is true so that (1d) is always valid.

(2) Definition: Let $\mathcal{P}^k = \{(x_1, \dots, x_k) \in \mathcal{R}^k \mid \text{for each } i, x_i \geq 0\}$.

We term the set $\mathcal{P}^k$ as the non-negative hyperoctant of $\mathcal{R}^k$.

(3) Definition: Let $V = (v_1, \dots, v_k)^t$ be a vector in $\mathcal{R}^k$. We define $\bar{V}$ to be the sum of the components of V , i.e.,

$$\bar{V} = \sum_{i=1}^k v_i \quad [3a]$$

Now, let B be any $r \times s$ matrix over $\mathcal{R}$. The row and column sums of B are defined, respectively, as

$$\bar{r}_i(B) = \sum_{j=1}^s B_{ij}, \quad i = 1, \dots, r \quad [3b]$$

$$\bar{c}_j(B) = \sum_{i=1}^r B_{ij}, \quad j = 1, \dots, s \quad [3c]$$

(4) Lemma: Let A be the formula matrix of the system S , b an element abundance vector for S , and n a species abundance vector satisfying the constraints

$$An = b, \quad n \in \mathcal{P}^{NS}.$$

Then

a) The column sums of A are positive.

$$b) \quad 0 \leq n_j \leq \min_{1 \leq i \leq NE} \left\{ \frac{b_i}{A_{ij}} \mid A_{ij} > 0 \right\}$$

$$c) \quad \frac{\bar{b}}{\max\{\bar{c}_1(A), \dots, \bar{c}_{NS}(A)\}} \leq \bar{n} \leq \frac{\bar{b}}{\min\{\bar{c}_1(A), \dots, \bar{c}_{NS}(A)\}}$$

Note that the lower bound on the total number of moles $\bar{n}$ in (c) above is a sharper bound than that presented in Reference 11.

(5) Definition: Let $\Omega = \{n \in \mathcal{P}^{NS} \mid An = b\}$. Ω is called the feasible set of solutions to the mass balance constraints.

(6) Lemma: The feasible set Ω is a compact convex polytope.

The convexity of the feasible set Ω follows straightforwardly from the linearity of the equations $An = b$. On the one hand, Lemma (4) shows that the set Ω is bounded; on the other hand, regarding A as a linear map $A: \mathcal{R}^{NS} \rightarrow \mathcal{R}^{NE}$ from $\mathcal{R}^{NS}$ to $\mathcal{R}^{NE}$, it immediately follows that Ω is closed. We merely need to invoke the Heine-Borel theorem (36,37) to claim compactness of Ω .

One of the results of convexity theory (39, Theorem 3.6.13) asserts that a compact convex subset is the convex hull of its extreme points, where, an extreme point of a convex set K is a point of K which cannot be written as a

convex linear combination of any pair points of K , neither of which is itself. [In the language of linear programming, an extreme point is a basic feasible solution (40, Theorem 3.1).] Hence,

(7) Corollary: The feasible set Ω is the convex hull of its extreme points.

The question that immediately arises is, of course, whether the set of extreme points of Ω is finite or otherwise.

Borrowing a result from linear programming again (40, 3.5.3) we have

(8) Corollary: The set E_Ω of extreme points of Ω is finite with

$$|E_\Omega| \leq \binom{r_A}{NS}, \text{ where, } r_A \text{ is the rank of the formula matrix } A \text{ and } \binom{r_A}{NS} \text{ is the}$$

binomial coefficient,

$$\binom{r_A}{NS} = \frac{NS!}{(NS-r_A)!r_A!}.$$

The final resolution of the solutions to the mass balance equations lies in the decomposition theorem for convex polytopes (40, Theorem 3).

(9) Theorem: Any vector $n \in \Omega$ can be written as the sum of two solutions,

$$n = n_p + n_h$$

where n_p is a convex linear combination of extreme points (basic feasible solutions) and n_h is a "homogeneous" solution solving

$$An = 0, n \geq 0. \quad [10]$$

Since Ω is bounded, all solutions to the mass balance equations are convex linear combinations of basic feasible solutions [cf: Corollary 7]. In other words, the only homogeneous vector solving Eq. 10 is the zero vector.

4.4.3 Gibbs Free Energy and Approximations

Given the system S comprising the NS species $s_1, \dots, s_{NS}$ and Gibbs free energy G , we want to establish that G attains its extremum values on the feasible set Ω . A sufficient condition for this to hold is that the free energy be a continuous function on Ω . Since the requirement of a continuous free energy for S is not all too restrictive and physically eminently reasonable, we shall from now on make the assumption that

(1) The Gibbs free energy G of the system S is a continuous function on the feasible set Ω .

Additionally, to make the problem meaningful, we also assume that

(2) The feasible set Ω is nonempty (and hence contains basic feasible solutions).

For any well-posed problem, Ω is usually nonempty: assumption (2) above is thus not all too restrictive either. (In any event, at the algorithm level, the algorithm can be made to terminate if it is determined that Ω is empty.)

With these two assumptions, the compactness of Ω then allows us to conclude that

(3) Theorem: The Gibbs free energy G of the system S attains its minimum and maximum values on Ω : i.e., there exist points n^* and n_* in Ω such that

$$G_{\min} = G(n_*) = \inf \{G(n) | n \in \Omega\}$$

$$G_{\max} = G(n^*) = \sup \{G(n) | n \in \Omega\}.$$

Likewise, the convexity of Ω , the continuity of G , and the fact that compact, connected subsets of $\mathcal{R}$ are closed, bounded intervals (37, Theorem 8.4) yield:

(4) Corollary: The image $G(\Omega)$ of the feasible set Ω under the Gibbs free energy G is a closed bounded interval in $\mathcal{R}$,

$$G(\Omega) = [G_{\min}, G_{\max}].$$

In general, the Gibbs free energy G may possess local minima in addition to the global minimum $G_{\min}$. However, if G is a convex function, then any local minimum is also a global minimum (41, Theorem 6.2.6). We state this in:

(5) Corollary: Let the Gibbs free energy G of S be convex. Then:

- a) Any local minimum of G is also a global minimum.
- b) The set $\Omega_{\star} = \{n_{\star} \in \Omega | G(n_{\star}) = G_{\min}\}$ of minimal points of G is a closed convex subset of Ω .
- c) If G is strictly convex, i.e., if for each $n, n' \in \Omega$ and $\alpha \in (0,1)$, $G(1-\alpha)n + \alpha n' < (1-\alpha)G(n) + \alpha G(n')$, then G has at most one minimal point.

It is to be noted that (5b) above is the mathematical statement of "indifferent" or "degenerate" equilibrium states discussed earlier in the introduction. It is to be also noted that, in contrast to linear optimization problems, G may well attain its minimal value at interior points of Ω .

In general, the Gibbs free energy of the system S may be written as

$$G = \sum_{\alpha} G^{\alpha} \quad [6]$$

where G^{α} represents the free energy of phase P_{α} and given by

$$\begin{aligned} G^{\alpha} &= \sum_{j \in P_{\alpha}} \mu_j^{\alpha} n_j^{\alpha} = \sum_{j \in P_{\alpha}} n_j^{\alpha} \{ \mu_{0j} + RT \ln a_j^{\alpha} \} \\ &= \sum_{j \in P_{\alpha}} n_j^{\alpha} \{ \mu_{0j} + RT \ln x_j^{\alpha} + RT \ln r_j^{\alpha} \} \end{aligned} \quad [7]$$

where μ_j^α is the chemical potential of species j in phase μ_{0j} is the standard or reference chemical potential of species j , a_j^α is the activity of species j in phase P_α , and r_j^α the activity coefficients. The symbols R and T represent, respectively, the universal gas constant and temperature, while x_j^α is the mole fraction of species j in phase P_α .

$$x_j^\alpha = \frac{n_j^\alpha}{\sum_{j \in P_\alpha} n_j^\alpha} = \frac{n_j^\alpha}{\bar{n}^\alpha} \quad [8]$$

Depending on the choices for the activities, or the activity coefficients, a variety of approximation to the Gibbs free energy of the system may be studied. (For instance, the Debye-Hückel formulas, 3-suffix Wohl equation, Wilson coefficients, sublattice models, etc. (3,8,10-11,12,17-18,22,23,26, 44-45)).

In particular, the activities defined by

$$a_j^\alpha = \begin{cases} 1, & \text{if } \alpha \text{ is a pure condensed phase} \\ P x_j^\alpha, & \text{if } \alpha \text{ is a gaseous phase (} P = \text{normalized pressure)} \\ x_j^\alpha, & \text{if } \alpha \text{ is a liquid phase} \end{cases} \quad [9]$$

constitute the ideal model which has been extensively discussed in the literature (3-9,12,17-18,23) and its relevance to silicate and coal conversion systems also emphasized (46-48). We note that the free energy of phase P_α can be written as

$$G^\alpha = F^\alpha + RT \sum_{j \in P_\alpha} n_j^\alpha \ln r_j^\alpha \quad [10]$$

and the overall Gibbs free energy of S as

$$G = \sum_{\alpha} F^{\alpha} + RT \sum_{\alpha} \sum_{j \in P_{\alpha}} n_j^{\alpha} \ln r_j^{\alpha} = F + RT \sum_{\alpha} \sum_{j \in P_{\alpha}} n_j^{\alpha} \ln r_j^{\alpha} \quad [11]$$

regardless of whether S is ideal or otherwise. (The functions F^{α} represent the free energies of the phases of the ideal model.) This observation, viz., that the Gibbs free energy can be written as the sum of the free energies of the ideal and non-ideal parts, forms the basis for an algorithm to determine the minima of G : reference (26) provides extensive details. We may note that explicit attention is given to the possibility of G and F not being differentiable along the boundary of Ω and the algorithm presented relies on the differentiability of G and F only in the interior of Ω .^a

Let $B: \Omega \rightarrow \mathcal{R}$ be the function defined by

$$B = \sum_{j \in IC} \mu_{0j} n_j + \sum_{j \in IL} n_j \left\{ \mu_{0j} + RT \ln \left(\frac{n_j}{\bar{n}_L} \right) \right\} + \sum_{j \in IG} n_j \left\{ \mu_{0j} + RT \ln \left(\frac{p n_j}{\bar{n}_G} \right) \right\} \quad [12]$$

where IC , IL , and IG denote, respectively, the index sets of the condensed, liquid, and gaseous species in S and $\bar{n}_L$ and $\bar{n}_G$ are the total moles of the liquid and gaseous species,

$$\bar{n}_L = \sum_{j \in IL} n_j, \quad [13a]$$

^a The assumption as to the uniqueness of the minimal point of F_x , $x \in H$ (in the notation of Ref. 26) may also be relaxed by suitably ensuring the operator T does not have finite cycles.

$$\bar{n}_G = \sum_{j \in IG} n_j \quad [13b]$$

Rewriting B as

$$B = \sum \tilde{\mu}_{0j}^0 n_j + RT \bar{n}_L \sum_{j \in IL} x_j \ln x_j + RT \bar{n}_G \sum_{j \in IG} x_j \ln x_j \quad [14a]$$

where

$$\tilde{\mu}_{0j} = \begin{cases} \mu_j^0, & j \in IC \\ \mu_j^0 + RT \ln P, & j \in IG \\ \mu_j^0, & j \in IL \end{cases} \quad [14b]$$

and

$$x_j = \begin{cases} \frac{n_j}{\bar{n}_L}, & j \in IL \\ \frac{n_j}{\bar{n}_G}, & j \in IG \end{cases} \quad [14c]$$

we have the inequalities

$$D(n) \leq B(n) \leq E(n), \quad n \in \Omega \quad [15]$$

where

$$D(n) = \sum_{j=1}^{NS} \tilde{\mu}_{0j} n_j - \frac{RT}{e} \bar{n}_L - \frac{RT}{e} \bar{n}_G,$$

$$E(n) = \sum_{j=1}^{NS} \tilde{u}_{0j} n_j,$$

NL = number of liquid species,

NG = number of gaseous species,

e = base of the natural logarithm ≈ 2.718 . [16]

The first inequality, $D(n) \leq B(n)$, $n \in \Omega$, is obtained by noting that the function

$$f : [0, 1] \rightarrow \mathcal{R} : t \rightarrow t \ln t$$

has a minimum at $t = 1/e$ with $f(1/e) = -1/e$, while the second inequality $B(n) \leq E(n)$ obtains from the fact that the function $t \ln t$ is non-positive.

Hence, if x_* , n_* , and y_* are minimal points of D , B , and E , respectively, we have

$$D(x_*) \leq B(n_*) \leq E(y_*). \quad [17]$$

4.4.4 Phase Distributions

The ideal approximation of Eq. 4.4.3.12, approximating the ideal Gibbs energy by the function B , seemingly approximates the number of liquid phases to be one. (The number of gaseous phases is, of course, one, while the number of solid condensed species can be determined only after B has been minimized.) This approximation of the number of liquid phases is not all too invalid for

complex aluminosilicate systems (24) wherein the melt is usually treated as a single homogenous phase. Additionally, standard methods of analysis (like SEM, XRD, TGA, etc.) also fail to provide satisfactory conclusions as to the number of liquid phases present and any data provided by the theory, unless verifiable otherwise, remains primarily of theoretical interest. Nevertheless, the function B in 4.4.3.12 captures all the "essential" information pertinent to the accounting of phases present at equilibrium, as we now proceed to show.

(1) Proposition: Let, in the ideal model, a solution species j be present in k phases $\alpha_1, \dots, \alpha_k$. If $x_{\star j}^{\alpha_1}, \dots, x_{\star j}^{\alpha_k}$ denote its equilibrium mole fractions in the k phases, then $x_{\star j}^{\alpha_1} = x_{\star j}^{\alpha_2} = \dots = x_{\star j}^{\alpha_k}$.

Proof: At equilibrium, the chemical potentials $\mu_j^{\alpha_1}, \dots, \mu_j^{\alpha_k}$ of solution species j are equal. Hence

$$\mu_{0j} + \ln x_{\star j}^{\alpha_1} = \mu_{0j} + \ln x_{\star j}^{\alpha_2} = \dots = \mu_{0j} + \ln x_{\star j}^{\alpha_k}$$

implying

$$x_{\star j}^{\alpha_1} = \dots = x_{\star j}^{\alpha_k}.$$

(2) Proposition: Let, in the ideal model, there be k solution phases. Assume that the species are numbered so that

$$IC = \{1, \dots, NC\}, \quad IG = \{NC + 1, \dots, NC + NG\}, \text{ and}$$

IL = {NC + NG + 1, ..., NS} and that the vector

$$f^3 = \{f_1^*, \dots, f_{NC}^*, f_{NC+1}^*, \dots, f_{NC+NG}^*, f_{NC+NG+1}^{*1}, \dots, f_{NS}^{*k}, \dots, f_{NC+NG+1}^{*k}, \dots, f_{NS}^{*k}\}$$

minimizes

$$\begin{aligned} B' = & \sum_{j=1}^{NC} \mu_{0j} + \sum_{j=NC+1}^{NC+NG} f_j \left\{ \mu_{0j} + \ln \left(\frac{f_j}{\bar{f}_G} \right) \right\} \\ & + \sum_{\alpha=1}^K \sum_{j=NC+NG+1}^{NS} f_j^\alpha \left\{ \mu_{0j} + \ln \left(\frac{f_j^\alpha}{\bar{f}^\alpha} \right) \right\}. \end{aligned} \quad [3]$$

Then there exists $\tilde{n} \in \Omega$ such that

$$\tilde{n}_j = f_j^*, \quad j = 1, \dots, NC + NG$$

$$\tilde{n}_j = \sum_{\alpha=1}^K f_j^{*\alpha}, \quad j = NC + NG + 1, \dots, NS. \quad [4]$$

and

$$B(\tilde{n}) = B'(f^*).$$

Proof: The existence of the vector $\tilde{n} \in \Omega$ follows easily by observing that the formula matrix for minimizing B' contains, for each solution species, k repeated columns corresponding to the k phases.

To observe that $B(\tilde{n}) = B^*(f^*)$ we utilize the result of proposition (1) and reorder the last sum in Equation 3 to obtain

$$\begin{aligned}
 & \sum_{\alpha=1}^K \sum_{j=NC+NG+1}^{NS} f_j^\alpha \left\{ \mu_{0j} + \ln \left(\frac{f_j^\alpha}{\bar{f}^\alpha} \right) \right\} \\
 &= \sum_{\alpha=1}^K \sum_{j=NC+NG+1}^{NS} f_j^\alpha \mu_{0j} + \sum_{j=NC+NG+1}^{NS} \sum_{\alpha=1}^K f_j^\alpha \ln \left(\frac{f_j^\alpha}{\bar{f}^\alpha} \right) \\
 &= \sum_{j=NC+NG+1}^{NS} \mu_{0j} \tilde{n}_j + \sum_{j=NC+NG+1}^{NS} \tilde{n}_j \ln \tilde{x}_j
 \end{aligned}$$

since from Equation 4 we have

$$\begin{aligned}
 \frac{\tilde{n}_j}{\tilde{n}_L} &= \frac{1}{\tilde{n}_L} \sum_{\alpha=1}^K f_j^{*\alpha} \\
 &= \frac{1}{\tilde{n}_L} \sum_{\alpha=1}^K x_j^{*\alpha} \bar{f}^{*\alpha}, \quad j = NC+NG+1, \dots, NS
 \end{aligned}$$

so that

$$\frac{\tilde{n}_j}{\tilde{n}_L} = \tilde{x}_j = x_j^{*1} = x_j^{*2} = \dots = x_j^{*K}, \quad j = NC + NG + 1, \dots, NS.$$

The primary consequence of the above two propositions is that, in the ideal case, the phase distribution provided for in the function B of Equation 4.4.3.12 is the most stable. In other words, it suffices to consider the function B for the minimization of the ideal case. Of course, if the vector f^* , which minimizes B' , is such that it minimizes B as well, the relative amounts of the phases present remain undetermined.

This indeterminacy, arising due to the inherent symmetries of the solutions to the mass balance constraints, may be, and usually is, removed by introducing terms describing non-ideal behavior. Unless there exists additional information regarding these non-ideal terms, which perhaps would then allow rejection of some phase distributions a priori, a minimization over all realizable phase distributions must, in general, be done. The algorithm of Ref. (26) may then be utilized to minimize G for a particular (assumed) phase distribution. If the minimization over the possible phase distributions is felt to be too prohibitive (in terms of program execution time or cost) simple phase splittings can be tried to approach the realistic phase distribution as described in Ref. (18), or a maximal phase distribution assumed and G minimized as described in the "phase elimination" technique of Ref. (8). This latter approach is preferred in that the process is not by "trial and error," and the algorithm automatically discards phases not present at equilibrium.

6. PHOEBE: Algorithm, Results and Conclusions

A computer program called PHOEBE has been developed at UNDEMRC implementing the ideas discussed above. PHOEBE essentially comprises two parts: (i) a data manipulation module and (ii) a computational module.

The data manipulation module (DDM) is a fully menu-driven front end or preprocessor designed to facilitate data entry, data-base retrieval/access and output of computational results (Fig. 6.1). This preprocessor is written in assembly level code and is targeted for PC users (specifically for IBM^a compatible machines). Facilities for file management, DOS^b commands, and a few desktop accessories are also provided to enable the user to work in an integrated manner under PHEOBE and to schedule or execute concurrent tasks. In terms of hardware, the minimal requirements are: (i) Monochrome/CGA/EGA adaptor (ii) IBM compatible PC; (iii) $\geq 600K$ RAM; and (iv) math coprocessor.

The computational module (see Fig. 6.2) accepts the input data as prepared by the preprocessor and after additional data verification proceeds with the computation of the equilibrium values. There are no restrictions on the number of elements, number of species, or the number of phases considered and the program dynamically allocates system memory depending on input parameters. The algorithm path depends on a user-dependent option and proceeds with the calculation of the equilibrium values with respect to the ideal model or a user-supplied, non-ideal model. At this stage of development, no library of standard/well-established non-ideal models are included with the program: we expect to include such a facility in the near future.

^a Trademark of the International Business Machines Corporation.

^b Product of Microsoft Inc.

Figure 6.1. PHOEBE: Pre-processor.

PHOEBE: Algorithm

Figure 6.2. PHOEBE: Computational module.

The results from PHEOBE, so far, look very promising. Two model outputs are presented in Tables 6.1 and 6.2. (Note that these are results obtained from only the linear approximation to G.) Table 6.1 represents the output for the $\text{Al}_2\text{O}_3\text{-SiO}_2$ binary system, while Table 6.2 is that for the $\text{Na}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2$ ternary system. As may be observed, the predicted and experimental values are in complete agreement for the binary system. The multiple minima indicated by the program for the $\text{Al}_2\text{O}_3\text{:SiO}_2$ ratio of 3:2 is also in accordance with phase diagram data which indicates a phase boundary for this composition ratio. For the ternary system (Table 6.2), the discrepancies between predicted and observed are especially pronounced for $\text{Na}_2\text{O:Al}_2\text{O}_3\text{:SiO}_2$ ratios of 2:1:2 and 3:3:4 while overall, the primary and secondary (or secondary and tertiary) phases are occasionally interchanged in the predicted values.

TABLE 6.1
COMPARISON OF PREDICTED AND EXPERIMENTAL PHASES
FOR THE $\text{Al}_2\text{O}_3\text{-SiO}_2$ BINARY SYSTEM

Composition (mol %)	Predicted Phases		Experimental Phases ^a	
	Primary	Secondary	Primary	Secondary
$\text{Al}_2\text{O}_3 = 10$	Mullite	Cristobalite	Mullite	Silica
$\text{Al}_2\text{O}_3 = 20$	Mullite	Cristobalite	Mullite	Silica
$\text{Al}_2\text{O}_3 = 30$	Mullite	Cristobalite	Mullite	Silica
$\text{Al}_2\text{O}_3 = 40$	Mullite	Cristobalite	Mullite	Silica
$\text{Al}_2\text{O}_3 = 50$	Mullite	Cristobalite	Mullite	Silica
$\text{Al}_2\text{O}_3 = 60$	Mullite ^b		Mullite ^c	
$\text{Al}_2\text{O}_3 = 70$	Corundum	Mullite	Corundum	Mullite
$\text{Al}_2\text{O}_3 = 80$	Corundum	Mullite	Corundum	Mullite

^a Phase diagram data obtained from Ref. 35.

^b Multiple optima predicted.

^c Phase boundary.

TABLE 6.2
COMPARISON OF PREDICTED AND EXPERIMENTAL PHASES
FOR THE $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ TERNARY SYSTEM

Composition (wt %)	Predicted Phases			Experimental Phases ^a		
	Primary	Secondary	Tertiary	Primary	Secondary	Tertiary
$\text{Al}_2\text{O}_3 = 10$ $\text{SiO}_2 = 40$	Corundum	Na_2O	-	See footnote b below.		
$\text{Al}_2\text{O}_3 = 20^c$ $\text{SiO}_2 = 40$	Corundum	Nepheline	Na_2SiO_3	Nepheline	Na_2SiO_3	-
$\text{Al}_2\text{O}_3 = 30^c$ $\text{SiO}_2 = 40$	Corundum	Nepheline	Na_2SiO_3	Nepheline	Na_2SiO_3	-
$\text{Al}_2\text{O}_3 = 40$ $\text{SiO}_2 = 40$	Corundum	Nepheline	Albite	Nepheline	Corundum	Albite
$\text{Al}_2\text{O}_3 = 50$ $\text{SiO}_2 = 40$	Corundum	Nepheline	Albite	Corundum	Nepheline	Albite
$\text{Al}_2\text{O}_3 = 10$ $\text{SiO}_2 = 50$	Nepheline	$\text{Na}_2\text{Si}_2\text{O}_3$	Na_2SiO_5	Na_2SiO_3	Nepheline	$\text{Na}_2\text{Si}_2\text{O}_5$
$\text{Al}_2\text{O}_3 = 20$ $\text{SiO}_2 = 50$	Nepheline	Na_2SiO_3	$\text{Na}_2\text{Si}_2\text{O}_5$	Nepheline	Na_2SiO_3	$\text{Na}_2\text{Si}_2\text{O}_5$
$\text{Al}_2\text{O}_3 = 30$ $\text{SiO}_2 = 50$	Nepheline	Albite	$\text{Na}_2\text{Si}_2\text{O}_3$	Nepheline	Albite	$\text{Na}_2\text{Si}_2\text{O}_5$
$\text{Al}_2\text{O}_3 = 10$ $\text{SiO}_2 = 60$	Nepheline	Albite	$\text{Na}_2\text{Si}_2\text{O}_3$	$\text{Na}_2\text{Si}_2\text{O}_5$	Nepheline	Albite
$\text{Al}_2\text{O}_3 = 20$ $\text{SiO}_2 = 60$	Nepheline	Albite	$\text{Na}_2\text{Si}_2\text{O}_3$	Nepheline	Albite	$\text{Na}_2\text{Si}_2\text{O}_5$
$\text{Al}_2\text{O}_3 = 30$ $\text{SiO}_2 = 60$	Corundum	Mullite	Albite	Corundum	Mullite	Albite
$\text{Al}_2\text{O}_3 = 10$ $\text{SiO}_2 = 70$	Cristobalite	Albite	$\text{Na}_2\text{Si}_2\text{O}_5$	Albite	$\text{Na}_2\text{Si}_2\text{O}_5$	Silica
$\text{Al}_2\text{O}_3 = 20$ $\text{SiO}_2 = 70$	Mullite	Cristobalite	Albite	Mullite	Albite	Quartz

^a Phase diagram data obtained from Ref. 35.

^b Phase diagram data not available.

^c See text.

In attempting to understand the prediction of corundum as the primary phase for the composition ratios $\text{Na}_2\text{O}:\text{Al}_2\text{O}_3:\text{SiO}_2$, 2:1:2 and $\text{Na}_2\text{O}:\text{Al}_2\text{O}_3:\text{SiO}_2$, 3:3:4 in Table 6.2, it was discovered that the μ_0 -values for nepheline(s) and nepheline(l) were computed from the SOLGASMIX coefficients reported in Ref. (49). As per these values, nepheline's melting point appears to be about 2300 K, while phase diagram data indicate a value of 1800 K. Furthermore, these compositions lie adjacent to a boundary to one side of which phase diagram data is nonexistent. All in all, we are reluctant to stand judgment on this misrepresentation of corundum as the primary phase and await further confirmation.

On the other hand, the intermixing of the primary and secondary phases (or the secondary and tertiary, etc.) that occurs in Table 6.2 is a more serious problem directly relating to the linear approximation made. The reasons are as follows: it may be recalled that the μ_0 values of the solid state of a species are less than that of the liquid state for temperatures below the melting point, while the liquid μ_0 values exceed the corresponding solid values for temperatures above the melting point. Therefore, if, for a species j , the mass constraints permit a nonzero amount x^j of it, the choice of assigning the x^j moles either to the liquid or the solid state of the species is clear cut: it must be assigned to the solid state if $\mu_{0j}(\text{s}) < \mu_{0j}(\text{l})$ and to the liquid state if $\mu_{0j}(\text{l}) < \mu_{0j}(\text{s})$. Thus for temperatures T below the melting point T_{mj} of species j , the solid state is always preferred, while for $T > T_{mj}$ the liquid state is preferred. Now, let the system contain species $k (\neq j)$ with $T_{mk} > T_{mj}$ and $\mu_{0k}(\text{s or l}) > \mu_{0j}(\text{s or l})$, and let the mass constraints allow the assignment of x^k and x^j -moles to j and k . Then it is easily seen that the species with the higher melting point (k in this case) will always be the primary phase, though it may be the case that species j

actually crystallizes first upon cooling the system. As remarked earlier, the linearized problem disregards mutual interactions between the various species, and the interchanges observed in Table 6.2 are precisely due to this reason. However, note that the overall list of phases predicted is indeed correct since the values obtained from the linearized version can be no more in error (than by a computable bound) than those obtained from the ideal version.

In conclusion we feel that the current version of PHEOBE is of great utility in thermodynamic phase equilibria calculations, not only in terms of its providing a fairly good estimate of the equilibrium state of the system, but also in terms of its intrinsic computational simplicity.

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U.S. DEPARTMENT OF ENERGY
FEDERAL ASSISTANCE MANAGEMENT SUMMARY REPORT

1. Program/Project Identification No.		2. Program/Project Title Gasification Ash & Slag Characterization		3. Reporting Period 4/01/88 through 6/30/89	
4. Name and Address University of North Dakota Energy & Mineral Research Center Box 8213, University Station, Grand Forks, ND 58202				5. Program/Project Start Date 4/1/86	
				6. Completion Date 3/31/92	
Milestone ID. No.	Description	Planned Completion Date	Actual Completion Date	Comments	
Task A	Mineral Transformations:				
a.1	Compile data base of coal ashes and model mineral mixtures.	07/88	07/88		
a.2	Compare crystalline phases observed with predicted phases.	08/88	10/88		
a.3	Model mineral transformation data.	12/88	12/88		
Task B	Volatilization Studies:				
b.1	Compile data base on loss of inorganic constituents during pressure pyrolysis.	07/88	03/89		
b.2	Compare and evaluate SOLGASMIX and PACKAGE.	08/88	08/88		
b.3	Correlate and model volatilization processes.	03/89	03/89		
b.4	Development of data bases for PHOEBE (thermochemical equilibrium code) to be used to study the inorganic phase transformation in gasification systems.	05/89			
b.5	Verification of data base.	06/89			
Task C	Physical Properties:				
c.1	Compile data base of experimental data on physical properties of slags.	07/88	07/88		
c.2	Develop model of physical properties of slags.	03/89	03/89		
c.3	Determine effects of gas composition (reducing) on mineral transformation/sintering behavior for 1 model glass.	06/89			

4.0 COMBUSTION RESEARCH

4.1 Fluidized Bed Combustion

FLUIDIZED-BED COMBUSTION OF LOW-RANK COALS

Third Year Technical Report for the period
April 1, 1988 - June 30, 1989,
including the Quarterly Technical Progress Report for the period
April through June, 1989.

By

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TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT.....	1
1.0 INTRODUCTION.....	1
2.0 GOALS AND OBJECTIVES.....	3
2.1 Three-Year Objectives.....	3
2.2 Third-Year Objectives.....	5
3.0 ACCOMPLISHMENTS.....	5
3.1 Agglomeration.....	5
3.2 Evaluation of Corrosion/Erosion during AFBC.....	6
3.2.1 Test Procedures.....	6
3.2.2 Chemical Analysis of Feed Coal, Limestone, and Bed Material.....	8
3.2.3 Results and Discussion.....	11
3.2.3.1 Wall Loss Measurements.....	11
3.2.3.2 Sulfide Penetration.....	20
3.2.3.3 Deposit/Scale Buildup.....	27
3.2.3.4 Deposition and Heat Transfer Effects.....	27
3.3 Advanced Concepts and Special Applications.....	31
3.3.1 Conceptualization of the Pretreatment Cell.....	31
3.3.2 Experimental Verification.....	34
4.0 SUMMARY.....	35
5.0 PUBLICATIONS AND PRESENTATIONS.....	37
6.0 REFERENCES.....	37

LIST OF FIGURES

<u>Figure</u>	<u>Page</u>
1 Isometric view of UNDEMRC's 0.44-ft ² AFBC.....	7
2 Cross-sectional view of UNDEMRC's 0.44-ft ² AFBC showing combustor dimensions and the metallurgies and approximate operational surface temperatures of heat transfer tubes and coupons.....	7
3 Diameter loss measurements for Tube #, 316-stainless steel. Greater-than-zero values refer to loss on all figures.....	15
4 Diameter loss measurements for Tube #8, Carbon Steel.....	15
5 Sum of all diameter metal loss measurements for all 29 tubes.....	16
6 Sum of diameter loss measurements as a function of coal type and metallurgy for all tubes.....	16
7 Sum of diameter loss measurements as a function of coal type and metallurgy for In-Bed Tubes.....	17
8 Sum of diameter loss measurements as a function of coal type and metallurgy for splash zone tubes.....	17
9 Sum of diameter loss measurements as a function of coal type and metallurgy for convective pass tubes.....	18
10 Sum of all tube wall loss measurements for a given location as a function of coal type.....	24
11 Overall heat transfer coefficient for Tube #6 at Run Hour 700 as a function of coal type.....	30
12 Experimental Unit for Testing Coal Pretreatment Cell Concept.....	35

LIST OF TABLES

<u>Table</u>	<u>Page</u>
1 Summary of Average Operating Conditions for the 1000-Hour Tests.....	9
2 Chemical Analysis of Coals Used for Testing.....	10
3 Chemical Analysis (in Wt%) of Limestone Feed.....	12
4 Chemical Analysis (in Wt%) of Bed Material (End of Run).....	13
5 Comparative Statistics on Diameter Loss.....	18
6 Comparative Statistics on Wall Loss.....	19
7 Analysis of Variance for Diameter Loss.....	21
8 Analysis of Variance for Wall Loss.....	21
9 Comparison of Means for Diameter Loss.....	22
10 Comparison of Means for Wall Loss.....	23
11 Comparative Statistics on Sulfide Penetration.....	24
12 Analysis of Variance for Sulfide Penetration.....	25
13 Comparison of Means for Sulfide Penetration.....	26
14 Comparative Statistics on Deposit/Scale.....	28
15 Analysis of Variance for Deposit/Scale.....	28
16 Comparison of Means for Deposit/Scale.....	29

FLUIDIZED-BED COMBUSTION OF LOW-RANK COALS

ABSTRACT

The University of North Dakota Energy and Mineral Research Center (EMRC) is currently performing research in fluidized bed combustion under Cooperative Agreement No. DE-FC21-86MC10637, Task 4.1. During the third year of this cooperative agreement, work focused mainly on the corrosion and erosion of heat transfer surfaces and on the development of a coal pretreatment cell. A minimal amount of effort focused on writing a topical report on agglomeration of bed material.

The corrosion and erosion work focused on analyzing data from seven 1000-hour tests previously performed. A topical report detailing these results is currently being prepared. Results from this effort indicate that coal type has a statically significant effect on the amount of tube metal wastage, the depth of sulfide penetration into the metal surface, and the thickness of the scale and deposits that form on the tubes. Other factors such as tube metal surface temperature, metal type, and location were found to impact the metal wastage rates. The results are summarized in this report. Detailed analysis will be presented in the forthcoming topical report.

A new concept was developed for use with fluidized bed combustion systems. A coal pretreatment cell was developed to have the ability to reduce the overall size of the FBC system, reduce operating costs, increase fuel flexibility, improve startup and load following capabilities, and have capabilities for modular construction and retrofitting. Work has proceeded through a detailed paper evaluation using data available from the literature. Current work is focusing on developing operational data using an experimental test rig.

Work in the area of agglomeration focused on the preparation of a topical report. Results from the analysis of deposits taken from utility systems is reported here. Preparation of the topical report is still in progress.

1.0 INTRODUCTION

The main driving forces behind the use of fluidized bed combustion have primarily been environmental concerns, fuel flexibility, and compatibility with low-cost fuels. Both bubbling and circulating designs have been developed for operation at atmospheric pressure, and many units of both types are currently in operation on the industrial scale. A limited number of larger utility boilers have recently been commissioned. In addition, pressurized fluidized-bed combustion (PFBC) is making its entrance on the utility scale with the PFBC being installed at the Tidd Station.

Even though fluidized-bed combustion technologies are being commercialized, a number of areas require further research. An integrated approach should be taken toward fluidized-bed combustion research to solve interrelated problems generic to bubbling, circulating, and pressurized fluidized-bed

combustion systems. The research program should also be designed to address specific problems related to each of these areas. Major issues facing fluidized-bed combustion are listed below:

- Methods are needed to minimize corrosion and erosion of in-bed and convective pass tubes, refractory and support surfaces, and expander turbines. Work should focus on:
 - Understanding mechanisms:
 - Mineralogical properties of bed and coal.
 - Fluid mechanics of bed.
 - Corrosion versus erosion mechanisms.
 - Stress forces on tubes.
 - Assessing acceptable wastages.
 - Identifying cost-effective methods of combating tube wastage.
 - Developing systematic test devices.
- Retrofit applications should be addressed for all types of FBCs. According to information from the American Boiler Manufacturing Association (ABMA), approximately 200 existing units are candidates for retrofit technologies. The FBC retrofits at NSP's Black Dog Station, MDU's Heskett Station, and Colorado Ute's Nucla Station have demonstrated the feasibility of such applications.
- Fuel flexibility and characterization issues should be addressed to help users understand constraints of fuel switching, design considerations, and, most important, the economics involved in having fuel flexibility for the FBC.
- Agglomeration/sintering of bed material and deposition on tubes, and support and refractory surfaces has been identified as a problem by both manufacturers and users of FBC technology. Problems have been documented for both bubbling and circulating beds using a variety of fuels, including coal.
- Scale-up effects need to be addressed so that vendors and users can take pilot-scale data and be assured that large-scale systems will perform as anticipated. This data base has been growing rapidly with all of the new units starting operation; however, much information is needed. UND will have an opportunity to observe scale-up effects when a CFBC is installed as a part of the University's steam system expansion project. This will make a 5,000- and a 150,000-lb steam/hr unit available for scale-up studies.
- Advanced systems should be designed to resolve problems and improve overall FBC performance. These systems should:
 - Increase volumetric heat release rates.
 - Improve overall boiler efficiency.

- Simplify fuel feed and ash removal systems.
- Decrease capital and operating costs.
- Improve turndown.
- Decrease the size of units to enable modular construction.
- Several problems related to emissions from FBC systems need to be addressed.
 - Better sorbent utilization would improve the economics of FBC.
 - NO_x control is currently not a major problem, but could become more difficult with bubbling beds if federal standards become more stringent.
 - Information indicates that particulate control problems may exist for certain types of ash. These ashes should be identified and the use of specific equipment, conditioning, or other methods should be applied to resolve the problem.
 - Hot-gas cleanup is required for PFBC to meet turbine specs, in addition to NSPS.

These problems and concerns could limit FBC from reaching its full potential. Special efforts should be made to perform the necessary research to help FBC evolve to a mature technology that meets the technical, economic, and environmental needs of the future. The University of North Dakota Energy and Mineral Research Center has addressed several of these problems and concerns through the research funded by DOE and reported herein.

2.0 GOALS AND OBJECTIVES

The overall objectives of the low-rank coal (LRC) fluidized bed combustion (FBC) program at the University of North Dakota Energy and Mineral Research Center is to conduct research and development programs aimed at providing a technology data base so that industry can bring economically competitive and environmentally acceptable coal technology options into the marketplace. Research will address those areas where data gaps exist in fuel flexibility and performance, potential operating problems, environmental compliance, and coal-water slurry applications. The focus is on the development of an atmospheric fluidized bed combustion (AFBC) system utilizing low-rank coal for the industrial, commercial, and residential sectors capable of economically meeting process steam and heating requirements.

2.1 Three-Year Objectives

Based upon coal ash composition, bed material characteristics, combustion studies, and results of laboratory ash sintering studies, an effort will be made to develop a technique to predict agglomeration in FBCs. This work will utilize samples obtained from UNDEMRC pilot-scale AFBC units as well as from

outside sources. The thermodynamic constraints of agglomerate formation will be studied to provide a theoretical understanding of coal ash and bed material interactions, and to apply kinetic formulations that may predict the rate of agglomerate development.

During the first Cooperative Agreement, UNDEMRC completed testing on three LRCs using the corrosion/erosion AFBC pilot plant to specifically evaluate the corrosion and erosion of in-bed, freeboard, and water wall heat transfer surfaces that occur during the combustion of low-rank coals in an AFBC. As an extension of this data base, four additional 1000-hour tests are proposed. These would include an eastern bituminous coal to serve as a reference to similar tests performed by other researchers, and three additional LRCs to be selected based on physical properties and market demand. At the completion of these tests, an evaluation will be made to determine whether additional 1000-hour tests are needed, or if the program should be modified to examine other aspects of corrosion and erosion.

Characterization studies of LRC will involve an evaluation of combustor performance and environmental impacts of an AFBC firing a variety of western coal at various modes of operation. Quantitative relationships between boiler performance and design and operational variables will be established for the various coals. Development of a greater knowledge and understanding of combustion efficiency, sulfur capture, heat transfer, bed dynamics, erosion, and load control should result. Several environmental issues will also be addressed to determine pollution controls that will be required based on characterization of the emissions of sulfur and nitrogen oxides, the ash generated from each of the coals, and the leachability of the ash and spent bed material. Characterization studies will include an eastern bituminous coal to be used as a reference to other researchers' results, and two low-rank coals.

The suitability of using LRC slurries produced by the UNDEMRC hot-water-drying process as feed to an AFBC will be evaluated. Items to be investigated will include combustion efficiencies, products of combustion, supplemental sorbent requirements, and in-bed heat transfer characteristics. In addition, method(s) of injection and the impact of the slurry feed on operation of the AFBC will be evaluated. Two slurries made from LRCs that have undergone extensive characterization will be tested. Based on the results of these tests, a decision will be made concerning which aspects of slurry feed applications need further refinement during third-year testing.

Using the results of the testing performed during the first two years of this Cooperative Agreement, an assessment of the suitability of LRCs and LRC slurries for use in advanced concepts and special application fluidized bed combustors will be performed. The findings of this evaluation will be used to develop a detailed scope of work for third-year activities. These activities are expected to lead to the demonstration of the use of LRC slurries in advanced FBC combustion systems.

2.2 Third-Year Objectives

Specific objectives of the Fluidized Bed Combustion Project for the third year of this Cooperative Agreement are as follows:

TASK 1. AGGLOMERATION

A detailed topical report will be prepared on coal ash, sorbent, and bed material agglomeration. All information generated at EMRC will be presented, as will utility and industrial operating and experimental data developed outside of EMRC. This report will present details of the agglomeration process and known methods of mitigating the problem, and will document occurrence of the problem (type of facility, feed type, sorbent type, and bed material if different than sorbent). This effort will include gathering and correlating existing data, interpreting the available data, and relating this information to operation of industrial and utility combustors. Minor experimentation will be performed as necessary to confirm observations and correlations.

TASK 2. EVALUATION OF CORROSION/EROSION

The data generated from the seven 1000-hour corrosion/erosion tests performed at EMRC will be correlated to determine the effects of the various coal, coal ash, and limestone properties on corrosion/erosion/deposition. Detailed metallographic characterization will be performed on samples from the runs, followed by a detailed statistical evaluation of the data to integrate the results of the seven tests and more clearly identify the general trends noted from the existing data. The detailed metallographic examination should be used to better understand and explain the underlying mechanisms associated with the different coal/ash/limestone combinations. The deliverable of this task will be a topical report.

TASK 3. ADVANCED CONCEPTS AND SPECIAL APPLICATIONS

Based on ideas generated during the first two years of this Cooperative Agreement, the suitability of LRCs and LRC slurries for use in advanced concepts and special application fluidized bed combustors will be assessed. The work will involve design and modeling of envisioned concepts and will be presented to program personnel at METC. Upon approval of an advanced concept, work will begin to prove the concept and to develop experimental data by firing LRC. These activities are expected to lead to the demonstration of the use of LRC in advanced FBC combustion systems.

3.0 ACCOMPLISHMENTS

3.1 Agglomeration

A low level of effort was maintained on this task during the past year. Literature was reviewed and data is being correlated to document occurrences of agglomeration and bed material sintering. Preparation of a topical report presenting EMRC experience in bench- and pilot-scale studies as well as results from full-scale plants is in progress.

During the year, a visit was made to the Montana-Dakota Utilities (MDU) 80-MW Heskett Station. The plant was down for a scheduled outage to clean boiler tube surfaces and perform other routine maintenance. EMRC personnel entered and inspected the boiler before any cleaning had taken place. It appears that MDU has been able to control agglomeration by using proper operating conditions. This includes operating at an average bed temperature of 1500°F, and turning the bed over every 50 hours. More interestingly, however, was the over ½-inch-thick deposition noted on the in-bed superheater surfaces. The deposits covered all the superheater surfaces in the bed. Generating surfaces in the bed, however, were clean and displayed fully exposed shiny metal over their entire surfaces. MDU operators feel that the deposition on the superheater surfaces is the cause of low steam temperatures (30 to 50°F below design). EMRC has noted a similar effect, where the in-bed tubes with cool surface temperatures (less than 400°F) were clean, while those with higher surface temperatures experienced severe deposition when burning Beulah lignite. EMRC will be receiving samples of this deposit material for analysis.

Some deposition was also noted on the convective pass tubes. This material was very tenacious and was being removed by air lances. The observed deposits were up to 1 inch thick, and their appearance resembled fouling deposits generated during pc-firing. These deposits may also account for the low steam temperature; however, their effect is thought to be minor compared to the effect of the in-bed superheater deposits. The deposits in the convective pass are very small in comparison to what MDU saw when burning the same coal in the stoker mode prior to the retrofit. A sample of this material was also collected and will be analyzed. These results, as well as other occurrences of agglomeration or deposition will be discussed in detail in the topical report.

3.2 Evaluation of Corrosion/Erosion During AFBC

A systematic study of the impacts of coal properties on corrosion and erosion of FBC boiler tube surfaces has been completed. Seven 1000-hour tests were completed utilizing two Texas lignites and a North Dakota lignite, a Montana and a New Mexico subbituminous coal, and an Illinois #6 and a Kentucky #9 bituminous coal. All tests were performed with the combustor and heat exchanger surfaces in the same location, and under similar operating conditions. This was done to remove the effects of parameters such as geometry, tube orientation, stresses, etc., from the test matrix. A detailed topical report is being prepared that will show the differences and similarities in the performances of various materials during these different tests, and relate performance to coal ash properties. A summary of the results is presented here.

3.2.1 Test Procedures

A pilot-scale AFBC was designed and constructed at EMRC specifically to investigate the effects of coal type on the corrosion and erosion of heat transfer elements. Figure 1 shows an isometric view of the overall system. A cross-sectional view of the combustor is shown in Figure 2. The facilities include an extractive flue gas analysis system for measuring oxygen, carbon dioxide, and sulfur dioxide levels, and a microprocessor-controlled data acquisition system for monitoring and recording temperature, pressure, and

Figure 1. Isometric view of UNDEMRC's 0.44-ft² AFBC.

Figure 2. Cross-sectional view of UNDEMRC's 0.44-ft² AFBC showing combustor dimensions and the metallurgies and approximate operational surface temperatures of heat transfer tubes and coupons.

flue gas concentration data. The combustor was designed to run at steady state conditions for 1000 hours with a bed temperature of 1550°F, a superficial gas velocity of 7.5 ft/sec, an excess air level of 25%, and 70% retention of sulfur. Actual operating conditions for each test are given in Table 1. Deviations from the set point were caused by operation of each test with the same heat transfer geometry, irrespective of coal properties.

During each test, 29 horizontally oriented tubes were distributed throughout the bed, splash zone, and convective pass. Metal surface temperatures of various tubes were maintained at preset limits by using either water- or air-cooling; other tubes not cooled. Figure 2 shows the location, method of cooling, and approximate surface temperatures of the 29 tubes. Different metallurgies were also tested as indicated in the figure. This configuration was kept the same for all seven tests, to remove tube configuration and geometry as a test variable.

Each sample was weighed and measured prior to exposure. After completion of the test, the tubes and coupons were removed, measured, weighed, and photographed. Detailed metallographic examination of the tube samples was performed to determine and record the color, texture, and location of features on the sample. Samples were cut for metallographic analysis. The cut sections were mounted in epoxy, polished, and examined using a research grade metallograph. These techniques were used to record metal loss, scale formation, deposition, sulfide penetration, pitting, and other changes that occurred to the samples during exposure. Selected polished samples were studied by scanning electron microscopy and electron microprobe techniques to analyze scale/deposit and scale/metal interfaces. Elemental mapping was also performed to ascertain the distribution of various elements.

A summary and analysis of total metal loss, sulfide penetration and deposit/scale measurements is presented here. Detailed procedures and data obtained during each of the corrosion/erosion tests have been presented in previous reports (1,2,3). Test data from all seven tests will be presented and discussed in detail in the forthcoming report entitled "Corrosion and Erosion of, and Deposition on AFBC Boiler Tube Surfaces: Topical Report."

3.2.2 Chemical Analysis of Feed Coal, Limestone, and Bed Material

The proximate, ultimate and ash analyses of the seven coals tested are listed in Table 2. The proximate analyses showed a wide variation between the coals tested. Moisture contents varied from 2.7 wt% for the Pyro Kentucky bituminous coal to 29.1 wt% for the South Hallsville Texas lignite. The other parameters of interest in the proximate analysis are the ash and higher heating values. Ash content ranged from 8.0% to 32.5% for the coals tested. Gibbons Creek had the lowest higher heating value and Pyro the highest.

Of interest in the ultimate analyses of the coals are the sulfur and chlorine levels. Sulfur contents, on a moisture-free basis, varied from 0.8 wt% for the Absaloka and Navajo subbituminous coals, to 4.2 wt% and 4.3 wt% for the River King and Pyro coals, respectively. The chlorine content of all the coals was below 0.05 wt%, except for the Pyro coal, which had a chlorine content of 0.25 wt%.

TABLE 1

SUMMARY OF AVERAGE OPERATING CONDITIONS FOR THE 1000-HOUR TESTS

Run	SC1-0185	SH1-0186	NJ1-0286	RK1-0386	B61-0187	GC1-0287	PY1-0188
Coal	Absaloka	So. Hallsville	Navajo	River King	Beulah	Gibbons Creek	Pyro
Limestone	Big Horn	Paris	Paris	Hannibal	Big Horn	Paris	Fredonia
Bed Temp., °F	1559	1551	1550	1547	1562	1544	1552
Gas Velocity, fps	7.8	7.2	7.3	7.8	7.1	8.1	7.1
Excess Air, pct	30.8	29.9	28.7	31.2	48.7	20.0	33.6
Coal Feed Rate, Btu/hr	243	278	244	291	208	280	256
Coal Feed Rate, lb/hr	27.5	36.7	27.8	32.6	27.6	57.2	20.9
Sorbent Feed Rate lb/hr	1.0	1.8	1.5	18.2	2.1	7.7	8.0
Alkali-To-Sulfur Ratio	3.0	1.9	3.1	5.0	3.1	5.0	2.8
O ₂ , pct	5.0	4.8	4.8	5.0	6.8	3.5	5.3
CO ₂ , pct	14.5	14.6	14.1	14.8	13.7	15.5	13.4
SO ₂ , ppm	216	710	294	431	40	326	402
Sulfur Emissions, lb/mmBtu	0.46	1.5	0.62	0.85	0.10	0.64	0.61
Sulfur Retention, pct	73	54	61	90	96	85	87
Limestone Feed Size, microns				1470	1360	1120	1600
Bed Material Size, d ₅₀ in microns	910	1100	910	1300	1000	1150	850
Solids Removal Rate, lb/hr							
Bed Material	0.1	0.1	0.8	10.9	1.9	2.4	2.6
Primary Cyclone Ash	3.3	4.3	5.9	9.9	1.3	14.9	7.9
Baghouse Ash	--	0.9	1.1	2.6	0.1	3.2	1.2

CHEMICAL ANALYSIS OF COALS USED FOR TESTING

10

The components of interest in the coal ashes are SiO_2 , Na_2O , K_2O and CaO . The Navajo and Gibbons Creek had high (60 wt%) SiO_2 contents. The other coal ashes had SiO_2 levels between 35 and 50 wt%, except for Beulah, which had a very low 20.4 wt%. Most coal ashes had very low sodium (Na_2O) levels (1.8 wt% or less) except for Beulah, which had 7.4 wt%. The bituminous coals, River King and Pyro, had relatively high K_2O contents (2.4 and 2.6 wt%, respectively). The other coal ashes had K_2O levels of about 1.0 wt% or less. The CaO content of the ashes varied markedly. Absaloka and Beulah had high CaO contents of about 21 wt%, and Navajo had the lowest value of 2.6 wt%.

The other factor affecting the bed chemistry is the limestone feed material. Limestone was added during each test at a rate necessary to meet 70% sulfur capture. The chemical compositions of the limestones used for each test are listed in Table 3. From these analyses, it can be seen that the limestones were relatively pure.

The chemical composition of the bed material from each of the tests was also determined. The data are listed in Table 4. Included in the table is the chemical composition of the bed material, calculated on an CaSO_4 -free basis, and the S/Ca molar ratio for each of the samples. The chemical composition of the bed on a CaSO_4 -free basis allows quantitative comparison of the components in the bed that are not associated with fully sulfated limestone. The Absaloka bed material contained high levels of SiO_2 and CaO . No sodium was observed. The South Hallsville bed material contained much SiO_2 and CaO , no Na_2O or CaO , and no measurable amounts of Na_2O or K_2O . The Navajo bed material, on a CaSO_4 -free basis, was very high in SiO_2 and low in CaO compared to the samples discussed above. The River King sample, however, was very high in CaO and low in the other components, notably the alkali oxides Na_2O and K_2O . The S/Ca molar ratio of 0.14 indicates an excess of "free CaO " in the River King bed material compared to the other samples. The Beulah bed material, on a CaSO_4 -free basis, had a high Na_2O content.

3.2.3 Results and Discussion

3.2.3.1 Wall Loss Measurements

The amount of metal lost from the heat transfer tubes was measured by two methods. The first method was to measure the diameter of the tube before and after the run, with the difference referred to as the diameter loss. The second method was to section the tube after the run and measure the thickness of the tube wall. The wall thickness lost was then calculated based on the tube wall thickness of a section of the tube that had not been exposed during the run. Values reported here will be specified as either "diameter loss" or "wall thickness lost." Because of the different measurement techniques, the trends noted for the wall loss measurements were not always the same as the diameter loss measurements. More confidence is placed in the diameter loss measurements, as they are comparing before-and-after measurements taken at the same location, whereas the wall loss measurements are comparing before-and-after measurements from two different locations.

TABLE 3

CHEMICAL ANALYSIS (IN WT%) OF LIMESTONE FEED

Run Limestone	SC1-0185 Big Horn, MT	SH1-0187 Paris, TX	NJ1-0286 Paris, TX	RK1-0187 Hannibal, MO	B61-0187 Big Horn, MT	GC1-0287 Paris, TX	PY1-0188 Fredonia, KY
SiO ₂	1.6	2.7	2.7	1.9	1.6	2.7	2.9
Al ₂ O ₃	0.3	0.4	0.5	0.3	0.3	0.5	0.7
Fe ₂ O ₃	0.2	0.5	0.5	0.3	0.2	0.5	0.6
CaO	53.9	55.1	54.9	55.7	53.9	55.0	51.4
MgO	0.3	0.3	0.3	0.7	0.3	0.3	1.6
SO ₃	0.2	0.2	0.2	0.3	0.2	0.2	1.7
Loss on Ignition	43.3	43.3	40.9	41.9	43.3	43.3	37.5

TABLE 4

Chemical Analysis (in Wt%) of Bed Material
(End of Run)

	SCL-0185	SHI-0186	NJI-0286	RK1-0386	B61-0187	GCL-0287	PY1-0188
SiO ₂	25.2 45.6	29.2 45.0	65.3 72.1	9.7 12.7	13.0 20.2	21.8 29.5	12.0 20.1
Al ₂ O ₃	3.8 6.9	5.2 8.0	12.2 13.5	3.0 3.9	6.5 10.1	6.5 8.8	4.1 6.9
Fe ₂ O ₃	1.6 2.9	3.2 4.9	2.3 2.5	2.2 2.9	6.3 9.8	1.9 2.6	3.7 6.2
TiO ₂	0.3 0.5	0.2 0.3	0.4 0.4	0.2 0.3	0.7 1.1	0.3 0.4	0.3 0.5
P ₂ O ₅	1.1 2.0	0.7 1.1	0.1 0.1	0.3 0.4	0.9 1.4	0.2 0.3	0.7 1.2
CaO	40.8 40.5	40.4 39.9	12.8 9.9	69.7 78.6	41.9 42.4	52.8 56.9	52.5 60.0
MgO	0.8 1.4	0.5 0.8	0.7 0.8	0.9 1.2	2.7 4.2	1.1 1.5	2.7 4.5
Na ₂ O	0.0 0.0	0.0 0.0	0.0 0.0	0.0 0.0	7.0 10.9	0.0 0.0	0.0 0.0
K ₂ O	0.1 0.2	0.0 0.0	0.6 0.7	0.0 0.0	0.0 0.0	0.1 0.1	0.4 0.7
SO ₃	26.3 --	20.7 --	5.5 --	13.9 --	20.9 --	15.3 --	23.7 --
S/Ca	0.45 --	0.36 --	0.30 --	0.14 --	0.35 --	0.20 --	0.32 --

CaSO₄-free basis analyses are listed in the second column for each test. S/Ca is molar ratio.

Individual measurements for metal loss were taken in microns. The graphs used in this report are in most cases a sum of several or all of the measurements for a given coal or metal type. This was done to average out data anomalies and present an overall picture of how metal loss was affected by the various parameters under study. Therefore, in most cases the y-axis should be taken as a relative scale, and not an absolute scale. Absolute numbers will vary from unit to unit, depending on geometry, operating conditions, and other factors. This report presents the relative trends and effects measured in this study.

An example of diameter loss data is given in Figures 3 and 4. Figure 3 shows the diameter loss for Tube #7, a 316-stainless steel tube, at the four measurement locations. Figure 4 shows similar data for Tube #8, a carbon steel tube. The measurements taken are the vertical diameter loss (VDL), Diagonal 1 diameter loss (D1DL), horizontal diameter loss (HDL) and the Diagonal 2 diameter loss (D2DL). These measurements were taken across the following clock positions: 12:00 to 6:00 (VDL), 1:30 to 7:30 (D1DL), 3:00 to 9:00 (HDL), and 4:30 to 10:30 (D2DL). The coal abbreviations used are the same as listed in Table 2. Raw data tables and figures will be presented for all the tubes in the topical report.

The metal loss data was examined in two ways. One method utilized the average of all four measurements around the circumference of each of the tubes to make comparisons between coal type, tube metal, surface temperature, and location. The second compared the maximum measurements taken for each tube. In most cases, the average values correlated well with the maximum value.

Figure 5 gives a comparison of the metal loss as measured by diameter loss. The diameter losses for all four locations for all 29 tubes have been summed. This data indicates that the highest metal loss resulted from burning the South Hallsville coal, followed by the Sarpy Creek and Pyro coals. Beulah and Gibbons Creek followed at a lower level, with the River King and Navajo being the lowest.

Figures 6, 7, 8, and 9 show the same diameter loss data broken down by location and metal type. These figures show differences in metal loss as a function of coal type, metal type, and location.

An analysis of variance was performed to determine which of these differences were statistically significant. The highest and lowest values for the diameter loss data, rather than the average or sum of the losses, were used in the statistical analysis. Maximum values were used because they represent worst case situations, and they indicate where tube failure would first appear.

Tables 5 and 6 present comparative statistics for the maximum measurements of wall loss and diameter loss as a function of surface temperature, coal type, metal type, and location. The difference between the lowest and highest readings is large in most cases, and reflects the fact that the data was not sorted into subcategories before determining the descriptive statistics. For instance, the lowest and highest values and standard deviations would be smaller (for each coal) for only those stainless steel tubes located in the bed than for the total number of tubes in the study. Even though including all of the data points increased the range of numbers reported, it also increased the degrees of freedom for a given category and improved the statistical analysis.

Figure 3. Diameter loss measurements for Tube #7, 316-Stainless Steel. Greater-than-zero values refer to loss on all figures.

Figure 4. Diameter loss measurements for Tube #8, Carbon Steel.

Figure 5. Sum of all diameter metal loss measurements for all 29 tubes.

Figure 6. Sum of diameter loss measurements as a function of coal type and metallurgy for all tubes.

Figure 7. Sum of diameter loss measurements as a function of coal type and metallurgy for In-Bed Tubes.

Figure 8. Sum of diameter loss measurements as a function of coal type and metallurgy for splash zone tubes.

Figure 9. Sum of diameter loss measurements as a function of coal type and metallurgy for convective pass tubes.

TABLE 5
COMPARATIVE STATISTICS ON DIAMETER LOSS

Temperature °F	Number of Observations	Lowest Value	Highest Value	Mean	Standard Deviation
250	28	- 38	165	23	40
400	33	-127	686	142	180
700	28	- 13	127	47	40
1100	45	-127	229	56	66
1200	26	- 63	965	196	279
1500	28	-177	127	-11	80
<u>Coal Type</u>					
Beulah	29	- 13	508	70	104
Gibbons Creek	29	- 25	965	74	181
Navajo	29	-165	394	41	94
Pyro	29	-127	686	122	197
River King	29	-114	673	70	156
Sarpy Creek	28	-177	457	54	120
South Hallsville	25	- 76	712	84	155
<u>Metal Type</u>					
304 SS	54	- 25	241	70	67
316 SS	56	- 25	228	50	58
347 SS	55	-177	153	4	73
Carbon Steel	33	- 38	965	234	277
<u>Location</u>					
In-Bed	96	-177	686	62	134
Splash Zone	20	- 63	965	86	175
Convective Pass	82	- 13	216	77	65

The highest and lowest values from each tube were used in the statistical analysis. All units are microns.

U.S. DEPARTMENT OF ENERGY
FEDERAL ASSISTANCE MANAGEMENT SUMMARY REPORT

Page ____ of ____

1. Program/Project Identification No. DE-FC21-86MC10637	2. Program/Project Title Fluidized Bed Combustion	3. Reporting Period 04-01-88 through 06-30-89
4. Name and Address University of North Dakota Energy and Mineral Research Center P.O. Box 8213, University Station, Grand Forks, ND 58202		5. Program/Project Start Date 04-01-86
		6. Completion Date 03-31-92

Milestone ID, No.	Description	Planned Completion Date	Actual Completion Date	Comments
SK A	AGGLOMERATION			
a.1	Survey of industrial/utility facilities	07/15/88	04/30/89	
a.2	Assemble and correlate EMRC data	08/15/88	09/01/88	
a.3	Analysis of selected material	10/15/88	10/15/88	
a.4	Draft report	03/31/89		
a.5	Final Topical report	05/30/89		
SK B	EVALUATION OF CORROSION/EROSION			
b.1	Complete metallographic analysis of tubes	09/01/88	03/30/89	
b.2	Complete statistical correlation of data	11/15/88	06/30/89	
b.3	Followup metallographic work on selected tubes	12/31/88	06/30/89	
b.4	Draft report	03/31/89		
b.5	Final Topical report	06/30/89		
SK C	CHARACTERIZATION STUDIES OF WESTERN COAL No work scheduled			
SK D	SLURRY FEED APPLICATIONS No work scheduled			
SK E	ADVANCED CONCEPTS AND SPECIAL APPLICATIONS			
e.1	Define advanced concepts for further study	06/30/88	06/30/88	
e.2	Preliminary modeling, calculations, experimentation	08/30/88	08/30/88	
e.3	Present concepts to METC personnel	09/30/88	10/30/88	
e.4	Assessment of development work on advanced concepts	06/30/89	06/30/89	

TABLE 6
COMPARATIVE STATISTICS ON WALL LOSS

<u>Temperature °F</u>	<u>Number of Observations</u>	<u>Lowest Value</u>	<u>Highest Value</u>	<u>Mean</u>	<u>Standard Deviation</u>
250	28	0	432	96	102
400	33	0	788	237	209
700	28	-25	483	133	133
1100	45	-25	559	127	121
1200	26	-25	1678	270	392
1500	28	-51	585	127	141
<u>Coal Type</u>					
Beulah	29	0	407	82	100
Gibbons Creek	29	0	1678	161	319
Navajo	29	-25	712	116	170
Pyro	29	25	712	185	167
River King	29	-25	788	285	199
Sarpy Creek	28	51	813	233	188
South Hallsville	25	-51	203	50	71
<u>Metal Type</u>					
304 SS	54	0	534	133	121
316 SS	56	-51	280	69	79
347 SS	55	-25	585	154	143
Carbon Steel	33	0	1678	372	347
<u>Location</u>					
In-Bed	96	-51	788	163	164
Splash Zone	20	-25	1678	164	249
Convective Pass	82	-25	559	135	156

The highest and lowest value from each tube were used in the statistical analysis. All units are microns.

Wall loss and diameter loss values are similar, with a few exceptions. Wall loss measurements, on a tube-by-tube basis, were consistently greater than the diameter loss measurements. This is believed to be a function of the measurement technique. The trends for metal loss as a function of coal type differed between the two measurement techniques, with the wall loss measurements showing higher values (relative to the other coal types) for the River King and Sarpy Creek, and lower values for the South Hallsville than did the diameter loss measurements. Metal losses for the 347-stainless steel were higher relative to the other stainless steels as measured by wall loss, and lower as measured by diameter loss. The relative measurements for temperature were similar for both wall loss and diameter loss, with the exception of measurements at 1550°C, where the relative diameter loss was less than the wall loss.

Results from the analysis of variance (ANOVA) are presented in Tables 7 and 8. Metal type and temperature were found to have significant effects on the metal loss at the 95%-confidence level for both wall and diameter measurements. Wall loss measurements indicated that coal type also played a significant role in the amount of metal lost during the testing. Several two- and three-level interactions, such as coal and metal type, were also found to be significant, indicating that the metal types, relative to each other, were affected differently by the different coals tested. The mean values of each category were compared to substantiate the differences indicated by the ANOVA. Tables 9 and 10 present the results.

A graphical representation of the amount of metal wear as a function of circumference location for the 29 tubes is presented in Figure 10. In this figure, the sum of all measurements at a given tube location for all tubes of a given coal type are plotted. The River King, Gibbons Creek, South Hallsville, and Sarpy Creek all show similar wear patterns, with the highest wear at 3:00 and the lowest at 9:00. An opposite trend is noted for the Navajo, which shows the lowest wear at 3:00 and the highest from 7:30 to 12:00. The Pyro and Beulah show less variance as a function of location on the tube.

The observations shown in Figure 10 differ from those made from test units experiencing high erosion rates. Under an erosive environment in a fluid bed, it would be expected that the highest wear would occur at the 4:30 and 7:30 locations, and that the wear pattern would be symmetrical about the 12:00/6:00 axis. The absence of this pattern in the current data indicates that erosion may have played only a minor role in the metal wastage observed in this testing, and that corrosion was the predominant force. Significant amounts of sulfide penetration, deposit/scale buildup, and evidence of spalling on the tubes also were indicative of corrosive action, rather than erosion. The effects of the wall in the small bed used for testing may have also impacted the erosion patterns. The geometry of the bed is not thought to impact the corrosion mechanisms.

3.2.3.2 Sulfide Penetration

Equally important to the amount of metal lost, is the depth of sulfide attack into the metal. Sulfidation within the metal will eventually lead to a destruction of the integrity of the metal, and spalling of layers of metal. This corrosive attack can lead to more metal loss than the erosive forces in the bed. Measurements of the depth of sulfide penetration were taken at four locations around the circumference of each tube. At each location, the maximum depth of the sulfide inclusion was recorded. Data from these measurements will be reported in the topical report. For this report, the maximum value reported for each tube was used to statistically determine the effects of coal type, metal type, metal surface temperature, and location.

Table 11 presents comparative statistics on sulfide penetration, and results from the ANOVA are given in Table 12. Coal type, metal type, metal surface temperature, and location all significantly affected the amount of sulfide penetration at the 95%-confidence level.

TABLE 7
ANALYSIS OF VARIANCE FOR DIAMETER LOSS

<u>Source</u>	<u>Degrees of Freedom</u>	<u>Pr > F</u>	<u>Significant</u>
Coal	6	0.2072	
Metal	3	0.0001	yes
Location	1	0.2146	
Temperature	4	0.0010	yes
Coal*Metal	18	0.4053	
Coal*Location	12	0.9689	
Metal*Location	5	0.8097	
Location*Temp	1	0.0919	
Coal*Temp	36	0.0643	
Metal*Temp	16	0.0001	yes
Loc*Temp*Coal	48	0.0409	yes
Temp*Metal*Loc	24	0.0001	yes
Coal*Metal*Loc	75	0.0091	yes

Pr > F of 0.0500 is equivalent to 95% confidence level.

TABLE 8
ANALYSIS OF VARIANCE FOR WALL LOSS

<u>Source</u>	<u>Degrees of Freedom</u>	<u>Pr > F</u>	<u>Significant</u>
Coal	6	0.0001	yes
Metal	3	0.0001	yes
Location	1	0.9857	
Temperature	4	0.0037	yes
Coal*Metal	18	0.0001	yes
Coal*Location	12	0.0001	yes
Metal*Location	5	0.0001	yes
Location*Temp	1	0.0049	yes
Coal*Temp	36	0.2046	
Metal*Temp	16	0.0001	yes
Metal*Temp*Loc	24	0.0001	yes
Coal*Temp*Loc	48	0.0787	
Coal*Metal*Loc	75	0.0001	yes

TABLE 9
COMPARISON OF MEANS FOR DIAMETER LOSS

<u>Temperature Comparison °F</u>	<u>Difference Between Means</u>	<u>Pr > F</u>	<u>Significant</u>
250- 700	24	0.4455	
250-1200	173	0.0001	yes
400-1100	85	0.0033	yes
400-1550	153	0.0127	yes
700-1200	149	0.0001	yes
1100-1550	68	0.0197	yes
<u>Coal Comparison</u>			
PY - SH	37	0.4663	
PY - GC	48	0.1184	
PY - BB	52	0.0949	
PY - RK	52	0.0911	
PY - SC	68	0.0487	yes
PY - NJ	80	0.0097	yes
SH - GC	11	0.4384	
SH - BB	14	0.3788	
SH - RK	15	0.3685	
SH - SC	31	0.2382	
SH - NJ	43	0.0769	
GC - BB	3	0.9125	
GC - RK	4	0.8966	
GC - SC	20	0.6678	
GC - NJ	32	0.2980	
BB - RK	1	0.9839	
BB - SC	16	0.7487	
BB - NJ	29	0.3517	
RK - SC	16	0.7639	
RK - NJ	28	0.3622	
SC - NJ	12	0.5465	
<u>Metal Comparison</u>			
CS - 304	164	0.0001	yes
CS - 316	184	0.0001	yes
CS - 347	239	0.0001	yes
304 - 316	20	0.3175	
304 - 347	66	0.0082	yes
326 - 347	46	0.0898	
<u>Location Comparison</u>			
Bed - Convective	24	0.2301	

TABLE 10
COMPARISON OF MEANS FOR WALL LOSS

<u>Temperature Comparison °F</u>	<u>Difference Between Means</u>	<u>Pr > F</u>	<u>Significant</u>
250- 700	27	0.3744	
250-1200	174	0.0002	yes
400-1100	110	0.0113	yes
400-1550	111	0.5388	
700-1200	136	0.0037	yes
1100-1550	0	0.0554	
<u>Coal Comparison</u>			
PY - SH	135	0.0051	yes
PY - GC	23	0.5717	
PY - BB	103	0.0135	yes
PY - RK	100	0.0157	yes
PY - SC	49	0.1688	
PY - NJ	69	0.0936	
SH - GC	111	0.0233	yes
SH - BB	32	0.6619	
SH - RK	235	0.0001	yes
SH - SC	184	0.0001	yes
SH - NJ	66	0.2215	
GC - BB	79	0.0556	
GC - RK	124	0.0031	yes
GC - SC	72	0.0536	
GC - NJ	45	0.2704	
BB - RK	203	0.0001	yes
BB - SC	151	0.0002	yes
BB - NJ	33	0.4125	
RK - SC	51	0.3021	
RK - NJ	169	0.0001	yes
SC - NJ	118	0.0027	yes
<u>Metal Comparison</u>			
CS - 304	240	0.0001	yes
CS - 316	303	0.0001	yes
CS - 347	217	0.0001	yes
304 - 316	63	0.0425	yes
304 - 347	22	0.4163	
316 - 347	85	0.0049	yes
<u>Location Comparison</u>			
Bed - Convective	1	0.9857

Figure 10. Sum of all tube wall loss measurements for a given location as a function of coal type.

TABLE 11
COMPARATIVE STATISTICS ON SULFIDE PENETRATION

Temperature °F	Number of Observations	Lowest Value	Highest Value	Mean	Standard Deviation
250	20	0	50	10	16
400	33	0	170	25	34
700	19	0	130	18	28
1100	51	0	420	43	60
1200	23	0	50	15	13
1550	27	8	120	54	32
<u>Coal Type</u>					
Beulah	29	10	170	47	39
Gibbons Creek	27	0	420	31	79
Navajo	29	0	50	18	16
Pyro	16	23	105	52	21
River King	24	0	50	12	13
Sarpy Creek	22	0	100	32	30
South Hallsville	26	0	138	31	39
<u>Metal Type</u>					
304 SS	48	0	420	44	64
316 SS	46	0	120	27	24
347 SS	47	0	120	24	27
Carbon Steel	32	0	170	28	38
<u>Location</u>					
In-Bed	93	0	170	37	32
Splash Zone	62	0	130	15	20
Convective Pass	18	0	420	55	96

The minimum and maximum values from each location were used in the statistical analysis. All units are microns.

TABLE 12
ANALYSIS OF VARIANCE FOR SULFIDE PENETRATION

<u>Source</u>	<u>Degrees of Freedom</u>	<u>Pr > F</u>	<u>Significant</u>
Coal	6	0.0130	yes
Metal	3	0.0050	yes
Location	1	0.0367	yes
Temperature	4	0.0099	yes
Coal*Metal	24	0.0344	yes
Coal*Location	6	0.0001	yes
Metal*Location	2	0.0076	yes
Location*Temp	0	NA	
Coal*Temp	22	0.6897	
Metal*Temp	10	0.8885	
Loc*Temp*Coal	45	0.0001	yes
Temp*Metal*Loc	24	0.0001	yes

A comparison of the means is given in Table 13. Temperatures in the convective pass (250, 700, and 1200°F) did not significantly effect the amount of sulfide penetration. Temperatures in the bed, however, did play a significant role in sulfide penetration, with more sulfide penetration occurring on the tube with the higher surface temperature. A comparison of the mean values for coal type indicate that the sulfide penetration was significantly higher for Pyro, Gibbons Creek, and Beulah compared to River King, and for Pyro and Beulah compared to Navajo. Differences between the other coal combinations were not significant at the 95%-confidence level.

The mean values of sulfide penetration for metal type are also compared in Table 13. The data indicate that at the 95%-confidence level, 347-stainless steel experienced less sulfide attack than did the 304-stainless and the carbon steel. No statistical difference existed between the 316- and 347-stainless steels. The 304-stainless not only displayed a higher sulfide penetration than the 347, but it was also higher than the carbon steel and the 316-stainless steel, if a 94% confidence level is used. The sulfide penetration for the 316 and the carbon steel showed no difference. Significantly greater sulfide penetration occurred in the bed as compared to the convective pass.

TABLE 13
COMPARISON OF MEANS FOR SULFIDE PENETRATION

<u>Temperature Comparison °F</u>	<u>Difference Between Means</u>	<u>Pr > F</u>	<u>Significant</u>
250- 700	8	0.5648	
250-1200	5	0.7360	
400-1100	17	0.2479	
400-1550	29	0.0006	yes
700-1200	3	0.7931	
1100-1550	12	0.1927	
<u>Coal Comparison</u>			
PY - SH	21	0.2904	
PY - GC	21	0.3411	
PY - BB	6	0.7660	
PY - RK	40	0.0091	yes
PY - SC	20	0.2897	
PY - NJ	34	0.0408	yes
SH - GC	0	0.8916	
SH - BB	15	0.1050	
SH - RK	19	0.0672	
SH - SC	1	0.9763	
SH - NJ	13	0.2495	
GC - BB	15	0.1341	
GC - RK	19	0.0475	yes
GC - SC	0	0.8730	
GC - NJ	13	0.1929	
BB - RK	34	0.0006	yes
BB - SC	15	0.1159	
BB - NJ	28	0.0047	yes
RK - SC	20	0.0852	
RK - NJ	6	0.4449	
SC - NJ	14	0.2867	
<u>Metal Comparison</u>			
CS - 304	16	0.9850	
CS - 316	1	0.1028	
CS - 347	4	0.0129	yes
304 - 316	18	0.0539	
304 - 347	20	0.0028	yes
316 - 347	2	0.2711	
<u>Location Comparison</u>			
Bed - Convective	23	0.0506	

3.2.3.3 Deposit/Scale Buildup

A similar analysis was performed for the deposit/scale buildup on the tube surfaces. Results are presented in Tables 14, 15, and 16. Coal, metal type, and metal surface temperature were all significant at the 95%-confidence level, as well as several two- and three-way interactions. The deposits from the test from the Beulah coal were significantly larger than deposit/scales from any of the other tests. The second greatest amount of deposit/scale was observed after the Pyro test, and these deposits/scales were significantly larger than those from the remaining coals, with the exception of the Gibbons Creek. No statistically significant difference existed between the amount of deposit/scale formation from the Gibbons Creek, Navajo, River King, Sarpy Creek, and South Hallsville tests.

The amount of deposit/scale noted on the in-bed tubes decreased with increasing temperature. The amount of deposit/scale measured is significantly different for the tubes at 400°F compared to those at 1550°F. The mean value measured at the intermediate value of 1100°C falls between the means at 400 and 1550°F, but does not differ statistically from either at the 95%-confidence level. The type of stainless steel did not affect the amount of deposit/scale; however, a significantly greater amount of deposit/scale was measured on the carbon steel tubes. More deposit/scale was found on the in-bed tubes as compared to the convective pass tubes; however, the difference was not significant at the confidence levels used in the statistical analysis.

This data is being further analyzed to determine the role of specific properties of the coal ash and bed chemistry on the amount of deposition/scale, sulfide penetration, and metal loss. Statistical analysis of bulk measurements will be used in conjunction with microprobe work. Results will be reported in the topical report.

3.2.3.4 Deposition and Heat Transfer Effects

When deposit layers are of sufficient thickness, heat transfer can be significantly reduced. The heat transfer surface can become insulated from combined effects of thermal radiation, gas convection, and conduction. During each corrosion/erosion test, all inlet and outlet air and water temperatures were monitored along with selected tube and coupon metal surface temperatures. For the tests conducted using Sarpy Creek, Navajo, River King, Gibbons Creek, and Beulah coals, heat transfer data was specifically obtained for Tube 6 (air-cooled). Air flow through Tube 6 was measured with a rotometer, the inlet and outlet air temperatures were measured at the combustor wall interfaces, and a surface thermocouple was embedded midway in the side of the tube.

The overall convective heat transfer coefficients measured for Tube 6 at Run Hour 700 are displayed as bar graphs for each coal type in Figure 11. The overall heat transfer coefficient (h_o) is determined from the relationship:

$$h_o = \frac{Q}{A_w (LMTD)}$$

where Q is the total heat removed from the tube, and A_w is the surface area of the tube wall.

TABLE 14
COMPARATIVE STATISTICS ON DEPOSIT/SCALE

Temperature °F	Number of Observations	Lowest Value	Highest Value	Mean	Standard Deviation
250	20	0	210	42	66
400	31	0	1560	317	473
700	20	0	580	115	193
1100	54	0	720	104	190
1200	23	0	600	105	132
1550	27	0	200	50	57
<u>Coal Type</u>					
Beulah	29	120	1560	502	349
Gibbons Creek	29	10	520	65	128
Navajo	27	0	150	19	34
Pyro	17	10	1240	188	385
River King	24	0	370	43	73
Sarpy Creek	23	3	150	30	31
South Hallsville	26	0	50	20	14
<u>Metal Type</u>					
304 SS	48	0	1100	104	215
316 SS	49	0	720	96	179
347 SS	47	0	910	82	175
Carbon Steel	31	0	1560	285	433
<u>Location</u>					
In-Bed	92	0	1560	163	319
Splash Zone	63	0	600	88	160
Convective Pass	20	0	650	91	177

The minimum and maximum values from each tube were used in the statistical analysis. All units are microns.

TABLE 15
ANALYSIS OF VARIANCE FOR DEPOSIT/SCALE

Source	Degrees of Freedom	Pr > F	Significant
Coal	7	0.0001	yes
Metal	3	0.0002	yes
Location	1	0.6284	
Temperature	4	0.0001	yes
Coal*Metal	18	0.0001	yes
Coal*Location	6	0.9942	
Metal*Location	8	0.0001	yes
Location*Temp	0	NA	yes
Coal*Temp	27	0.0001	yes
Metal*Temp	13	0.0420	yes
Coal*Loc*Metal	72	0.0001	yes
Coal*Loc*Temp	46	0.0001	yes
Temp*Metal*Loc	24	0.0287	yes

TABLE 16
COMPARISON OF MEANS FOR DEPOSIT/SCALE

<u>Temperature Comparison (°F)</u>	<u>Difference Between Means</u>	<u>Pr > F</u>	<u>Significant</u>
250-700	73	0.3411	
250-1200	63	0.3544	
400-1100	213	0.4707	
400-1550	267	0.0036	yes
700-1200	10	0.9539	
1100-1550	54	0.4930	
<u>Coal Comparison</u>			
PY - SH	168	0.0113	yes
PY - GC	123	0.0806	
PY - BB	314	0.0001	yes
PY - RK	145	0.0280	yes
PY - SC	158	0.0058	yes
PY - NJ	168	0.0228	yes
SH - GC	45	0.3129	
SH - BB	482	0.0001	yes
SH - RK	23	0.7058	
SH - SC	10	0.7821	
SH - NJ	0	0.7341	
GC - BB	437	0.0001	yes
GC - RK	22	0.5459	
GC - SC	35	0.2054	
GC - NJ	46	0.4976	
BB - RK	459	0.0001	yes
BB - SC	473	0.0001	yes
BB - NJ	483	0.0001	yes
RK - SC	13	0.5214	
RK - NJ	23	0.9599	
SC - NJ	10	0.5415	
<u>Metal Comparison</u>			
CS - 304	182	0.0134	yes
CS - 316	189	0.0096	<
CS - 347	203	0.0154	yes
304 - 316	8	0.9099	
304 - 347	22	0.9969	
316 - 347	14	0.9152	
<u>Location Comparison</u>			
Bed - Convective	74	0.7615

Figure 11. Overall heat transfer coefficient for Tube #6 at Run Hour 700 as a function of coal type.

The log mean temperature difference (LMTD) is calculated by

$$\text{LMTD} = (\text{Tao} - \text{Tai}) / \ln [(\text{TB} - \text{Tai}) / (\text{TB} - \text{Tao})]$$

where Tai = temperature of air in °F,

Tao = temperature of air out °F, and

TB = temperature of bed (°F).

Ash deposition had a significant impact on the heat transfer coefficients measured during each of the runs. The overall heat transfer coefficient varied from 11 to 19 Btu/hr·ft²·°F for the coals reported here. Tube 6 was air cooled and had a surface temperature approximating that of the in-bed superheater surfaces (approximately 1100°F). This result could seriously impact the design and operation of a bubbling bed unit. A reduction in the heat transfer coefficient of this magnitude will cause a boiler derate, as these deposits build up over time. The heat transfer coefficients measured are low in comparison to those in steam generating units because of the low inside coefficient for the cooling air. For a steam- or water-cooled tube, higher values would be observed.

3.3 Advanced Concepts and Special Applications

3.3.1 Conceptualization of the Pretreatment Cell

EMRC has begun work on developing a new process for an advanced fluidized-bed combustion system. The impetus of this program is to develop a new system or improve existing equipment to realize a reduction in overall capital and operating costs, increase boiler and overall efficiency, and/or reduce emission levels. EMRC is striving to match specific goals of the DOE METC Advanced Concept Program as outlined in an earlier RFP. These include:

- Decrease NO_x emissions to 0.11b/MMBtu or lower;
- Decrease SO_x emissions to meet standards with more efficient sorbent use (Ca/S molar ratio < 1.5);
- Increase volumetric heat release rate to above 0.5 million Btu/hr ft³;
- Simplify fuel feeding to handle as-received coal with minimum preparation;
- Increase boiler thermal efficiency to $>90\%$;
- Decrease capital and operating costs in comparison to conventional AFB;
- Extend fuel flexibility range.

A several-phased approach is being taken to accomplish the goals of this task. Initially, a systematic listing of identifiable problems in current FBC technology was developed. This list of problems, and the goals outlined in the METC Advanced Concept Program, were used to direct future work. A second step involved breaking down the FBC process into individual processes, such as calcination, sulfation, drying devolatilization, carbon burnout, etc. Conditions needed to optimize each of these processes, independent of the rest of the process, were determined, based on EMRC experience, FBC theory, and published results.

Using the list of problems and the individual process constraints developed in the first two steps, new concepts that could be incorporated into a design to solve a particular problem or improve performance of a certain subsystem were formulated. These ideas have been qualitatively screened and refined based on technical, environmental, and economic criteria. Since the ideas and concepts have not been analyzed in detail, only those ideas that had obvious problems were screened out. Those that seemed to have merit based on this qualitative screening were pursued further.

Based on these preliminary efforts, EMRC is focusing attention on developing a pretreatment cell to be used in conjunction with any number of combustor designs. The operation and function of the pretreatment cell, as envisioned thus far, is based on previous studies. Details are left out at this time while patentability is being checked. The process, as envisioned,

will feed raw coal into the pretreatment cell. In the pretreatment cell, moisture will be driven off, some devolatilization will occur, and the coal will be fragmented into smaller pieces. The extent or severity of these processes can be controlled by varying several operating parameters. These reactions and changes will occur using heat generated from combusting a small portion of the coal and no external heat source will be required.

The pretreatment cell will be operated as a fluid bed. Velocity and vessel design will be chosen to allow classification of the fuel. Existing data show that an optimal size exists for fuel feed into an FBC, in terms of both top and bottom size. As a result, coal preparation is often a significant operating cost. Data show that size reduction of all coals tested will occur under the conditions planned for the pretreatment cell. Large-sized coal (top size to be determined by testing) can be fed into the pretreatment cell. The vessel will be designed with less surface area on the bottom (high velocity) than at the top of the bed surface (lower velocity) so that segregation will occur. Smaller chunks of coal will be removed from the top of the bed to be fed into the combustor. The larger chunks will remain in the lower level of the bed until they become reduced in size due to drying, volatilization, and the action of the bed. This action will allow the use of coal with a larger top size, thereby reducing coal preparation costs.

In most combustor designs, excessive fines cause reduced combustion efficiency due to elutriation. In the pretreatment cell, velocities will be maintained at a sufficient level to remove fines below 200 mesh. These fines will be removed from the top of the pretreatment cell with the moisture and volatiles, and will become a part of a low-Btu gas stream that can be burned using conventional burners as will be discussed later. Therefore, only a minimal amount of fines will be fed into the combustor and carbon burnout should increase.

Moisture and some volatiles will be driven off in the pretreatment cell. This will be done at a very low air-to-fuel ratio using only heat from the coal. The gas stream from this process, combined with the coal fines, will make up a low-Btu gas that can be used somewhere else in the system, such as in the freeboard or the convective pass of the combustor. Pretreatment can have several applications, but maintaining steam quality during turndown may have the greatest potential benefit. Coal pretreatment can not only smooth out the steps when load is controlled by removing segments of bed, but should also increase the range of turndown.

Removal of the moisture and volatiles in the pretreatment cell will also act as an "equalizer" for the fuel being fed into the main combustor. All fuels burned in the combustor will be similar in terms of moisture and volatiles, and should vary only in the ash. This feature should increase the overall fuel flexibility of the unit.

Mass and energy balances have been performed using this concept. A comparison was made using a conceptual 200-MW bubbling FBC with and without a pretreatment cell. Data for the FBC under normal operation was taken from a previous EPRI study (4). For the case using the pretreatment cell, data taken from previous work was used to generate material and energy balances around the pretreatment cell. For the combustor, velocities and excess air levels

the same as the base case FBC were used. This analysis showed a reduction of 17% in the overall plan area, even with the pretreatment cell included. This will be accompanied by a significant reduction in height for the pretreatment cell versus the height of the fluid bed it replaces. This should result in substantial reductions in capital costs.

Mass and energy calculations also indicated an optimum total air-to-fuel ratio of 1.105. This calculation was done assuming an air-to-fuel ratio of 1.20 for all combustion processes, and is compared to an overall air-to-fuel ratio of 1.20 for the base case FBC. The resulting lower air-to-fuel ratio indicates higher overall boiler efficiency and should result in lower capital cost because of reduced fan requirements.

To summarize, the proposed advanced concept should have many advantages over conventional fluid bed combustion, including the following:

- Minimal coal preparation will be required. Both fines and large coal particles will be efficiently handled.
- The pretreatment cell will be smaller, requiring less feed points and less plan area than the equivalent amount of combustor that it replaces. The total height requirement for the pretreatment cell will also be less than that of the combustor it replaces.
- Fuel flexibility will increase by "equalizing" the fuel (in terms of moisture and volatiles) that is being fed into the combustor.
- Sorbent utilization may be improved by precalcining the sorbent material before feeding it into the combustor.
- The total plan area of the pretreatment bed, the combustor, and the calciner would be approximately 17% less than for an equivalently sized conventional FBC.
- Turndown will be improved by maintaining steam quality at low load conditions.
- Higher volumetric heat release rates are expected.
- Tighter constraints on coal size, both top size and bottom size, will result in higher combustion efficiency and higher heat removal in the fluid bed.
- Staging of air, and lower total air usage should result in lower NO_x emissions.
- Startup may be accomplished without the use of an auxiliary burner.
- The pretreatment cell may be retrofittable to existing units, with similar benefits realized.
- The pretreatment cell will be small enough to allow for modular construction.

The net result of these benefits is the realization of several of the initial goals defined in the DOE METC Advanced Concept Program. Although none of these have been quantified, the system being developed is expected to result in lower capital and operational costs, higher overall boiler efficiencies, higher utilization of sorbent alkali, lower overall NO_x emissions, higher volumetric heat release rates, a simplified fuel feed system, extended fuel flexibility, and improved turndown. Bench-scale tests are being developed to help quantify these advantages and to further define the process. It is anticipated that a patent will result from this effort.

3.3.2 Experimental Verification

The data used to generate the preliminary mass and energy balances for the coal pretreatment cell were taken from previous work performed on an entrained carbonizer (5,6,7). Although conditions will be different when operated as a fluidized bed, the general trends and reactions are expected to be similar. To verify this, and to generate data that can be used to refine earlier mass and energy balances, a pilot unit was designed. This pilot unit was designed to operate under conditions similar to those that will be used in the envisioned commercial unit. Data from this set of experiments will be used to prepare a preliminary plant design for the process.

A general schematic of the pilot test unit is presented in Figure 12. In the pilot unit, coal is fed via a screw feeder into the bottom of the bed. The fluidizing gas will be made up of air and nitrogen. Air flow is varied to get the correct air-to-fuel ratio, and the addition of nitrogen will allow variations in velocity. In an actual unit, flue gas would be used rather than nitrogen to produce the desired velocity. During initial startup of the unit, the incoming air will be preheated to initiate drying and pyrolysis. Once these reactions start, it is expected that they will be self-sustaining and no additional external heat will be required.

Treated char (sized, dried, and partially devolatilized) will be collected via a gravity overflow into a barrel. After each test period, this char will be weighed for material balance calculations. Ultimate, heating value, and sieve analyses will be performed. The coal fines, moisture, and volatiles driven off in the pretreatment cell will be carried out of the pretreatment cell and will ultimately be burned in an existing pc-fired system. Samples will be taken to determine the amount, size, and composition of the coal fines, and the amount and chemical composition of the gas stream.

A test matrix has been designed to study the effects of residence time, superficial gas velocity, air/fuel ratio, coal size, and expanded bed height on the amount and quality of each of the product streams. Results will allow the determination of the optimal operating conditions, and the range and method for turndown and control of the pretreatment cell. A lignitic, subbituminous, and a bituminous coal will be tested to help determine the effect of rank on the performance of the pretreatment cell.

Design and construction of the test unit has been completed during this reporting period. Shakedown activities included testing of the coal feed system, checking for leaks, and testing the gas sampling train. These systems have been checked and modified as necessary. Cold flow testing was initiated. Analytical data was not available at the writing of this report; however,

Figure 12. Experimental Unit for Testing Coal Pretreatment Cell Concept.

visual observations during the test indicate that the device was very successful in achieving the desired sizing of the coal. Surface moisture also appeared to be removed from the coal. The test matrix consisting of 40 different test conditions will be executed in the first quarter of the next program year.

4.0 SUMMARY

Work in the area of agglomeration focused on the preparation of a topical report. Preparation of this report is still in progress.

Corrosion and erosion work focused on analyzing data from seven 1000-hour tests previously performed. A topical report detailing these results is currently being prepared. Results from this effort are summarized.

- Coal type, metal type and surface temperature had significant effects on the amount of metal loss. As determined by diameter loss measurements, the following trends were observed:
 - The ranking of metal loss as a function of coal type, from highest to lowest, was Pyro, South Hallsville, Gibbons Creek, Beulah, River King, Sarpy Creek, and Navajo.
 - Metal loss was most severe for the carbon steel, followed by 304-, 316-, and 347-stainless steel respectively.

- Metal loss decreased with increasing surface temperature for the in-bed tubes.
- Coal type, metal type, surface temperature, and location all had statistically significant effects on the amount of sulfide penetration resulting from the 1000-hour exposure. The observed trends were:
 - The greatest amount of sulfide penetration was observed for the test using Pyro coal, followed by Beulah, Gibbons Creek, Sarpy Creek, South Hallsville, Navajo, and River King.
 - Sulfide penetration was the greatest for the 304-stainless steel tubes, and was similar for the 316-stainless, 347-stainless, and the carbon steel.
 - Depth of sulfide penetration increased with increasing metal surface temperature.
 - Sulfide penetration was the greatest in the splash zone, followed by the bed, with the least amount of penetration occurring in the convective pass tubes.
- Coal type, metal type, and surface temperature had statistically significant effects on the amount of deposit/scale buildup on the heat transfer tubes. Trends are as follows:
 - The largest amount of scale/deposit was observed with the Beulah test, followed by Pyro, Gibbons Creek, River King, Sarpy Creek, South Hallsville, and Navajo.
 - The carbon steel tubes had almost 3 times as much buildup as the stainless steel tubes. Little difference was noted between the stainless steels.
 - Deposit/scale was much greater for the in-bed tubes when compared to the splash zone and convective pass.
 - For the in-bed tubes, the amount of deposit/scale buildup decreased with increasing metal surface temperature.
 - The heat transfer coefficient was significantly reduced as a result of deposit/scale buildup on the tube surfaces.

A new concept was developed as a part of the Advanced Concepts and Special Applications task. A coal pretreatment cell was developed to reduce the overall size of the FBC system, reduce operating costs, increase fuel flexibility, improve startup and load-following capabilities, and enable modular construction and retrofitting. Work has proceeded through a detailed evaluation of available data. Current work is focusing on developing operational data using an experimental test rig. Experimental data will be used to refine mass and energy balances and improve the design concept.

5.0 PUBLICATIONS AND PRESENTATIONS

The following papers were presented during the program year:

Mann, M.D., D.P. Kalmanovitch, and D.R. Hajicek, "The Impact of Coal Properties on Corrosion and Erosion of FBC Boiler Tubes," 1989 Biennial Low-Rank Fuels Symposium, Minneapolis, MN, May, 1989.

Kalmanovitch, D.P., D.R. Hajicek, and M.D. Mann, "The Effects of Coal Ash Properties on the Corrosion/Erosion/Deposition of FBC Boiler Tubes," 10th International Conference on Fluidized-Bed Combustion in San Francisco, CA, April 30-May 3, 1989.

Kalmanovitch, D.P., D.R. Hajicek, and M.D. Mann, "Corrosion and Erosion in a Fluidized Bed Combustor: Effect of Bed Chemistry," Corrosion 89, Paper No. 547, April, 1989.

Mann, M.D., and D.R. Hajicek, "Fuel Flexibility and the CFBC," Presented at the 1988 Pittsburgh Coal Conference, Pittsburgh, PA, September 12-18, 1988.

Mann, M.D., B.J. Zobeck, and D.R. Hajicek, "Comparison of FBC Performance as a Function of Coal Rank," Presented at the Joint Power Generation Conference, Philadelphia, PA, September 25-29, 1988

6.0 REFERENCES

1. Mann, M.D., et al., "Fluidized-Bed Combustion of Low-Rank Coals," Final Report for the Period Ending June 30, 1986, Work Performed under DOE Contract DE-DC21-83FE60181-2127, Grand Forks, North Dakota, September, 1986.
2. Mann, M.D., et al., "Fluidized-Bed Combustion of Low-Rank Coals," First Year Technical Report for the Period April 1, 1986 - March 31, 1987, Work Performed under DOE Contract DE-FC21-86MC10637-T3, Grand Forks, North Dakota, April, 1987.
3. Mann, M.D., et al., "Fluidized-Bed Combustion of Low-Rank Coals," Second Year Technical Report for the Period April 1, 1987 - March 31, 1988, Work Performed under DOE Contract DE-FC21-86MC10637-T3, Grand Forks, North Dakota, April, 1988.
4. Dunlop, W., "Evaluation of Alternative Steam Generation Designs for Atmospheric Fluidized-Bed Combustion Plants," EPRI CS-5296, July 1987.

U.S. DEPARTMENT OF ENERGY
FEDERAL ASSISTANCE MANAGEMENT SUMMARY REPORT

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4. Name and Address University of North Dakota Energy & Mineral Research Center P.O. Box 8213, University Station, Grand Forks, ND 58202		5. Program/Project Start Date 04-01-86
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	C	
	P	
	C	
B. Evaluation of Corrosion/Erosion	P	1 2 3 4
	C	
	P	
	C	
C. Characterization Studies of Western Coal	P	No work scheduled
	C	
	P	
	C	
D. Slurry Feed Applications	P	No work scheduled
	C	
	P	
	C	
E. Advanced Concepts and Special Applications	P	1 2 3
	C	
	P	
	C	
	P	
	C	
	P	
	C	
	P	
	C	
	P	
	C	
	P	
	C	

12. Remarks

13. Signature of Recipient and Date

Michael D. Mann

8/29/89

14. Signature of DOE Reviewing Representative and Date

4.2 Beneficiation of Low-Rank Coals

BENEFICIATION OF LOW-RANK COALS

Annual Technical Report for the Period, April 1, 1988 - June 30, 1989,
including Quarterly Technical Progress Report
for the Period April-June 1989

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July, 1989

Work Performed under Cooperative Agreement No. DE-FC21-86MC-10637

For

U.S. Department of Energy
Office of Fossil Energy
Pittsburgh Energy Technology Center

By

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TABLE OF CONTENTS

	<u>Page</u>
List of Tables.....	ii
List of Figures.....	iii
Abstract.....	1
1.0 INTRODUCTION.....	1
2.0 GOALS AND OBJECTIVES.....	2
3.0 ACCOMPLISHMENTS.....	2
3.1 Physical Cleaning.....	2
3.1.1 Dense-Media Cone Separator.....	2
3.1.1.1 Background.....	2
3.1.1.2 Results.....	3
3.1.2 Comparison of Bench- to Pilot-scale Physical Cleaning....	6
3.1.3 Froth Flotation.....	7
3.1.3.1 Background.....	7
3.1.3.2 Results.....	7
3.2 Chemical Cleaning.....	8
3.2.1 Background.....	8
3.2.2 Bench-scale Testing.....	8
3.2.2.1 Experimental Methods.....	8
3.2.2.2 Results.....	9
3.2.3 Pilot-scale Testing.....	10
3.2.4 Acid Leaching Column Residence Time Tests.....	12
3.2.5 Design Modifications.....	14
3.2.6 Operational and Safety Procedures.....	15
3.3 Coal Product Quality.....	15
3.3.1 Coal Analyses.....	15
3.3.1.1 Proximate, Ultimate And Heating Value Analyses.....	15
3.3.1.2 X-ray Fluorescence Analyses.....	18
3.3.1.3 Particle Size Distributions.....	20
3.3.2 Pilot-scale Material Balance.....	21
3.3.3 Overall Product Recovery for Deep-Cleaned Fuels.....	24
3.3.4 Conceptual Fuel Economics.....	24
3.3.4.1 Background.....	24
3.3.4.2 Operating Costs and Revenues.....	24
3.3.4.3 Capital Costs.....	28
3.4 Water Treatment Studies.....	28
3.4.1 Ultrafiltration.....	28
3.4.1.1 Background.....	28
3.4.1.2 Operating Costs and Revenues.....	28
3.4.1.3 Capital Costs.....	29
3.5 Activated Sludge Treatment of Ultrafilter Permeate.....	29
4.0 CONCLUSIONS.....	31
5.0 RECOMMENDATIONS.....	32
6.0 REFERENCES.....	32

LIST OF TABLES

<u>Table</u>	<u>Page</u>
1. Results for Beulah PDU-Scale Physical Cleaning.....	3
2. Dense-Media Cone Separator Results for Usibelli, Kemmerer, and Beulah.....	5
3. Bench-Scale Washability of PDU-Scale Physically Cleaned Usibelli.....	6
4. Bench-Scale Washability of PDU-Scale Physically Cleaned Beulah.....	6
5. Continuous Bench-Scale Acid Leaching Results for Beulah Using York-Scheibel Extraction.....	9
6. Bench-Scale Acid Leaching Results of PDU-Scale Physically Cleaned Coal Samples to Predict Ash Levels Obtainable for PDU-Scale Acid Leaching.....	9
7. Acid Leaching Material Balance for Usibelli, Kemmerer, and Beulah....	12
8. Results for Acid Leaching Residence Time Tests.....	13
9. Proximate, Ultimate, and Heating Value Analyses for Kemmerer Coal/Water Fuels.....	17
10. Proximate, Ultimate, and Heating Value Analyses for Usibelli HWD Products.....	18
11. Proximate, Ultimate, and Heating Value Analyses for Beulah HWD Samples.....	19
12. Kemmerer Subbituminous X-ray Fluorescence Analysis.....	19
13. Usibelli Subbituminous X-ray Fluorescence Analysis.....	20
14. PDU #40 Beulah X-ray Fluorescence Analysis.....	21
15. Material Balance for Acid-Cleaned Kemmerer Fuels.....	24
16. Overall Material Balance for Deep-Cleaned Fuels.....	25
17. Processing Performance Ranges for Low-rank Coals.....	25
18. Operating Costs for an 800,000-ton/year CWF Plant.....	26
19. Reagents for Deep-Cleaned CWF Production.....	27
20. Operating and Capital Costs for an Ultrafiltration System.....	30

LIST OF FIGURES

<u>Figure</u>	<u>Page</u>
1. Physical Coal Cleaning Dense-Media Cone Separator.....	3
2. Baffle Modification to Dense-Media Cone Separator.....	5
3. Infrared Analysis of Wet- and Dry-Milled Beulah Lignite.....	8
4. Continuous Acid Cleaning Column and Supporting Equipment.....	11
5. Centrifuge Cake Ash Reduction versus Residence Time.....	13
6. Centrifuge Cake Ash Reduction versus Wash Water Rate.....	14
7. Modified Continuous Acid Cleaning Column.....	16
8. Particle Size Distribution for PDU #40 Beulah.....	22
9. Particle Size Distribution for PDU #38 Kemmerer.....	22
10. Particle Size Distribution for PDU #38 Usibelli.....	23
11. Clean Coal/Water Fuel Processing Scheme.....	23
12. Schematic of Ultrafiltration Test System.....	29

BENEFICIATION OF LOW-RANK COALS

ABSTRACT

A continuous, integrated beneficiation process development unit (PDU) for low-rank coals (LRCs) was developed to allow production of nominally 200 lbs/hr of cleaned LRCs for end-use testing. Processing involved physical cleaning by dense-media cone separation, chemical cleaning by dilute acid column leaching and thermal upgrading by hot-water drying (HWD). Intermediate dewatering was accomplished with on-line centrifugation. The clean, upgraded coal products were prepared for utilization testing as either thermally dried, micronized dry powder fuels or micronized, coal/water fuels (CWFs). Micronizing was performed with a continuous, vertical Attritor wet-grinding mill.

Bench-scale results, which yielded products with ash levels of less than 1 wt% (dry basis) for several LRCs, were the basis for PDU development. PDU operation has produced over 10 tons of cleaned coal products containing 1.5 to 3.0 wt% ash (dry basis) in the past year, with most of the material prepared as micronized CWF. Modifications to the PDU processing and cleaning equipment eliminated product contamination and helped reduce the difference between PDU and bench-scale cleaning performance. Beulah lignite from North Dakota and Kemmerer subbituminous coal from Wyoming were used extensively for process development and fuel production. Additional testing in the PDU was performed on Usibelli subbituminous coal from Alaska in much smaller amounts. CWFs with 48-62 wt% solids (dry basis) and energy densities of 5500 to 8000 Btu/lb were prepared from beneficiated coals with heating values of 11,400 to 13,000 Btu/lb (dry basis).

In addition to development of the PDU, bench-scale froth flotation tests were completed. Emphasis was placed on the effect of wet versus dry grinding on froth flotation performance. This investigation was not successful with the LRCs tested regardless of wet or dry grinding. Other bench-scale investigations included acid leaching with a variety of acids, and Certigrav washability testing. Work on ultrafiltration and activated sludge treatment of process water was concluded with an economic assessment for the two processes.

1.0 INTRODUCTION

This report summarizes progress towards previously (1) and newly established goals and objectives. Product coals were generated from PDU preparation of low-ash, LRC fuels for combustion testing. Modifications and additions to the PDU facilities were made to improve product quality.

Investigations were performed to identify and improve the pilot-scale processing steps that yielded higher ash products than comparative bench-scale processing steps. This involved analyses and bench-scale testing of various coal products from intermediate steps of the PDU. Alternate cleaning techniques, such as froth flotation, were investigated on the bench-scale to

determine their effectiveness on LRCs. Recommended HWD process water treatment designs and their estimated commercial-scale costs were also determined.

2.0 GOALS AND OBJECTIVES

The objectives of the Low-Rank Coal Beneficiation Project were to study methods of reducing the inorganic content and increasing the heating value of LRCs. Integrating physical and chemical coal cleaning technologies with the established HWD process allowed EMRC to produce a clean, energy-dense LRC for dry solid or CWF preparation. Tasks were performed to further develop bench-scale and PDU-scale methods to produce fuels for advanced combustion systems including turbines, diesel engines and small-scale combustors. The PDU-scale processing work has been performed under both the Pittsburgh and Morgantown Energy Technology Centers programs on Combustion, Gasification, and Heat Engines which have run concurrently with the Low-Rank Coal Beneficiation Program.

The specific objectives of the EMRC LRC Beneficiation group for the past year were to: 1) complete integration and modification of PDU facilities for physical cleaning, chemical cleaning and HWD fuel production at a minimum of 200 lb/hr, 2) perform and improve on fuel production for various advanced combustion applications, 3) summarize HWD process water treatment options and economics, 4) continue to investigate alternate methods to established coal cleaning techniques, and 5) continue to evaluate methods for froth flotation of LRCs.

3.0 ACCOMPLISHMENTS

3.1 Physical Cleaning

3.1.1 Dense-Media Cone Separator

3.1.1.1 Background

Heavy-media static separation was used to physically clean coal by removing extraneous inorganic ash. Results have shown a 95% pyritic sulfur content reduction in Beulah lignite utilizing heavy-media separation (1). Figure 1 shows the dense-media cone separation cleaning apparatus currently used as part of the EMRC PDU. The process consists of classifying coal to 1/4 inch x 20 mesh size, feeding it into an air actuated cone separator system, and washing the float (clean coal) to remove magnetite. Magnetite is recycled to the cone separator to maintain a constant media specific gravity (sp. gr.). Classification of the feed coal was done to minimize mineral contamination from coal fines in the float product and facilitate product separation from the media suspension. The coal fines were also removed to ensure a low viscosity of the media.

Viscosity or internal friction of the media is an important property in the recovery of the product particles. The viscosity must be low enough to permit high particle velocities. The volume of the media used should be kept

Figure 1. Physical Coal Cleaning Dense-Media Cone Separator

at a minimum to maintain a low liquid viscosity. Magnetite (Fe_3O_4) was selected as the media because of its high sp. gr. (5.17) and availability. The volume of the magnetite within the solution ranged from 0.35 to 0.40. The particle size of the magnetite is critical to the stability of the heavy-media solution. To insure adequate tangential force to the magnetite particles, the magnetite particles must be smaller than 75 microns. At these fine sizes, a minimal force is required to suspend the particles. The calculated viscosity was approximately 2 cp for a 1.3-sp. gr. mixture (3, 4).

3.1.1.2 Results

Table 1 shows the results of physically cleaning Beulah lignite using the PDU-scale physical cleaning equipment at EMRC. The yield is lower than expected because of the 1.25 sp. gr. that was used in this test.

TABLE 1
RESULTS FOR BEULAH PDU-SCALE PHYSICAL CLEANING.

Coal Sample	Spec. Grav.	Feed Ash (%)	Product Ash (%)	Ash Reduct. (%)	Yield (%)
Beulah	1.25	9.4	6.7	17.3	46

The ash content of physically cleaned product coal from the dense-media cone separator is slightly higher than bench-scale cleaning results. It is uncertain whether the higher ash content is due to inadequate mineral matter removal or incomplete washing of magnetite from the product coal. Magnetite, a naturally occurring ore, oxidizes to hematite after chemical cleaning, lowering the fuel ash fusion temperatures and causing slagging to occur in pressurized combustion systems. Therefore, it is imperative to remove carryover magnetite from the float product during physical cleaning.

Optimizing the dense-media cone separator operation required a further understanding of theoretical dense-media coal cleaning principles, and equipment and operating modifications. In order to assess whether incomplete washing of magnetite from the coal product was contributing to the high ash content, a preliminary test was performed.

A dissecting microscope (10X to 50X) was used to examine the dense media cone separator product, tailings, product material after wet micronizing, and product material after HWD, and centrifugation. Magnetite was identified in the product and tailings but identification became difficult after micronization. Identification of the magnetite became easier after the demagnetized magnetite (magnetic poles randomly oriented) was again polarized by passing a magnet under the sample. Particles that had associated magnetite reacted to the magnet and showed a preferred orientation. Magnetite appeared as a chain-like, branching, gray metallic-looking, fine-grained substance. Based on laboratory experiments, theoretical considerations, and operational judgement, the cone separator was modified to reduce magnetite carryover and increase operating efficiency.

To increase the washing efficiency during product recovery, five baffles (3/16" high, full screen width) were installed on the screen, as shown in Figure 2. In addition, two high volume sprayers were added to the second washing stage. All sprayers were directed to strike the product coal as it moved over the baffles. Washing residence time was also increased by decreasing the screen gradient.

With the new washing efficiency apparatus, dense-media separation tests were performed on Usibelli and Beulah to determine what run conditions produce the highest ash reduction with acceptable yields. Yields range from 55% to 75% recovery of the feed coal. Trials were run at specific gravities of 1.2, 1.25, and 1.3. From these tests, it was determined that the most acceptable yields were achieved at a sp. gr. of 1.3 for both coals. Specific gravities higher than 1.3 were not included in the test matrix since the product quality would be greatly reduced. Table 2 shows the results from 1.3-sp. gr. runs for both coals.

Also included in Table 2 are the physical cleaning data for Kemmerer. Kemmerer was physically cleaned to determine if lower ash contents were achievable than for fuel prepared with only chemical cleaning (2). Kemmerer coal, due to its low ash level, was initially chemically cleaned and directly fed to the HWD process. However physical cleaning prior to the chemical cleaning reduced the content of the heavier components of the coal ash such as silica, aluminum, and iron pyrite. The ash analysis results will be discussed

Figure 2. Baffle Modification to Dense-Media Cone Separator

in the section on coal product quality. The run parameters for Kemmerer coal were optimized to produce a low ash product; however, product yield suffered greatly, with only 39 wt% recovery.

Results for Beulah using the improved process were compared to the initial physically cleaned Beulah samples, which were plagued with poor ash reductions and magnetite contamination. The comparison showed that the overall ash content of clean Beulah lignite was lowered from 6.9 to 6.0 wt% improving the coal product quality at a higher yield.

TABLE 2
DENSE MEDIA CONE SEPARATOR RESULTS
FOR USIBELLI, KEMMERER AND BEULAH

Coal Sample	Spec. Grav.	Feed Ash (%)	Product Ash (%)	Ash Reduct. (%)	Yield (%)
Usibelli	1.30	8.7	6.4	26.4	68
Kemmerer	1.26	4.3	2.9	32.6	39
Beulah #3	1.30	8.1	6.0	26.0	58

3.1.2 Comparison of Bench- to PDU-Scale Physical Cleaning

A comparative approach was drawn from the specific gravities of bench-scale physical cleaning (which uses true liquid solutions) and dense-media PDU-scale physical cleaning. The PDU-scale sp. gr. reading was determined from the recycle media, which has a lower sp. gr. than the media in the cone separator. During processing, medial losses occur in the float, sink, and spilled media solution. On the average, the bench-scale sp. gr. of 1.4 compares to a 1.25-specific gravity PDU-scale value.

Samples of PDU-scale cleaned Beulah and Usibelli were reworked in the bench-scale washability analyses used for the comparison test. The PDU-scale specific gravities for the coals were 1.2 for Usibelli and 1.25 for Beulah. A small washability test was run on the samples using true liquid solutions of various specific gravities. Tables 3 and 4 contain results on the bench-scale washabilities of the PDU-scale cleaned coals. The results indicate that the Usibelli product ash level and recovery compare to those of the 1.4-specific gravity float product of the bench-scale sample. The Beulah dense-media sample compares with a bench-scale product with a sp. gr. between 1.4 and 1.5.

TABLE 3
BENCH-SCALE WASHABILITY OF PDU-SCALE
PHYSICALLY CLEANED USIBELLI

<u>Product</u>	<u>Direct</u>		<u>Cumulative</u>	
	<u>Yield, wt%</u>	<u>Ash, wt%</u>	<u>Yield, wt%</u>	<u>Ash, wt%</u>
1.3 - Float	1.2	-	1.2	-
1.35 - Float	47.6	4.45	48.8	4.45
1.4 - Float	43.9	5.68	92.7	4.97
Total	7.3	16.20	100	5.79

TABLE 4
BENCH-SCALE WASHABILITY OF PDU-SCALE
PHYSICALLY CLEANED BEULAH

<u>Product</u>	<u>Direct</u>		<u>Cumulative</u>	
	<u>Yield, wt%</u>	<u>Ash, wt%</u>	<u>Yield, wt%</u>	<u>Ash, wt%</u>
1.3 - Float	1.8	3.41	1.8	3.41
1.35 - Float	24.2	3.94	26.0	3.90
1.4 - Float	58.9	5.71	84.9	5.16
1.5 - Float	12.8	7.59	97.7	5.48
Total	2.3	16.00	100	5.72

3.1.3 Froth Flotation

3.1.3.1 Background

Investigations of froth flotation of LRCs previously focused on dry ground sample preparation. Part of the work performed during this year was to assess the process using wet ground coal. It was felt that wet grinding would not oxidize the coal to the same extent as dry grinding, possibly improving coal floatability.

Additional work performed included screening froth flotation reagents for hydrophilic LRCs. The role and effectiveness of flotation reagents is reasonably well understood for hydrophobic higher-rank coals. Since fuel oil was effective in previous studies on LRCs (1), and is the principal collector used in nearly all coal froth flotation, it was used in these experiments, along with two frother/promoters from the Sherex Chemical Company. These were Shur-Coal 164A (SC164A) and Shur-Coal 168A (SC168A), which were developed primarily for hard to float coals, such as lignite and subbituminous coal. The traditional bituminous coal frother, MIBC (methyl isobutyl carbinol), was also tested. Finally, as a follow-up to research performed last year (1), limited froth flotation experiments were carried out using the collector enhancer, cetyltrimethylammonium chloride. The reagents were not able to significantly improve results over those obtained with MIBC (2,5,6).

3.1.3.2 Results

None of the froth flotation tests during the year produced any significant ash removal, compared to the washability results. This included the flotation of wet-milled samples, which was not as successful as initially expected (5). Infrared analysis was performed on four of the flotation samples to evaluate any differences in coal oxygen functionality during the final quarter. The samples analyzed were wet-milled and dry-milled Jacobs Ranch subbituminous coal and Beulah lignite.

All the infrared analyses of dry-milled and wet-milled coals were similar with respect to aliphatic-to-aromatic ratios; thus, it is unlikely that there was any substantial difference in the extent to which the grinding operations oxidized the coals. The FTIR analyses for the wet- and dry-grind Beulah lignite samples are shown in Figure 3, as an example. The only difference in the spectra of the samples is that the wet-milled samples exhibited a smaller carbonyl absorption ($1630\text{--}1780\text{ cm}^{-1}$) than did the dry-milled samples. An appropriate explanation for this decrease is that the wet-milling converted some of the carboxylic acid groups to the corresponding carboxylate anion (salt form). The wet-milling may have mobilized some of the clay cations, which then combined with the organic carboxylic acid groups.

The carboxylate ionic form would be expected to increase the hydrophilic tendency more than the carboxylic acid. Therefore, air bubbles would be less likely to stick to the ionic surface and flotation would be depressed in the wet-milled coal. These differences in the infrared spectra are very small and the model for explaining the flotation results needs further verification. Chemical methods that determine coal carboxylate and carboxylic acid content, and corroborate infrared analysis, should be investigated.

Figure 3. Infrared Analysis of Wet- and Dry-Milled Beulah

3.2 Chemical Cleaning

3.2.1 Background

The production of cleaned coals with less than 1 wt% ash (dry basis) has been achieved for some LRCs with combined physical and chemical cleaning on the bench-scale. A continuous, PDU-scale acid leaching process was incorporated with physical cleaning for the production of clean LRCs tailored according to the bench-scale results.

3.2.2 Bench-scale Testing

3.2.2.1 Experimental Methods

The equipment that was used for acid leaching was a York-Scheibel liquid-liquid extraction column (6). Samples were collected from 9-30 minutes residence time at 3 minute intervals. When it was determined that the bench-scale column provided an acceptable method to continuously chemically clean the coal, the process was incorporated on the PDU-scale. After bench-scale acid leaching was performed using batch methods, testing was performed to ascertain what levels of cleaning were possible with the coals on the PDU-scale. The bench-scale procedure was modified to be similar to a PDU-scale continuous process (6). Instead of heating the sample to 80°C as done previously (1), the sample was mixed in a 4 wt% nitric acid solution with the only heat generated by chemical reaction.

3.2.2.2 Results

Table 5 is a summary of the bench-scale results from the York-Scheibel extraction column for Beulah lignite. Raw combustion grind coal and physically cleaned combustion grind coal were used in the testing. Coal concentrations are weight percent on a wet basis. Average ash content is on a dry basis. The ash contents of the raw combustion grind and the physically cleaned combustion grind were 9.9 wt% and 6.8 wt%, respectively.

TABLE 5
CONTINUOUS BENCH-SCALE ACID LEACHING RESULTS
FOR BEULAH USING YORK-SCHEIBEL EXTRACTION

<u>Coal Type</u>	<u>Coal Conc., wt%</u>	<u>Final Acid Conc., wt%</u>	<u>Average Ash, wt%</u>	<u>Average Ash Reduction, wt%</u>
Raw	27	7.3	3.2	67.6
Raw	40	4.7	2.2	77.7
Phys. Cleaned	27	7.6	1.6	76.5
Phys. Cleaned	27	4.2	0.9	86.6

The results in Table 5 indicate that the best conditions at which to attain a product with less than 1 wt% ash for Beulah lignite by acid leaching, are to use a physically cleaned coal sample at an acid concentration of around 4 wt%. Additional bench-scale acid leaching tests were performed to ascertain what should be possible on the PDU-scale. These results are summarized in Table 6. The table contains results for Beulah lignite, and Kemmerer and Usibelli subbituminous coals.

TABLE 6
BENCH-SCALE ACID LEACHING RESULTS OF PDU-SCALE
PHYSICALLY CLEANED COAL SAMPLES TO PREDICT ASH LEVELS
OBTAINABLE FOR PDU-SCALE ACID LEACHING

<u>Coal Sample</u>	<u>Phys. Cleaned Ash, wt% (dry basis)</u>	<u>Phys. Cleaned, Chem. Cleaned Ash, wt% (dry basis)</u>
Beulah	6.4	1.8
Kemmerer	3.1	2.2
Usibelli	6.4	2.6

The results in the table compare favorably with the acid leaching results obtained at the PDU-scale for Beulah and Usibelli samples. However, the Kemmerer PDU-scale results were much lower than the bench-scale results, as the PDU-scale results showed a product with an ash content of 1.4 wt% (dry basis). This difference was partially attributed to the fact that the ash content of the physically cleaned sample used on the bench-scale for acid leaching was slightly higher than the PDU-scale sample.

3.2.3 PDU-scale Testing

Processing involved crushing -1/4 inch x 10-mesh coal to minus 60 mesh, mixing into a coal/water slurry, and pumping the slurry into the top of an agitated column, co-currently with nitric acid. The concentration of the coal slurry was approximately 25 wt% (dry basis) with a column acid concentration of 4 wt%. The level in the column was controlled by a valve at the bottom. After passing through the column the sample was stored at 50-60°C in a steam jacketed tank to provide an additional 30 minutes residence time prior to centrifugation. The slurry was pumped from the tank to the solid bowl centrifuge where the acid was washed out with excess wash water and the coal was collected as a moist cake.

Initial column leaching indicated a need for modification to the existing design. The size of the paddles were increased to provide more vigorous mixing and the screen separators were removed to prevent coal build-up. The removal of the screens decreased the solids residence time and slurry mixing in the column. However, improving the mixing in the column helped compensate for the changes. Figure 4 shows the acid cleaning column and related equipment.

After modifications, PDU-scale acid leaching was conducted on four physically cleaned samples of Kemmerer and Usibelli subbituminous coals, and two samples of Beulah lignite. A raw Kemmerer sample, Kemmerer #2, was also PDU-scale acid cleaned for turbine simulator combustion fuel production.

Prior to acid leaching, the float products from the dense media separator were pulverized to 80% -74 microns. The coal sample was then slurried to 25 wt% and fed continuously into the acid cleaning column. Initially, the column acid concentration was 4 wt% nitric acid. The samples were then washed with 1.5 gal/min of water during the centrifugation process. Table 7 summarizes the cleaning efforts.

The results for Kemmerer #1 indicate a fuel produced containing less than 1.5 wt% ash on a dry basis. With Kemmerer #1 a slightly lower ash content was obtained for the PDU-scale acid leached sample than for the bench-scale cleaned sample (results in Table 6). The PDU-scale Usibelli results, which were similar to bench-scale results, indicate that the ash contents of the physically cleaned samples were nearly identical.

Two trials for acid leaching results on Beulah lignite are also contained in Table 7. The two trials were performed with nitric acid concentrations of 5.2 and 3.7 wt%, respectively. The results indicated no significant change in

Figure 4. Cont. Acid Cleaning Column and Supporting Equipment

TABLE 7
ACID LEACHING MATERIAL BALANCE
FOR USIBELLI, KEMMERER AND BEULAH

Coal Sample	Acid Conc. (%)	Feed Ash (%)	Product Ash (%)	Ash Reduction (%)	Product Yield (%)
Kemmerer #1	6.3	2.9	1.4	52	83
Usibelli	8.9	6.3	2.6	59	87
Beulah	5.1	6.3	2.1	67	89
Kemmerer #2	5.2	3.5	2.4	31	97
Beulah #40	3.7	6.0	2.1	65	91

cleaning efficiency with the higher concentration of nitric acid, since both tests yielded products with an ash content of 2.1 wt%.

Acid leaching of raw Kemmerer (Kemmerer #2 in Table 7) was performed to determine whether physical cleaning costs could be eliminated and still produce a low ash fuel. The acid concentration was kept at about 5.2 wt% for the entire run. The results showed only a 31% ash reduction, compared to the 52% reduction yielded for the physically and acid cleaned sample.

3.2.4 Acid Leaching Column Residence Time Tests

A series of tests were performed to determine the effects of residence time and centrifuge wash water rate on ash reduction during continuous acid leaching of Kemmerer subbituminous coal. A slurry consisting of 25 wt% coal and 75 wt% deionized water was mixed with nitric acid to achieve an acid concentration of approximately 4 wt%. The slurry and acid feed rates were adjusted to achieve residence times of 5, 10, 15, 30 and 60 minutes. The centrifuge wash water rates were 0.5, 1.5 and 3.0 gal/min for the 30-minute residence time tests. For the 5, 10, 15 and 60-minute tests the wash water rate was maintained at 1.5 gal/min. Residence time was considered the interval between the introduction of reactants (slurry and acid) and the initiation of centrifugation.

Table 8 presents the acid concentrations, wash water rates, centrifuge cake ash contents and ash reductions at the various residence times. The desired acid concentration was 4.0%; however, acid flow control was difficult and consequently, the concentration varied between tests. The ash content of the raw Kemmerer coal was 3.54 wt% (dry basis) and the ash content of the leached coal varied from 1.97 to 2.41 wt%. Product moisture and ash-free coal yields were all 85-90%. Figure 5 depicts ash reduction as a function of residence time for a wash water rate of 1.5 gal/min. Ash reduction increased as residence time increased; however, ash reduction was essentially unchanged after a 30 minute residence time.

TABLE 8
RESULTS FOR ACID LEACHING RESIDENCE TIME TESTS

Residence Time (min)	5	10	15	30	30	30	60
Acid Concen. (%)	5.8	2.9	3.2	3.9	3.9	3.9	3.9
Wash Water Rate (gal/min)	1.5	1.5	1.5	0.5	1.5	3.0	1.5
Cent. Cake Ash (%)	2.26	2.41	2.04	2.12	2.12	1.97	2.08
Ash Reduction (%)	36.2	31.9	42.4	40.1	40.1	44.4	41.2

Figure 5. Centrifuge Cake Ash Reduction versus Residence Time

The wash water rate was varied during the 30-minute tests to determine the effect of wash rate on removal of solubilized mineral matter. Figure 6 indicates that a wash rate of 3.0 gal/min is superior to the normal wash rate of 1.5 gal/min for removing liberated minerals. On a pilot scale, the higher wash rate may be practical. However, on a commercial scale, the higher value of the lower ash-content fuel may not be sufficient to offset the higher water usage and treatment costs.

3.2.5 Design Modifications

Due to desired improvements to the current acid leaching column and its potential use in another project, the LRC Beneficiation group decided to design and construct a replacement column. The criteria for design were to increase capacity from a 300 to a 400 lb/hr slurry feed rate and a 30 minute hydraulic residence time. A residence time of 30 minutes was considered optimal for ash reduction and was based upon residence time tests described in section 3.2.4.

It was determined that a nominal 8-inch diameter 10-foot long column would provide sufficient volume for the desired feed rate and residence time. The new column was constructed of PVC to reduce material cost. Soak tests using concentrated nitric acid confirmed that the PVC was acid resistant. The new internals include four-bladed, stainless steel turbine impellers capable of variable pitch, to optimize mixing.

Figure 6. Centrifuge Cake Ash Reduction versus Wash Water Rate

Previously, level measurement and control were done visually using a manually operated ball valve. On the new column, level control is performed by a pneumatically actuated ball valve and a displacement-type pneumatic level controller. The existing acid and slurry feed systems, product surge tank and centrifuge were sufficiently oversized and modifications were not necessary. A schematic of the new acid leaching column is shown in Figure 7.

3.2.6 Operational & Safety Procedures

The operational procedure for the acid column began with a check to ensure that process lines were clear and all pumps were calibrated. The column was then filled with a 4 wt% nitric acid solution, so that feeding of 25 wt% coal/slurry feed begin with a flooded situation. The mixing system was started at this point. Concentrated nitric acid and the 25 wt% dry coal slurry were co-currently fed at proportionate rates to maintain approximately 4 wt% nitric acid based on the water content of the slurry feed. Flowrates were monitored every 15 minutes, to ensure feed and residence times. After a column residence time of 20-30 minutes, the product was collected in a circulated and agitated product surge tank to allow an additional 30-60 minutes of residence time. Once a 75% level was achieved in the tank, the centrifuge was started with a 1-2 gallon/minute water wash rate.

All personnel involved with the operation of the acid cleaning process wore protective full face shields and acid resistant gloves. Samples were only taken from sampling points below knee level. A vacuum system was operated on the product tank to evacuate any acid fumes to an incinerator. Process wash water from the centrifuge was carefully neutralized with pelletized sodium hydroxide before discharge.

3.3 Coal Product Quality

3.3.1 Coal Analyses

3.3.1.1 Proximate, Ultimate, and Heating Value Analysis

Tables 9, 10, and 11 contain the proximate, ultimate, and heating value analyses for HWD products made from Kemmerer and Usibelli subbituminous coals and Beulah lignite, respectively. Table 9 contains the proximate, ultimate, and heating value analyses for several CWFs made from Kemmerer subbituminous coal. Analyses are given for the raw coal, PDU #35 and #36, and two samples from PDU #38. The fuel produced in PDU #35 was chemically cleaned prior to HWD. The fuel produced in PDU #36 was only hot-water dried. The fuel produced in PDU #38A was a chemically cleaned fuel similar to the fuel made in #35, and PDU #38B was physically and chemically cleaned coal prior to HWD.

The data in Table 9 indicates that the fuel produced in PDU #35 was oxidized by nitration during acid leaching, as evidenced by the increase in nitrogen and oxygen contents, and by the decrease in heating value in comparison to the raw coal. The fuel produced in PDU #36 without acid cleaning did not show similar increases in oxygen and nitrogen contents, but showed a higher carbon content, which led to a higher heating value.

Figure 7. Modified Continuous Acid Cleaning Column

TABLE 9
PROXIMATE, ULTIMATE, AND HEATING VALUE ANALYSES FOR
KEMMERER COAL/WATER FUELS

Sample:	<u>Raw</u>	<u>PDU #35</u>	<u>PDU #36</u>	<u>PDU #38A</u>	<u>PDU #38B</u>
Prox. Analysis (mf, wt%)					
Vol. Matter	41.9	39.4	38.5	41.1	39.7
Fixed Carbon	53.8	57.7	56.9	56.6	58.1
Ash	4.3	2.9	4.7	2.3	2.2
Ult. Analysis (maf, wt%)					
Carbon	76.7	75.4	77.5	77.5	76.5
Hydrogen	5.5	4.4	5.2	5.1	4.8
Nitrogen	1.4	2.3	1.4	1.3	1.4
Sulfur	0.2	0.2	0.3	0.3	0.3
Oxygen ^a	16.2	17.7	15.6	15.8	17.0
Heating Value (mf, Btu/lb)	12,650	12,540	12,840	12,930	12,920

^a by difference

The fuel from PDU #38A was prepared like that of PDU #35 but at a lower overall acid concentration. Note the lower nitrogen and oxygen levels of the PDU #38A fuel obtained while maintaining excellent cleaning efficiency. The fuel has a higher carbon contents, lower ash, nitrogen, and oxygen content, and a higher heating value.

The fuel made in PDU #38B was physically cleaned prior to chemical cleaning and HWD. The physical cleaning prior to acid leaching helped to decrease the post acid leaching ash content to less than 1.5 wt% as reported earlier (5). The ash level increased to 2.2 wt% during HWD, which can be attributed to the loss of volatile matter. The best Kemmerer fuels were produced during PDU #38, acid concentration was maintained low enough that little oxidation occurred.

Table 10 contains the proximate, ultimate, and heating value analyses for a HWD product made from Usibelli subbituminous coal. The results have been discussed in detail in a previous report (5). In summary, the increase in nitrogen and oxygen contents indicate that an excess amount of nitric acid was used in the process, thus lowering the heating value of the final product. This fuel did not attain the goal of 2.0 wt% or lower ash, as was produced on the bench-scale (1). This may be attributable to inadequate optimization of the processing steps.

TABLE 10
PROXIMATE, ULTIMATE, AND HEATING VALUE ANALYSES FOR
USIBELLI HWD PRODUCT

	Raw	Phys. Cleaned	Chem. Cleaned	Cent. Cake
Prox. Analysis (mf, wt%)				
Vol. Matter	47.0	49.1	51.1	45.4
Fixed Carbon	44.3	44.7	46.3	51.1
Ash	8.7	6.2	2.6	3.5
Ult. Analysis (maf, wt%)				
Carbon	69.6	69.2	68.5	73.0
Hydrogen	5.2	5.1	5.3	5.0
Nitrogen	0.7	0.7	1.1	1.0
Sulfur	0.1	0.1	0.1	0.1
Oxygen ^a	24.4	24.9	25.0	20.9
Heating Value (mf, Btu/lb)	10,850	11,090	11,360	12,070

^a by difference

Table 11 contains the results for proximate, ultimate, and heating value analyses of Beulah lignite. All of the fuel preparation schemes involved physical and chemical cleaning followed by HWD. The fuels prepared in PDU #34 and #36 were physically and chemically cleaned by AMAX prior to HWD at EMRC. The fuel made in PDU #40 was processed entirely at EMRC. The overall analyses of products from each step in the processing of the fuels have been presented in previous reports (2, 5, 6).

Table 11 compares the final fuels for each of the PDU runs performed on Beulah lignite. There was an increase in the fixed carbon content for each of the fuels, compared to the raw coal, which can be attributed to the HWD process. The table indicates no significant difference between any of the final fuels.

3.3.1.2 X-ray Fluorescence Analyses (XRFA)

The x-ray fluorescence analysis presented in Table 12 summarizes all the final fuels produced using Kemmerer subbituminous coal. The XRFA of each individual fuel has been interpreted in earlier reports (2, 5). The data in Table 12 indicates that when the fuels were prepared by HWD only, as in PDU #36, the soluble cations such as sodium, calcium, and magnesium were removed or reduced. Sodium was completely removed in the process. When cleaning steps were incorporated in the process, additional reductions were achieved, as discussed in previous reports (2, 5). A comparison between the replicate tests, PDU #35 and #38B, indicated differences attributed to the concentration

TABLE 11

PROXIMATE, ULTIMATE, AND HEATING VALUE ANALYSES FOR
BEULAH LIGNITE HOT-WATER DRIED SAMPLES

	<u>Raw</u>	<u>PDU #34</u>	<u>PDU #36</u>	<u>PDU #40</u>
Prox. Analysis (mf, wt%)				
Vol. Matter	42.5	41.2	38.2	41.6
Fixed Carbon	49.7	56.4	59.6	56.0
Ash	7.8	2.4	2.2	2.4
Ult. Analysis (maf, wt%)				
Carbon	70.6	74.0	73.2	73.0
Hydrogen	4.6	4.2	4.1	4.5
Nitrogen	0.9	1.3	1.2	1.2
Sulfur	0.9	0.5	0.5	0.8
Oxygen ^a	23.0	20.0	21.0	20.5
Heating Value (mf, Btu/lb)	11,010	11,850	11,910	11,920

^a by difference

of acid used. The most noticeable difference was in the calcium oxide content of the fuels. The calcium oxide content in PDU #35 was lower than in PDU #38B, due to the higher acid concentration used in PDU #35.

TABLE 12

KEMMERER SUBBITUMINOUS X-RAY FLUORESCENCE ANALYSIS

High Temperature Ash Results (% of ash, SO ₃ -free)	<u>Raw</u>	<u>35</u>	<u>PDU Run #</u>		
			<u>36</u>	<u>38A</u>	<u>38B</u>
Silica	50.0	60.6	50.3	49.0	44.5
Aluminum Oxide	19.1	19.8	19.6	22.0	20.3
Ferric Oxide	6.1	9.0	7.9	14.5	19.0
Titanium Oxide	0.9	1.3	1.0	1.2	1.3
Phosphorous Pentoxide	1.1	0.4	0.8	0.4	0.4
Calcium Oxide	15.7	5.8	14.5	9.1	10.2
Magnesium Oxide	5.6	2.6	5.1	3.5	4.3
Sodium Oxide	0.7	0	0	0	0
Potassium Oxide	0.8	0.5	0.8	0.3	0
Percent Ash	4.3	2.9	4.7	2.3	2.2

The XRFA of physically and chemically cleaned and HWD Usibelli subbituminous coal is presented in Table 13. The results from this data indicate that physical cleaning reduced the silica and aluminum oxide concentrations in the ash. Instead of a decrease in ferric oxide content as has been observed with other coals (5), the ferric oxide content was increased. This same pattern was observed with Usibelli on the bench-scale (1). Chemical cleaning reduced the contents of soluble cations such as sodium, calcium, and magnesium. Chemical cleaning of Usibelli removed all the sodium. Additionally, the HWD process reduced the calcium and magnesium concentrations. There was an increase in iron content after HWD, which could be attributed to the leaching of non-stainless steel equipment used in the HWD process.

The data in Table 14 is for the Beulah fuel prepared in PDU #40, showing similar trends (1, 5). When this data is compared to that for earlier fuel preparation, the improved fuel quality reflects the process improvements (2, 5). One obvious improvement was the ferric oxide removal, whereas an earlier test did not result in comparatively low levels due to magnetite contamination (2). Another noticeable difference with this fuel was the calcium oxide content, which was not reduced to the levels of prior tests, due to the use of a lower acid concentration.

3.3.1.3 Particle Size Distributions

Figures 8, 9, and 10 depict the particle size distributions for deep-cleaned Beulah, Kemmerer, and Usibelli coals. The average size of the physically cleaned coal in all cases was 2.8 mm in mass mean diameter (MMD). The coal was then pulverized to a 30-to 50-micron MMD for chemical cleaning.

TABLE 13
USIBELLI SUBBITUMINOUS X-RAY
FLUORESCENCE ANALYSIS

High Temperature Ash Results (% of ash, SO ₃ -free)	<u>Raw</u>	<u>Phys. Cleaned</u>	<u>Chem. Cleaned</u>	<u>PDU Cent. Cake</u>
Silica	36.8	21.5	49.8	36.9
Aluminum Oxide	15.3	12.9	23.6	19.0
Ferric Oxide	8.7	11.7	11.4	32.0
Titanium Oxide	1.4	1.3	1.8	1.4
Phosphorous Pentoxide	0.1	0	0.3	0.1
Calcium Oxide	32.0	46.2	10.6	8.4
Magnesium Oxide	3.7	4.7	1.5	1.1
Sodium Oxide	1.1	1.3	0	0
Potassium Oxide	0.9	0.3	1.1	1.0
Percent Ash	8.7	6.3	2.6	3.5

TABLE 14

PDU #40 BEULAH X-RAY FLUORESCENCE ANALYSIS

High Temperature Ash Results (% of ash, SO ₃ -free)	Raw	Phys. Cleaned	Chem. Cleaned	PDU Cent. Cake
Silica	21.0	15.8	30.1	27.4
Aluminum Oxide	13.8	16.4	24.8	24.4
Ferric Oxide	10.1	6.3	10.6	21.0
Titanium Oxide	1.6	0.9	1.8	1.9
Phosphorous Pentoxide	1.5	1.1	2.0	1.7
Calcium Oxide	30.3	36.6	22.3	18.0
Magnesium Oxide	8.4	10.6	6.0	5.2
Sodium Oxide	13.2	12.2	2.0	0
Potassium Oxide	0.1	0.1	0.3	0.1
Percent Ash	7.8	5.9	2.2	2.4

A slight increase in the average size, from 35 to 40 microns, occurred after chemical cleaning due to the removal of small particles from the feed slurry during centrifugation. The clean coals were screened to a top size of 600 microns prior to hydrothermal treatment. Figures 8, 9, and 10 show the size reductions due to screening and HWD, with the MMD reductions averaging 10 to 20% in comparison to the feed. After HWD, the centrifuge cake was reslurried and then micronized to a final product size of 10 to 15 microns MMD.

3.3.2 PDU-scale Material Balance

Beulah lignite from North Dakota, Usibelli subbituminous from Alaska, and Kemmerer subbituminous coal from Wyoming, were selected for PDU-scale processing because of their ability to be cleaned to less than 1 wt% ash on the bench-scale (1). Figure 11 shows the process steps for production of deep cleaned LRCs.

The HWD conditions were 626°F, 2200 psi, and a residence time of 5 minutes. System material balances for each process run were completed to determine percent product recoveries and losses. Material losses occurred during mixing and transferring of the coal, conversion of coal to gas, and removal of minerals during processing.

After chemical cleaning, the clean coal was slurried and fed into the HWD Process Development Unit (PDU). The HWD product was concentrated by centrifugation, reslurried to approximately 55 wt% solids and fed into the Attritor mill for final grinding. Final clean-coal recovery from the PDU processing was 87% of the feed coal weight. Table 15 summarizes the complete process material balance for PDU Run #38.

Figure 8. Particle Size Distribution for PDU #40 Beulah

Figure 9. Particle Size Distribution for PDU #38 Kemmerer

Figure 10. Particle Size Distribution for PDU #38 Usibelli

Figure 11. Clean Coal/Water Fuel Processing Scheme

TABLE 15
MATERIAL BALANCE FOR ACID-CLEANED KEMMERER FUELS

Run #	Feed Coal wt. (lb)	Acid Cleaned (lb)	HWD Product (lb)	Final Fuel (lb)	Final Yield (%)
36	558	---	525	505	91
38	2620	2530	2330	2280	87

A small batch of acid cleaned Kemmerer was processed during PDU run #36. The first processing step included HWD the coal at a solids loading of about 30 wt%. The final Kemmerer fuel was a bimodal blend of 80 wt% coarse particles (40-micron average) and 20 wt% fine particles (10-micron average). Blending was done to achieve an optimum solids loading. An excellent solids recovery of 91 wt% was achieved for the Kemmerer.

3.3.3 Overall Product Recovery for Deep-Cleaned Fuels

Three coals were processed using the complete deep-cleaned scenario illustrated in Figure 11, which incorporates both physical and chemical cleaning of the raw coal. The product recoveries for Usibelli, Kemmerer, and Beulah coals at different stages of processing are presented in Table 16. The physical cleaning step was not optimized for the Usibelli or the Kemmerer, as indicated by low recoveries (30 to 40 wt%), compared with 65 to 75 wt% for bench-scale Certigrav washability testing. PDU #40 with Beulah is more representative of an acceptable yield for physical cleaning. Table 17 is a summary of projected PDU-scale performances for deep-cleaned LRCs. The low total energy recoveries were due to a 30- to 45-wt% coal loss during physical cleaning. At a commercial-scale CWF plant, the energy of the middlings or tailings could be utilized in a coal slurry preheat system, thus saving on the overall energy costs.

3.3.4 Conceptual Fuel Economics

3.3.4.1 Background

Using physical data determined by PDU-scale preparation at EMRC, costs for production of CWFs from Kemmerer, Usibelli and Beulah coals were estimated based on the coal product and rheological performance of the fuels. Estimations of cost per million Btu (MMBtu) and per ton of CWF were based on revision of an October 15, 1986, clean, low-rank CWF feasibility study (7).

3.3.4.2 Operating Costs and Revenues

Table 18 lists operating costs for various production schemes for a combustion-ground, LRC fuel plant producing 800,000 tons of fuel per year. Process parameters that varied during production included physical cleaning, chemical cleaning, hot water drying, and composition of an additive package of

TABLE 16
OVERALL MATERIAL BALANCE FOR DEEP-CLEANED FUELS

Coal Type	Feed (lb)	Phys. (lb)	Acid (lb)	HWD (lb)	Final Fuel(lb)	Final Yield (%)
Usibelli	223	82	71	55	50	22
Kemmerer	295	96	80	61	57	20
Beulah #40	3054	1780	1620	1275	1230	40

anionic dispersant and xanthan gum. Micronizing the fuel would result in a \$0.25 - \$0.35/MMBtu increase in fuel costs due to the additional processing required and the reduced rheological performance (7). Cost estimations for Kemmerer CWF ranged from \$3.18/MMBtu to \$3.73/MMBtu, the Usibelli estimations varied from \$4.00/MMBtu to \$4.62/MMBtu, while Beulah ranged from \$2.63/MMBtu to \$4.20/MMBtu, depending on which production scheme was implemented.

Included in the operating cost estimates were the cost of coal at the mines and physical cleaning costs, labor costs, utilities expenses, general maintenance costs, fixed charges on capital investment, and reagent costs.

TABLE 17
PROCESSING PERFORMANCE RANGES FOR LOW-RANK COALS

Process Step	Ash Reduction (wt%)	Coal Yield (wt%)	Energy Recovery (%)
Physical Cleaning	25 - 40	55 - 70	62 - 72
Chemical Cleaning	40 - 60	86 - 91	90 - 93
Hot Water Drying	-10 - 0	80 - 93	82 - 95
Micronizing	0	93 - 99	93 - 99
Total Process Performance	60 - 80	40 - 60	45 - 70

* Values are based on dry coal processed

A. Coal at Mine and Physical Cleaning

Coal-at-mine rates were conservatively determined to be \$8/ton for the Kemmerer subbituminous coal, \$20/ton for the Usibelli subbituminous coal and \$12/ton for the North Dakota lignite, respectively.

TABLE 18
OPERATING COSTS FOR AN 800,000 TON/YEAR
CWF PLANT (\$/MMBtu)

	<u>Kemmerer</u>	<u>Usibelli</u>	<u>Beulah</u>
Coal Cost	0.49	1.27	0.76
Physical Cleaning	0.12	0.12	0.13
Chemical Cleaning	0.91	0.95	0.95
Hot-Water Drying	1.22	1.27	1.34
Additives*	0.47	0.48	0.49
Micronizing	0.52	0.53	0.51
Chem. Cleaning, Hot-Water Drying, Micronized, w/ Additives	3.47	4.15	3.86
Phys. Cleaning, Chem. Cleaning, Hot-Water Drying, w/ Additives	3.18	4.00	3.63
Physical Cleaning, Chemical Cleaning, Hot-water Drying, Micronized w/ Additives	3.73	4.62	4.20

* Additives: Fractionated Ammonium Ligno-Sulfonate (D319-2)
and Xanthan Gum

B. Labor

Estimated labor requirements for a coal slurry fuel plant were determined using the state of Wyoming employee wage rates.

C. Utilities

Utility costs include electricity, estimated to be \$0.07/kwh, and others. A majority of the electricity cost is created by operating the 2000 hp Attritor wet grinder used to micronize the coal during final fuel production. A direct heating fluid bed combustion system was used to heat the coal to HWD conditions to eliminate additional costs of heating the slurry. The category, others, includes estimations for natural gas, process and cooling water, reverse osmosis, and ion exchange water (18).

TABLE 19
REAGENTS FOR DEEP-CLEANED CWF PRODUCTION

	Process Area	Price	Source
1. Magnetite	Area 200	(\$120/ton)	from AMAX report
2. Dispersant	Area 600	(\$0.30/lb)	Reed Lig.
3. Formaldehyde	Area 600	(\$0.25/lb)	Chem. Mark. Rep.
4. Nitric Acid	Area 300	(\$195/ton)	Chem. Mark. Rep.
5. Xanthan Gum	Area 600	(\$0.20/lb)	Pfizer Corp.(R.K.)
6. Ammonia	Area 300	(\$210/ton)	from AMAX report
7. Filter Aid	Area 300		from AMAX report

D. Reagents

The amount of each reagent used is dependent upon which processing steps were used to produce the fuel. The reagents are listed in Table 19.

E. Maintenance and Materials

Maintenance and materials costs include a general maintenance cost of 3% of the total capital outlay and any grinding supplies needed to micronize the fuel.

F. Fixed Charges

Charges include an estimation for capital amortization at 12% for 20-year life based on total capital cost, assuming a salvage value of \$4,000,000.

G. Revenue and Payback Period Estimations

Estimations were also calculated on the revenue that would be generated by the various production methods. Using a before-tax minimum rate of return of 20%, prices for the CWFs were determined on a \$/MMBtu basis. Applying the three CWF production schemes described in Table 18, the Kemmerer prices ranged from \$4.35/MMBtu for the combustion grind fuel to \$5.20 for the deep-cleaned micronized fuel. The Usibelli prices ranged from \$5.25/MMBtu to \$6.1/MMBtu, while the Beulah fuel prices varied from \$4.90/MMBtu to \$5.8/MMBtu.

The amount of time needed to pay off the plant was determined by dividing the fixed capital investment by the sum of the average after-tax cash flow and the average depreciation per year. The payback period was determined to be about 6 years.

3.3.4.3 Capital Costs

A. Major Equipment Costs

Current prices for the major equipment items were obtained as either written or verbal quotations from suppliers. Other equipment prices were obtained from internal files and published sources. Costs were last updated to the last quarter of 1988 using cost index values.

B. Installation Costs

Equipment installation costs were estimated as 40 percent of original equipment costs when manufacturer's estimates could not be obtained. Other components of the capital cost estimate such as piping, electrical, instrumentation, engineering and construction costs, and others were determined as direct percentages of equipment costs.

3.4 Water Treatment Studies

3.4.1 Ultrafiltration

3.4.1.1 Background

Results of ultrafiltration studies at EMRC have been presented previously (2). Testing has concluded ultrafiltration is effective at removing fine solids from hot-water drying centrifuge centrate. An additional attribute of ultrafiltration is rejection of soluble alkali material with the permeate (ultrafilter waste). Without this separation, recombination of the recovered solids with the centrifuge cake is not possible and water recycle for processing cannot be performed.

Ultrafilter tests indicated that the permeate flux rate is primarily dependent upon liquid temperature, centrate solids concentration, and ultrafilter membrane type (8). A linear equation, as a function of these variables, was modeled to predict the average ultrafilter permeate flux rate for a commercial hot-water drying plant producing 800,000 ton/yr of CWF. The centrifuge centrate, containing 3 wt% dry solids, is concentrated to 10 wt% dry solids for addition to the centrifuge cake. The product is a 60 wt% dry solids CWF. A diagram of a feed and bleed ultrafilter system, envisioned for use in a commercial hot-water drying plant, is shown in Figure 12.

3.4.1.2 Operating Costs and Revenues

Operating expenses for the system include the cost of electricity for pumps, three-year membrane replacement costs, 10% interest expenses on the capital cost, labor, cleaning solution, and miscellaneous costs. Table 19 summarizes these costs for the conceptual system.

The value of the recovered fines produced in a HWD plant can be determined by the estimated value of the CWF. The cost of nominally \$2.00/MMBtu for a HWD CWF product, including coal costs, has been cited by three different studies (9, 10, 11). Depending upon coal rank, a HWD coal, cleaned to less than 2 wt% ash (dry basis), costs \$3.00 to \$4.00/MMBtu. Recovering 7380 lb/hr of centrate coal fines with a heating value of 11,900

Btu/lb, can save \$1,405,000 to \$2,810,000/yr based upon 8000 hours of yearly operation. Based on this scenario, ultrafilter recovery of the centrate coal fines would be economically justified.

3.4.1.3 Capital Costs

After applying the linear equation to a 3 wt% dry solids centrate stream at 120°F, a flux rate of 109 gal/ft²-day was determined. Producing 469,300 gallons/day of ultrafilter permeate requires 4740 ft² (including a 10% safety factor) of ultrafilter surface area. Five 1200 ft² membrane units were selected for the commercial system at an estimated price of \$200,000 per unit. The price estimate includes the membranes, permeate collection systems, recycle pumps, and instrumentation. Additional capital costs are installation costs at 20% of the membrane cost, make-up pump costs and make-up storage tank costs. The system items and their estimated capital costs are listed in Table 20.

3.5 Activated Sludge Treatment of Ultrafilter Permeate

Results of treatment of ultrafilter permeate have been presented in a previous report (2). The permeate from the ultrafiltration process is a liquid waste stream containing some soluble organic, as well as inorganic contaminants. These contaminants must be removed prior to recycle or

Figure 12. Schematic of Ultrafiltration Test System

discharge. A treatability study was performed to verify the ability of the activated sludge process to reduce organic contaminant levels to assumed discharge standards. Removal of inorganic contaminants was beyond the scope of this wastewater treatability study.

Activated sludge effluent quality targets were based on New Source Performance Standards (NSPS) for related industries such as petroleum refining and coke making. After treatment at a 30-day mean cell residence time (MCRT), all target effluent discharge criteria were met except phenol content and chemical oxygen demand (COD). Also, soluble inorganic contaminants may be effectively removed by ion exchange or reverse osmosis processes. Future ultrafilter permeate treatment studies should investigate effects of reduced hydraulic retention times of COD removal.

TABLE 20
OPERATING & CAPITAL COSTS FOR AN ULTRAFILTRATION SYSTEM

TOTAL OPERATING COSTS	
Pump Electrical Costs	\$190,000
Membrane Replacement	227,000
Cleaning Solutions	7,000
Labor	26,000
Miscellaneous	18,000
Interest on Capital Costs	157,000
Total Operating Expenses	\$625,000
TOTAL CAPITAL COSTS	
Ultrafilter Membranes	\$1,000,000
Installation	200,000
Make-up Pumps	45,000
Storage Tanks	113,000
Electrical Transformers	76,000
Buildings	17,000
Piping	93,000
Contingency	154,000
Total Capital Costs	\$1,698,000

4.0 CONCLUSIONS

1. Heavy-media separation is a viable method of reducing the ash levels from some LRCs, with reductions as high as 40 wt%. Proper washing techniques are essential during the operation of the unit to avoid contamination.
2. The PDU-scale physical cleaning results approach the results from bench-scale physical cleaning. Yet additional modifications are needed to insure clean coal quality.
3. A screening of froth flotation reagents showed none of the reagents tested were viable for LRC froth flotation.
4. Continuous bench and PDU-scale chemical cleaning reduced the ash levels of the physically cleaned samples by an additional 25 to 40 wt%.
5. Modifications to the mixers in the acid column will improve the mixing action, thus increasing exposure to the acid media.
6. Proximate, ultimate, and heating value analyses can indicate if too much acidification was performed on the coal by an increase in both nitrogen and oxygen content and a decrease in carbon content and heating value.
7. X-ray Fluorescence Analysis can indicate possible magnetite contamination of the coal/water fuel products by substantial increases in the amount of ferric oxide present in the ash.
8. The overall recovery of the coal yield from the complete deep-clean micronized process scenario varied from 40 to 60 %. A majority of the coal was lost during physical cleaning. Without physical cleaning, coal recoveries ranged from 65 to 85% of the original coal.
9. Ultrafiltration has been shown to be a technically feasible concept for removing fine solids, from 2 to 10 wt%, from the centrate water produced during concentration of the hot-water dried product. An economic study indicates that the fine solids recovered would pay for the cost of ultrafiltration.
10. Soluble organic and inorganic contaminants contained in the permeate can be removed prior to reuse or discharge to the environment. A bench-scale activated sludge process was used to reduce permeate contaminants to levels that meet the criteria in the targeted discharge standards.

5.0 RECOMMENDATIONS

1. To improve material balances on the UNDEMRC beneficiation treatment scheme of physical and chemical cleaning, followed by hot-water drying, a nitrogen-free, gas accumulation system should be included in the hot-water drying pilot plant. This would allow collection of gas samples for more accurate analyses.
2. To increase the yields on the heavy media cone separation physical cleaning, it may be prudent to use a cyclone or spiral in place of the cone. This would also allow the physical cleaning of smaller particle sizes.
3. The necessity of performing the physical and chemical cleaning steps in series is taxing on the process economics. A combination physical, chemical process to achieve similar cleaning results, like an oil agglomeration technique, might prove more economically feasible, if comparable cleaning results are obtainable.
4. It may be possible, due to the high quality of the ultrafiltration permeate, to directly feed a reverse osmosis unit with this water. This would allow direct recycle of cation-free, organic-rich water for process reuse. This scenario should be tested on a small reverse osmosis unit to complete economic feasibility studies on water treatment for the hot-water drying process.

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U.S. DEPARTMENT OF ENERGY
FEDERAL ASSISTANCE MANAGEMENT SUMMARY REPORT

Page ____ of ____

1. Program/Project Identification No. DE-FC21-86MC10637	2. Program/Project Title Beneficiation of Low-Rank Coals	3. Reporting Period 04-01-88 through 06-30-89
4. Name and Address University of North Dakota Energy and Mineral Research Center Box 3213, University Station, Grand Forks, ND 58202		5. Program/Project Start Date 04-01-86
		6. Completion Date 03-31-92

Milestone ID. No.	Description	Planned Completion Date	Actual Completion Date	Comments
a.1	Implementation of wet grinding equipment to pilot-scale coal fuel production scheme	05-31-88	04-30-88	
a.2	Implementation of physical coal cleaning equipment to pilot-scale coal fuel production scheme	04-30-88	05-31-88	
b.1	Bench-scale testing on HWCD process water	06-30-88	07-31-88	
b.2	Refinement of process sequences developed to treat the process water	07-31-88	07-31-88	
b.3	Economic evaluation of process treatment scheme	08-31-88	12-31-88	
b.4	Pilot-scale testing of Alaskan subbituminous coal	05-31-89	04-30-89	
c.1	Development of new bench-scale coal cleaning techniques	05-31-89	06-30-89	
c.2	Screening of coal fuel candidates for pilot-scale production	12-31-88	09-31-88	
c.3	Implementation of chemical cleaning equipment to pilot-scale coal fuel production scheme	07-31-88	09-31-88	
c.4	Feasibility study on intermediate products from the preparation steps	10-30-88	03-31-89	
d.1	Screening of froth flotation reagents	12-31-88	09-31-88	
d.2	Refinement of bench-scale froth flotation apparatus	01-31-89	02-28-89	
d.3	Determination of the effects of wet grinding versus dry grinding by froth flotation	02-28-89	03-31-89	
e.1	Final Reporting	06-30-89	08-20-89	

4.3 Combustion Characterization of Low-Rank Coal Fuels

COMBUSTION CHARACTERIZATION OF LOW-RANK COALS

Final Technical Report for the Period
April 1, 1988 - June 30, 1989
Including the Quarterly Technical Progress Report
for the Period April - June, 1989

Submitted by:

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TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT.....	iv
1.0 INTRODUCTION.....	1
2.0 GOALS AND OBJECTIVES.....	2
3.0 PROPOSED WORK FOR THE THIRD YEAR (4/88 - 6/89).....	3
3.1 Task A. Stationary Packed-Bed Combustor Optimization.....	3
3.2 Task B. Construction of the Rotating Packed-Bed Combustor...	3
3.3 Task C. Design of a Dry, Ultra-Fine, Low-Rank Coal Combustion System.....	3
3.4 Task D. Optimization of the Coal/Water Fuels Rheological Properties.....	3
4.0 ACCOMPLISHMENTS.....	4
4.1 Bench-Scale Testing.....	4
4.1.1 Ignition Testing.....	5
4.1.2 Combustion Temperature and Rate Tests.....	6
4.1.3 Emissions Testing.....	11
4.2 Results of Task A. Stationary Packed-Bed Combustor Optimization.....	11
4.2.1 Bed Material.....	12
4.2.2 Fuel Distribution.....	13
4.2.3 Continuous Operation.....	15
4.2.4 Emissions Control.....	16
4.3 Results of Task B. Rotating Packed-Bed Combustor.....	17
4.4 Results of Task C. Design of an Ultra-Fine Coal Combustion System.....	18
4.5 Results of Task D. Rheological Evaluation of Low-Rank CWF...	19
5.0 SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS.....	25
6.0 REFERENCES.....	26

LIST OF FIGURES

<u>Figure</u>	<u>Page</u>
1 Experimental Packed-Bed Combustor.....	4
2 Flue Gas CO Concentration Versus Time. Effect of Slow Heating Rate on Minimum Ignition Temperature.....	5
3 Minimum Restart Temperature and Restart Time Versus Flow Rate.....	7
4 Predicted Versus Actual Maximum Combustion Temperatures.....	9
5 Predicted Versus Actual Combustion Rates.....	10
6 Stationary Packed-Bed Combustor and Modular Test Rig.....	12
7 Rotating-Bed Combustor and Modular Test Rig.....	18
8 Apparent Viscosity of Treated and Untreated CWFs.....	20
9 Yield Stress of Hydrothermally Treated Kemmerer CWFs.....	22
10 Viscosity of Hydrothermally Treated Kemmerer CWFs.....	22
11 Viscosity Effect of High Temperature and High Pressure on Two Coal/Water Fuels Prepared with Different Additives.....	24

LIST OF TABLES

<u>Table</u>	<u>Page</u>
1 Independent Variables and Responses for Maximum Bed Temperature and Combustion Rate.....	8
2 Statistical Model for Maximum Bed Temperature.....	6
3 Statistical Model for Combustion Rate.....	10
4 Properties of Kemmerer CWF.....	21
5 Rheological Evaluation Results for Kemmerer CWFs.....	21
6 Summary of Power Law Flow Behavior for Kemmerer CWFs at 25°C and 500 cP.....	23

ABSTRACT

Slurry combustion research at the University of North Dakota Energy and Mineral Research Center (UNDEMRC) began in 1983 and has continued under the U.S. Department of Energy (DOE). Coal research by DOE is directed toward increasing coal usage in existing markets and introducing new, premium-quality, coal-based fuels to markets currently dependent on oil or natural gas. The overall objective of the UNDEMRC project was to expand the scientific and engineering data base on combustion of advanced low-rank coal (LRC) fuels for residential and commercial applications (1). To accomplish the overall goal, three-year goals were to design, construct, and evaluate two prototype coal/water fuel (CWF) combustors suitable for providing space and water heat to residential and commercial buildings. These small-scale combustion systems would burn the fuel on a packed bed, eliminating the need for atomization, and would be dedicated to the combustion characterization of beneficiated low-rank CWFs.

Combustion of coal/water fuel in the packed-bed system was studied on the bench and pilot scale. Bench-scale testing studied ignition, combustion rate, bed material size, and control of maximum bed temperatures. More than 80 bench-scale tests were run in batch mode using CWFs in the range of 46 to 54 wt% solids and gravel sizes in the range of 1/4 to 1 inch in diameter. Results of a statistical analysis were used to design the stationary packed-bed and rotating-bed combustion systems for pilot-scale testing.

The stationary packed-bed combustor was designed to burn a beneficiated (1.0%-ash, low-sulfur), low-rank CWF in batch mode with heat storage in the packing. Pilot-scale tests were designed to study ignition, combustion rate, thermal rating, ash removal and collection, gaseous emissions, and continuous cycling. The fuels used for testing were non-beneficiated, high-ash (up to 7%, dry basis) slurries, which accelerated the ash build-up rate in the packing. Initial testing indicated that ordinary gravel and quarried granite were unacceptable bed materials. Ceramic spheres were used to replace the rock as packing for the combustor and were found to be very compatible with the combustion of CWFs.

Pilot-scale combustion results indicated that fuel distribution across the packing surface, ash deposition within the packing, and gaseous emissions were the parameters that must be controlled to successfully burn CWF in the packed-bed system. Fuel distribution was a function of the rheological properties of the fuel, and in general, fuel with a viscosity between 500 and 700 cP and a yield stress between 5 and 10 Pa would distribute itself both radially and vertically through the packing. Ash removal from the packing was increased by vibrating the packing for 10 minutes at the end of each combustion cycle. Vibration of the packing reduced ash levels in the packing from 84% with no vibration to below 30% with vibration. The ash was also more evenly distributed through the packing after vibration, indicating a steady state removal of ash from the system. During normal operation, levels of CO were observed at more than 25,000 ppm. A platinum/palladium catalyst was put on line, and when operated at 600°F with 5% excess air, the CO emissions were reduced to below 40 ppm (2).

Continuous cycling tests of up to 52 hours were performed, burning nearly two million BTUs of 2.8%-ash CWF. This was equivalent to approximately 1/9th the amount of 1.0%-ash CWF required (providing a similar BTU yield) prior to maintenance during a typical residential heating season. Recommendations were made to incorporate the various modules into a compact design with special attention given to the conversion of gaseous emissions. Design of heat exchange equipment would also be required (2).

The rotating-bed combustor was designed to operate in semibatch mode with the combustion chamber rotating at between 1 and 5 rpm. The rotation would ensure ash removal through the packing and an even temperature profile in the combustion zone, lowering CO, hydrocarbon, and NO_x emissions. Shakedown testing of the rotating bed was not completed and further evaluation testing was recommended.

Rheological evaluation of two low-rank CWF additive packages indicated that D319-2, an anionic lignosulfonate dispersant, and T-Mulz, a non-ionic surfactant, can both be used in conjunction with xanthan gum to provide stability and improve flow behaviors of the fuel. Rheological analysis of the additive packages indicated relatively little difference between the anionic and non-ionic additives, as each had a pseudoplastic or shear-thinning effect on the fuel. No significant differences were noted under freeze/thaw conditions; however, when tested under high temperature/high pressure conditions, the non-ionic surfactant tended to agglomerate and gel at higher temperatures (>180°C), increasing the viscosity of the fuel. Therefore, the anionic dispersant, D319-2, was considered the best additive for high temperature applications.

Work on the stationary packed-bed and rotating-bed combustors was discontinued as of June 30, 1989. Future work under the cooperative agreement with DOE will focus on combustion characteristics such as flame stability, carbon burnout, ash fouling, and ESP performance for industrial- and utility-scale coal-fired systems.

COMBUSTION CHARACTERIZATION OF LOW-RANK COALS

Final Technical Report

Including the Quarterly Technical Progress

Report for April - June, 1989

Submitted by: Michael D. Mann, Project Manager

Prepared by: Jay R. Gunderson
Michael D. Mann

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1.0 INTRODUCTION

Coal research by the Pittsburgh Energy Technology Center (PETC) of the U.S. Department of Energy (DOE) is directed toward increasing coal usage in existing markets and introducing new, premium-quality coal-based fuels to markets currently dependent on oil or natural gas (3). Accordingly, the work concentrates on coal cleaning, fuel formulation and handling, combustion, and flue gas cleaning -- all necessary technologies in the direct use of coal. Progress achieved over the past several years through PETC and related federal- and private-sector research activities has considerably strengthened these technologies, consequently enhancing the possibility of meeting DOE's coal research goals.

In the area of coal beneficiation, processes to reduce ash concentrations to less than 1.0% have progressed to advanced stages of development and are also capable of extracting most of the pyritic sulfur from the raw coal. Coal fuels of this quality are becoming available in either slurry or dry powder form, in quantities necessary for engineering performance evaluation.

In parallel with these advancements, technologies for mixing ultra-fine (top size of 40 microns) beneficiated coal products with water or liquid carriers have also progressed to the pilot-production level. Handling of coal liquid mixtures from bulk transport and storage to ultimate transfer to a combustion device has been investigated for a variety of projected applications. Injection and combustion characteristics have also been studied in relation to the requirements of specialized applications. Other technical advances have been made in the design of combustors, heat exchangers, improved materials, and gas cleaning processes.

At present, gas- and oil-fired furnaces and boilers dominate the market for space heating and the production of process steam. However, recent technological developments offer the prospect that premium coal-based fuels such as coal/water mixtures or dry, ultra-fine coal, when combined with advanced fuel handling, storage, and combustion concepts, can approach standards of performance expected by users of natural gas and petroleum in small- to moderate-scale applications.

DOE research is currently directed toward the development of coal-based advanced combustion system technologies suitable for the following applications:

- New boilers/fluid heaters for producing steam and process heat for industrial purposes.
- Space and water heating in commercial buildings.
- Residential space and water heating.
- Combustors for retrofitting existing oil- and gas-fired boilers, and process heat applications.

The introduction of coal-based fuels into the residential, commercial, and industrial markets is dependent upon successful pursuit of high-risk R&D programs. DOE has developed a multi-year program to address the R&D needs relevant to each of the four application areas. The work completed by the University of North Dakota Energy and Mineral Research Center (UNDEMRC) over the past three years was directed toward fulfilling those needs. While work to date had concentrated on developing an alternative to oil- and gas-fired combustion systems on the residential and commercial scale, the overall objective for the project was changed for the upcoming year and will involve combustion characterization for industrial- and utility-scale coal-fired systems. This final report is a summary of the work performed at UNDEMRC over the past three years.

2.0 GOALS AND OBJECTIVES

The purpose of the slurry combustion project at UNDEMRC was to expand the scientific and engineering data base on combustion of advanced low-rank coal (LRC) fuels for residential, commercial, and moderate industrial processes by investigations into the operational and environmental effects of burning slurry fuels made with low-rank coal. To achieve this goal, planned three-year objectives included:

- Design of an LRC/water combustion system with future applications in the residential, commercial, or moderate industrial sectors.
- Investigation of effects of LRC fuel type on slurry combustion characteristics such as ignition limits and flame stability, and on operational problems such as fouling and slagging.
- Production of selected LRC fuels for off-site testing in industrial-scale boilers. Combustion runs would be performed with slurry produced by UNDEMRC's hot-water-drying process.

Specific goals for the third year were to:

1. Evaluate and optimize the stationary packed-bed slurry combustor built during FY87. The combustion and operational characteristics to be

evaluated include ignition limits; start-up and response time; CO, particulate, and hydrocarbon emissions; combustion and steady-state efficiencies; and heat transfer characteristics.

2. Construct the rotating packed-bed slurry combustor designed in FY87 and begin evaluation testing, focusing on combustion characteristics and operational problems.
3. Finalize the design of, and construct a combustion system to be used in the combustion characterization of dry, ultra-fine, low-rank coal.

3.0 PROPOSED WORK FOR THE THIRD YEAR (4/88-6/89)

To achieve the specific goals for the third year, a four-task program was developed. The tasks included optimization of the stationary packed-bed slurry combustor built during FY87; construction of the rotating packed-bed slurry combustor designed during FY87; finalization of the design of a dry, ultra-fine, low-rank coal combustor; and performance of rheological studies including optimization of an additive package to upgrade the coal/water slurries.

3.1 Task A. Stationary Packed-Bed Slurry Combustor Optimization

Task A involves evaluating and optimizing the stationary packed-bed slurry combustor built in FY87, focusing on combustion characteristics and operational combustor problems. Characteristics to be evaluated include ignition limits; start-up and response time; CO, particulate, and hydrocarbon emissions; combustion and steady-state efficiencies; and heat transfer characteristics.

3.2 Task B. Construction of the Rotating Packed-Bed Slurry Combustor

Task B consists of the construction of the rotating packed-bed slurry combustor designed in FY87. Evaluation testing of the unit will also be initiated to investigate the effects of LRC fuel types on combustion characteristics and operational goals. Performance goals are similar to those outlined for the stationary packed-bed slurry combustor.

3.3 Task C. Design of a Dry, Ultra-Fine Low-Rank Coal Combustion System

Task C is directed at finalizing a design of a commercial-scale combustion system to be used in the combustion characterization of dry, ultra-fine, low-rank coal. The prototype combustion system will be constructed and evaluation testing initiated, focusing on the combustion characteristics, operational problems, and the safety and reliability of firing dry LRC.

3.4 Task D. Optimization of the Coal/Water Fuels Rheological Properties

The focus of Task D will be on performing rheological studies of an additive package to enhance CWF transport, storage, handling, and combustion for a residential- or commercial-sized slurry combustion system. The effect

of temperature on the rheology of clean CWF, including freeze-thaw and high-temperature and pressure effects, will be investigated, as will additive degradation and CWF dilatancy at high temperatures. The changes in system and combustion characteristics as a result of these rheological phenomena will be determined.

4.0 ACCOMPLISHMENTS

The milestones not met in the previous annual project plan were rolled into this year's annual project plan. Accomplishments for the first three years of the project include the completion of bench-scale testing, the design and construction of two prototype combustors, and testing on the pilot scale. This section is a summary of those accomplishments.

4.1 Bench Scale Testing

A 5.5-inch-inside diameter incinerator was modified to serve as a packed bed combustor for initial studies and is shown in Figure 1. The combustor was lined with 3.5 inches of an insulating refractory, and nine thermocouples were placed in the combustor. The combustion air, bed material and exit gas temperatures were monitored continuously on a chart recorder. Analysis of the flue gas for CO, O₂, CO₂ and NO_x was performed with on-line analyzers. Air flow was from the top to the bottom and was monitored with an orifice plate; the air was preheated electrically to ignite the coal/water fuel. The bed material and fuel were pre-mixed prior to placement within the incinerator, with the weight of the packing recorded before and after saturation with the fuel (4).

Figure 1. Experimental Packed Bed Combustor.

4.1.1 Ignition Testing

Tests were performed to determine the effects of flow rate, bed material size, slurry density, and rate of heating on the minimum ignition temperature required to ignite the slurry, which was indicated when the outlet air temperature became greater than the inlet air temperature. The effects of air flow rate, bed material size, and slurry density were found to be minimal. When any two of the three effects were held constant, the minimum ignition temperature required ranged from just above 400°F to just below 500°F. Low air flow rates, small rock sizes, and highly concentrated slurries were the most favorable conditions for lowering the minimum inlet air temperature required for ignition (4).

The heating rate was found to have the greatest impact on the required ignition temperature. As the CWF was heated, small exothermic reactions released heat and carbon monoxide. The additional heat generated by these reactions caused further oxidation of the volatile matter within the fuel, releasing more heat and promoting additional oxidation, until combustion was sustained. Figure 2 shows the carbon monoxide concentration versus time when very slow increases in inlet air temperature were made. As the temperature was increased from 350 to 500°F over a period of eight hours, the CO concentration increased with each step change for a short period, and then decreased with no indication of ignition. Additional testing indicated that the CWF would ignite each time with a step change from room temperature

Figure 2. Flue Gas CO Concentration Versus Time.
Effect of Slow Heating Rate on Minimum Ignition Temperature.

to 375°F. Apparently, the heat generated by the small exothermic reactions was dissipated before appreciable changes in bed temperature could occur when the fuel was heated slowly, whereas those reactions occurred simultaneously, generating enough heat to sustain combustion, when the fuel was heated quickly.

To study the maximum turndown ratio possible, reignition tests using cold air were performed. The slurry-saturated bed was ignited with preheated air. As soon as ignition was indicated, room temperature air was introduced for the combustion air. When any of the thermocouples in the bed indicated 1500°F, the fan was turned off and the inlet valve to the combustor was closed. The bed temperature was allowed to drop until a preset temperature was reached. The inlet valve was then opened and the fan restarted. If the bed reignited, the temperature was allowed to increase until the highest temperature in the bed reached 1500°F and the system was again shut down. The temperature in the bed was then allowed to decrease to a temperature below that of the original set point. This procedure was repeated until the bed could not be reignited with cold air (4).

The tests evaluated the minimum restart temperatures of the bed as a function of air flow rate. Figure 3 illustrates the average minimum bed temperature needed to restart the combustor at various combustion air flow rates. Clearly, by using lower air flow rates for reignition, the fan could be shut off for longer periods of time. Apparently, when large amounts of cold air were introduced into the warm bed, the cooling effect overcame the heating effect of the exothermic reactions. While the lower combustion air flow rates lowered the temperature at which the bed would reignite, the time required to reignite the bed was significantly increased (4). Figure 3 also shows the time required to achieve 1500°F in the packing after reignition at various combustion air flow rates, and indicates that higher air flow rates will reignite the packing much more quickly than low air flow rates. These results indicate that a trade-off between response time and turndown ratio must be made during continuous operation of the combustor on the pilot scale.

4.1.2 Combustion Temperature and Rate Tests

To determine the effect of bed material size, slurry concentration, and air flow rate on the maximum combustion temperature and rate of combustion, a 2-by-3 matrix with four midpoints was designed. After completing the matrix and statistically analyzing the data, curvature of the model was indicated and nine additional tests were performed to develop a quadratic model (4). The run conditions, maximum observed temperatures, and combustion times are shown in Table 1.

The experimental procedure used in the matrix was designed to yield results applicable to both the stationary packed-bed and the rotating-bed combustion systems. For each test, the bed material was saturated with slurry and the excess slurry allowed to drain off. The weight of the bed material and remaining slurry was carefully measured and recorded. To ignite the slurry, an inlet combustion air flow rate of 20 scfm

Figure 3. Minimum Restart Temperature and Restart Time Versus Flow Rate.

was maintained at a temperature of 550°F. When the highest thermocouple temperature in the bed reached 1500°F, the preheater and fan were turned off and the inlet air valve to the packed bed was closed. The bed was allowed to cool until the highest thermocouple reading in the bed was 600°F. The fan was then restarted by drawing cool air through the packing, reigniting the fuel. The run was terminated when the fuel was completely oxidized and the temperature of the packing was below 100°F. The time in minutes to burn one linear foot of the bed and the maximum combustion temperature were recorded (4).

The equations for prediction of the maximum bed temperature and combustion rate were arrived at using three different statistical procedures: a forward selection procedure, a backward selection procedure, and a maximizing R-Square procedure (5). The three different statistical procedures produced the same equation for the maximum bed temperature at the 95% confidence level for all terms. The equation was determined to be:

$$\text{Maximum Bed Temperature} = 1829 - 67X + 237Y + 47Z - 133X*Z + 74Y*Z - 152Y^2$$

where $X = (\text{Bed material diameter in inches} - 0.578)/0.297$
 $Y = (\text{Dried slurry wt. in grams} - 707.5)/247.9$
 $Z = (\text{Scfm} - 17)/15$

The test variables, parameter estimates for those variables, standard error of the parameter estimates, F ratios, and significance of the F ratios for each term in the model are shown in Table 2. It should be noted that the

TABLE 1
INDEPENDENT VARIABLES AND RESPONSES
FOR MAXIMUM BED TEMPERATURE AND COMBUSTION RATE TESTS

Packing Size (inches)	Air Flow Rate (scfm)	Slurry Conc. (wt%)	Dried Slurry Wt. (grams)	Maximum Temperature (°F)	Combustion Time (minutes)
0.375 x 0.53	17.0	50	782.0	1,883	8.9
0.75 x 1.0	2.0	54	553.61	1,685	43.1
0.75 x 1.0	2.0	46	68.72	*	*
0.25 x 0.3125	32.0	54	950.29	2,234	9.0
0.375 x 0.53	17.0	50	667.0	1,766	7.9
0.25 x 0.3125	32.0	46	459.59	1,619	5.08
0.375 x 0.53	17.0	50	699.25	1,865	8.8
0.75 x 1.0	32.0	46	131.28	*	*
0.25 x 0.3125	2.0	46	401.03	1,325	45.0
0.25 x 0.3125	2.0	46	468.51	1,417	38.1
0.375 x 0.53	17.0	50	632.45	1,782	6.1
0.75 x 1.0	32.0	54	775.71	1,751	2.3
0.25 x 0.3125	2.0	54	938.52	1,747	56.1
0.25 x 0.3125	17.0	50	711.75	1,931	10.6
0.375 x 0.53	2.0	50	573.65	1,635	41.4
0.375 x 0.53	2.0	50	595.50	1,546	39.1
0.375 x 0.53	2.0	54	955.26	1,760	47.4
0.375 x 0.53	17.0	46	258.98	*	*
0.375 x 0.53	17.0	46	255.76	*	*
0.75 x 1.0	17.0	50	198.0	*	*
0.375 x 0.53	32.0	50	536.5	1,663	4.3
0.375 x 0.53	2.0	50	600.5	1,666	34.2

* Indicates no ignition

TABLE 2
STATISTICAL MODEL FOR MAXIMUM BED TEMPERATURE
R-SQUARE = 0.96813797

Intercept	Coefficient	Standard Error	F Ratio	Prob > F
X	-67.52544377	19.48330150	12.01	0.0071
Y	237.16920854	17.48787256	183.93	0.0001
Z	46.88639016	15.75244891	8.86	0.0155
X*Z	132.53087165	18.28537194	52.53	0.0001
Y*Z	73.79573524	17.80162944	17.18	0.0025
Y	-152.12503544	32.19504068	22.33	0.0011

least significant term in the model is significant at the 2% level. This fact, coupled with the fact that all three statistical procedures produced the same equation, is a very good indication that the model is sufficient. A plot of the actual data versus the predicted data from the model is shown in Figure 4, and indicates good agreement between the model and the actual data. Since low temperatures are undesirable in terms of combustion efficiency and heat transfer, and high temperatures can fuse the packing with ash and produce excess NO_x , this model will be used to determine the operating conditions for the pilot-scale combustors.

The equation for prediction of the combustion rate measured in minutes to combust one linear foot of the bed was determined to be:

$$\text{Combustion Rate} = 729 + 4.46Y - 19.6Z - 4.4Y*Z + 6.97X^2 + 11.96Z^2$$

where X, Y, and Z are as defined previously.

The variables, parameter estimates for those variables, F ratios, and significance of the F ratios for each term in the model are shown in Table 3. Again, the least significant term in the model is significant at the 2% level. A plot of the actual data versus the data predicted by the model is shown in Figure 5 -- the close scatter of data points about the 45-degree line indicates that the model is sufficiently accurate. This model will be used to determine the minimum combustor size required for a given thermal load.

Figure 4. Predicted Versus Actual Maximum Combustion Temperatures.

TABLE 3
STATISTICAL MODEL FOR COMBUSTION RATE
R-SQUARE = 0.98746072

Intercept	Coefficient	Standard Error	F Ratio	Prob > F
Y	4.46391284	1.05606293	17.87	0.0018
Z	-19.64221197	0.83612451	551.87	0.0001
Y*Z	-4.38840282	1.16687810	14.14	0.0037
X ²	6.97391414	2.36783309	8.67	0.0147
Z ²	11.95841802	2.00355459	35.62	0.0001

Figure 5. Predicted Versus Actual Combustion Rates.

4.1.3 Emissions Testing

High levels of carbon monoxide were noted during bench-scale testing of the packed bed. The temperature profile through the bed when the top of the packing was ignited ranged from above 1500°C to below 300°F. Since the temperature range was a continuum through the bed, there were low-temperature combustion reactions occurring that produced CO levels in excess of 10,000 ppm. Two methods were proposed to minimize CO emissions. The first method was to use a platinum/palladium catalyst similar to the types used in automobile or woodburning stove catalyst systems, which oxidizes the CO to CO₂. The second method was to slowly agitate the packing in a rotating bed so that the temperature distribution was uniform and CO would not be formed.

A honeycomb catalyst was purchased from a wood stove vendor and placed in the outlet piping of the combustor. The minimum operating temperature for the catalyst was 400°F, so the outlet pipe was heated externally to ensure that the proper operational temperature was reached. Each test used 2 scfm of combustion air to permit adequate residence time in the catalyst. The first test showed a 98% reduction in CO from 11,500 to 180 ppm at catalyst operating temperatures of just under 500°F. Because an open flame was used to heat the outlet piping from the combustor (which could possibly cause hot spots on the piping, subsequently oxidizing CO), a repeat run was performed without the catalyst in place. The CO concentration remained above 10,000 ppm for the entire run, indicating that the catalyst was responsible for the reduction in CO observed in the first test. A third test was conducted to determine if the results of the first test could be repeated. Again, large decreases in the CO concentration were observed (6).

4.2 Results of Task A. Stationary Packed-Bed Combustor Optimization

The information generated in the bench-scale tests was used to design the stationary packed-bed combustor and the rotating packed-bed combustor. The objective of the pilot-scale systems was to investigate the operational and environmental effects of burning low-rank CWF in a residential/moderate commercial-sized combustion device. To accomplish this goal, the combustion systems were designed in modules so that each aspect of the combustion cycle could be studied independently. Optimization of these individual components would ultimately lead to the design of an actual combustion device, incorporating each module into a compact design suitable for installation in residential and commercial buildings. The modules in the designed test rig include the combustor (the prototype combustors are interchangeable in the test rig), the storage tank and feed pump, the catalyst test section, and the baghouse (6). A schematic of the stationary packed-bed combustor and the modular test rig is shown in Figure 6.

4.2.1 Bed Material

Preliminary testing of bed material for the packed-bed slurry combustor indicated that locally procured gravel would not be a viable bed material for combustion of coal/water slurries. The gravel used contained limestone, which disintegrated when it came into contact with water. As the limestone (CaCO₃) is heated, carbon dioxide is driven off leaving calcium oxide, which readily dissolves in water. Breakup of the packing would lead to plugging of the bed, air distribution problems and, eventually, shutdown of the combustor (1).

Figure 6. Stationary Packed-Bed Combustor and Modular Test Rig.

The second bed material tested was 3/8-inch by 5/8-inch granite obtained from a quarry in Ortonville, Minnesota. During shakedown testing, the slurry was pumped onto the rocks, ignited, and allowed to burn through. The packing was then removed and screened. Approximately 11 percent of the granite fell through a 1/4-inch screen. Samples of the unaffected and thermally affected bed material were then analyzed by x-ray diffractometry to determine their respective bulk mineralogical compositions, and to see if changes in the character of the original mineral components might be detected, and, in turn, related to the breakdown of the material at elevated temperatures. The analyses were done by Dr. R.J. Stevenson, director of the National Materials Analytical Laboratory. Careful comparison of the diffractograms revealed no discernible differences in the mineral suites of the two samples or in the character of the minerals that were identified. This suggests that the observed breakdown was not due to thermally related mineral transformations. The possibility that partial dehydration may have had some effect still exists; however, that was unable to be determined. Another possibility is that breakdown was controlled by structural weaknesses in the material resulting from stress experienced during or subsequent to its formation. Detailed petrographic analysis would be required to investigate this alternative; this was not done. The instability of the granite under the conditions required for the combustion of CWF in the packed bed make it an undesirable bed material (1).

In subsequent tests, 3/8-inch by 5/8-inch gabbro obtained from a quarry in Duluth, Minnesota, was used as packing for the combustor. In each run the slurry was ignited and allowed to burn completely. Again the packing was removed and screened to 1/4-inch. Less than two percent of the gabbro fell through the screen, suggesting that gabbro may be a suitable packing for combustion of coal/water slurries in a stationary packed-bed combustor.

Further combustion testing used 3/4-inch ceramic spheres obtained from Norton Ceramics, which were found to show no significant signs of degradation. Because this packing was compatible with the combustion of CWF in the packed-bed system and because it was very easy to handle, it was chosen as the bed material for the majority of the combustion tests performed. The only other bed material tested was ceramic Berl saddles (1).

Half-inch Berl saddles, with a void space of 60%, were used as packing to determine whether greater void space could facilitate ash removal from the combustor. Testing indicated that combustion of CWF over the saddles was independent of slurry distribution through the packing; however, combustion temperatures in excess of 2000°F caused fusion of the ash in the packing and inhibited removal of the ash from the packing. For these reasons, the 1/2-inch Berl saddles were determined to be an unacceptable bed material (7).

4.2.2 Fuel Distribution

Distribution of the CWF throughout the packing was considered the most critical step in the batch mode operation of the stationary packed-bed combustor. It dictates the distribution of air during combustion and impacts nearly all other phases of the combustion cycle. For this reason, much of the testing over the past year centered around evaluation of the fuel distribution phase and on improving distribution over a wider range of fuel properties and characteristics.

The fuel distribution phase begins as the fuel is pumped to the surface of the packing, where it spreads radially across the surface of, and vertically through the packing. An even distribution of the fuel ensures that the entire bed is available for combustion and increases the combustor's thermal output (6). More importantly, even distribution of the fuel prevents areas of low pressure drop from developing in the packing. As the fuel coats the packing, the void space in that region is reduced and the pressure drop is increased accordingly. The areas not coated with fuel will have a substantially lower pressure drop than coated areas and will allow ignition and combustion air to bypass the coated regions, decreasing the combustion rate and the thermal rating of the combustor.

As a result of distribution testing, the internal diameter of the combustor -- which was originally 24 inches -- was reduced to 15 inches. The reduced cross-sectional area enabled the pump to easily flood the packing surface, and in subsequent testing the combustion rate was greatly improved. Because the pressure drop was basically the same at all points across the surface, there was no preference for combustion air flow and the air by-pass problem was eliminated (8).

Further testing indicated that bed material size and fuel properties such as yield stress and viscosity played important roles in the distribution of

the fuel (6). Yield stress dictated the radial extent of slurry distribution across the packing surface when the yield stress was in the range from 3 to 10 Pascals. Outside of this range, the fuel tended to remain in the central portion of the packing. An increase in viscosity of the fuel tended to decrease the rate at which the fuel was delivered to the packing surface. The viscosity of the fuel limited the amount of fuel that could be drawn into the suction side of the peristaltic pump, decreasing the pressure-side flow rate even though the pump was positive displacement on the pressure side.

The physical size of the packing plays an important role in the distribution of the fuel. As the fuel is delivered to the center of the packing surface, it quickly fills the void space in that region and begins to flow radially toward the walls of the combustor. The larger packing sizes have a greater local void space between adjacent particles, requiring a larger portion of the fuel to fill the void, simultaneously slowing the radial flow of the fuel. Distribution tests were conducted using uniform ceramic spheres with diameters of 3/8, 1/2, and 3/4 inch. Results indicated that smaller packing sizes increased radial flow at a given yield stress, but generally hindered ash removal from the packing (6). The limited success of the physical redirection of the fuel using the smaller packing size led to the development and testing of metal screens that could accomplish the same task over a much smaller volume of total packing space (9). A 304-SS screen was used during a continuous combustion run in an attempt to evenly distribute a fuel with a yield stress and viscosity outside the range of the fuels previously used. The test was successful; however, further testing was deemed necessary to optimize this method of fuel distribution.

In conjunction with the development of the metal screens, a number of spraying methods (non-atomizing) were tested to determine their effect on fuel distribution in the packing (9). Again, the properties of the fuel tended to inhibit the performance of the nozzles. Each nozzle tested provided a spray pattern that would adequately cover the packing surface when using water, but when used to spray the CWF they were not effective. A solid cone pattern could be achieved at fuel solids loadings of <50%; however, the fuel is highly unstable at this level and would be expected to settle in the storage tank and feed line during continuous operation. Under these conditions, spraying of the CWF to achieve good distribution in the packing is not feasible. The conditions that would favor development of spray nozzles for this purpose would preclude the production of a stable CWF whose rheological properties more closely resembled those of water -- low yield stress and low viscosity.

4.2.3 Continuous Operation

The stationary packed-bed combustor was designed to burn a beneficiated (1.0%-ash, low-sulfur), low-rank coal/water fuel in batch mode with heat storage in the packing. Pilot scale tests were designed to screen various bed materials and to study ignition, combustion, thermal rating, ash removal and collection, gaseous emissions control, and continuous cycling during the combustion of these beneficiated fuels (6). Fifty-nine combustion tests were conducted, with a number of the tests using multiple cycles to study various aspects of combustion during continuous operation.

Each combustion cycle has five stages. First, the fuel is pumped from the storage tank to the packing surface where it spreads radially across the

surface and downward through the packing. A small purge of water follows the fuel to clean the delivery pipe. Electrical heaters located above the packing surface are then turned on until a set temperature is reached, indicating ignition of the fuel. During the ignition phase, an induced draft fan is used to draw air through the packing, transferring heat from the elements to the fuel. The induced draft is a safety precaution that prevents products of combustion from leaking into the area surrounding the combustor. When ignition is indicated, a computer-controlled bypass is closed to increase the amount of air drawn by the fan through the packing during the combustion phase. The flue gas, which is laden with particulate and gaseous emissions, is then drawn through the baghouse for particulate removal and through the catalyst test section for oxidation of CO and hydrocarbon emissions to CO₂ and H₂O. When complete combustion of the fuel has been achieved, the packing is air-cooled to a set temperature, preparing the packing for the next cycle. In the last phase of the combustion cycle, a vibrator is turned on to facilitate ash removal through the packing. Temperatures and air flow rates are recorded by a computer-controlled data acquisition system that is also used to control the feed pump, water flush, heaters, fan, and vibrator. Gaseous emissions are monitored on-line and are manually recorded throughout the cycle (6).

The main objective of the continuous cycling tests was to simulate the long-term operation of a small-scale combustor for the purpose of providing space- and water-heat for residential and commercial applications. The most recent of the cycling tests burned more than 277 lbs of CWF over a period of approximately 50 hours and 17 combustion cycles. The time required for ignition of the fuel was typically 12 minutes and the average cycle time was 2.9 hours. Air flow for the stationary packed-bed combustor is typically in the range from 10 to 15 scfm during ignition and between 20 and 25 scfm during the combustion phase (9). At these flow rates, the pressure drop across the packing is normally between 1 and 3 inches of water, depending upon the amount of fuel in the packing and the degree of ash removal from the packing.

Bench-scale testing and shakedown testing on the pilot-scale indicated that ash removal from the packing and control of gaseous emissions needed to be addressed to make the packed-bed combustion system a viable alternative to oil- and natural gas-fired systems. With an operational goal of twice-annual maintenance, cycling tests were designed to burn the equivalent of a beneficiated 1.0%-ash coal/water fuel for a duration of one-half of a heating season. To accomplish this goal, fuels with much higher ash levels were used to accelerate the process and more quickly evaluate the results of each continuous test. The fuels used during continuous operation included a 4.9%-ash Spring Creek, a 7.1%-ash Jacob's Ranch, a 4.7%-ash Kemmerer, and an acid-cleaned Kemmerer with 2.8% ash. Initial tests indicated that ash build-up within the packing (84% of the total ash) hindered continuous operation of the combustor (10). To alleviate this problem, an electric vibrator was mounted on the outside combustor wall and used as described above. Subsequent long-term testing indicated that vibration of the packing reduced the level of ash in the packing from 84% to below 30% in the most recent continuous test, and also evenly distributed the ash throughout the packing, indicating a steady state removal of ash from the system (9).

4.2.4 Emissions Control

Emissions control in the modular design of the pilot-scale packed-bed combustion system was accomplished using a baghouse for particulate capture and a platinum/palladium catalyst for conversion of carbon monoxide and various hydrocarbons. The baghouse and catalyst test sections are shown as part of the modular test rig in Figure 6.

The baghouse was constructed to measure the pressure drop and required cleaning frequencies for the bags at various air-to-cloth ratios. When both bags were used, the air-to-cloth ratio was 3 to 1. By using only one chamber and by using bags that have had their collection area reduced by intentional blinding, air-to-cloth ratios as high as desirable could be studied. The baghouse was oversized to ensure that an adequate air-to-cloth ratio could be obtained for any prototype combustion device (6). For the testing completed on the packed-bed combustion system, the baghouse was used primarily as a collection device to quantify the levels of ash in the system. Further testing is required to determine collection efficiency and optimum operating parameters.

The primary function of the catalyst test section was to study the effects of various catalyst types and configurations on the conversion of carbon monoxide and hydrocarbons. The test section was designed to study optimal operating temperature, catalyst life, required residence time, and overall catalytic conversion efficiency. A natural gas preheater was used to control the temperature of the flue gas entering the test section. Gaseous emissions were monitored on-line for CO, CO₂, and O₂ before and after the catalyst (6). Initial pilot-scale testing used the same platinum and palladium catalyst described in section 4.1, Bench-Scale Testing.

Five combustion tests were designed to monitor the effectiveness of the catalytic converter while varying the operating conditions. Initial testing had shown sporadic reduction of carbon monoxide emissions. A maintenance check of the bench-scale catalyst indicated that flue gas passed through the test section in plug-flow, bypassing a major portion of the available surface area of the catalyst. Before the first combustion test, a standard platinum/palladium automotive catalyst was installed that had more surface area than the bench-scale catalyst. The greater pressure drop across this catalyst forced even distribution of the flue gas through the test section, and as a result, carbon monoxide emissions were reduced from above 20,000 ppm to below 40 ppm. Subsequent testing varied inlet flue gas temperature and excess oxygen levels to determine the optimum operating conditions for the reduction of carbon monoxide in the flue gas. Results from these combustion tests indicated that effective catalyst operation could be achieved by maintaining a flue gas temperature of 600°F and an excess oxygen level of 5% (8).

An increase in temperature from catalyst inlet to exit of more than 500°F was observed in these tests. This rise in temperature could not be accounted for by the conversion of CO alone and was most likely due to the conversion of hydrocarbons in the flue gas. To evaluate the level of hydrocarbons in the flue gas and their effective level of conversion in the catalyst test section, a sampling system was designed using methylene chloride as the solvent. A metering pump was used to draw the flue gas through an impinger filled with methylene chloride. A reflux condenser and fabric filter were used to reduce

any hydrocarbon loss through the system and to protect the pump from contamination. Samples were taken at three points in the system: 1) post-combustor, 2) pre-catalyst, and 3) post-catalyst. The samples were then submitted for gas chromatographic analysis to qualitatively determine the effect of the platinum/palladium catalyst on the conversion of hydrocarbon emissions. Results of the analyses indicated that straight-chain and aromatic hydrocarbons in the range from C_1 through C_{40} are evolved as a result of the slow heating of the fuel caused by the transfer of heat from the combustion zone through the packing. Initial studies indicated that the catalyst converted all straight chain and aromatic hydrocarbons below C_8 . No quantitative results were available to determine the extent of conversion of higher order hydrocarbons or the relative distribution of the various hydrocarbon emissions. However, an on-line hydrocarbon analyzer indicated that hydrocarbons were present at the post-combustor and post-catalyst locations at levels of 10,000 and 5,000 ppm, respectively. The heating value of the hydrocarbon emissions was significant and conversion was considered essential to obtaining the desired thermal rating and meeting environmental regulations. Future studies burning coal/water fuel in the packed-bed combustor would require the testing of different catalyst types and the effect of surface area and residence time on hydrocarbon conversion in those catalysts.

Other gaseous emissions, SO_x , NO_x , and CO_2 , were monitored during testing and were present at low levels during the cyclic operation of the combustor. Further testing would be required to determine the environmental impact of SO_x and NO_x , and also to determine the level of reduction required for continuous operation.

4.3 Results of Task B. Rotating Packed-Bed Combustor

The rotating packed bed combustor was designed to run in semi-batch mode, with fuel delivered to the packing surface intermittently to achieve the desired thermal output. The combustor chamber could be rotated between 1 and 5 rpm to create an even temperature profile in the combustion zone, reducing the level of carbon monoxide and hydrocarbon emissions. The slow rotation imparts a mixing action in the packing, moving the fuel into the combustion zone and removing the ash from the packing for collection in a hopper below the rotating chamber. The packing temperature was to be maintained during non-use hours by feeding small amounts of fuel to the packing surface where rotation of the chamber would move the fuel into the combustion zone. The bed was also designed to study combustion at angles of inclination between 30 and 90 degrees from horizontal. A schematic of the rotating packed-bed combustor and modular test rig can be seen in Figure 7. The arrows show the direction of air flow through the combustor. During continuous operation, combustion air surrounds the rotating chamber, insulating the combustor and preheating the combustion air.

Shakedown testing attempted to evaluate ignition procedures and determine the impact of air flow rate, fuel feed rate, angle of inclination, and rotational speed on the combustion characteristics of low-rank CWF. A number of modifications to the system were made to reduce local velocities and increase the residence time of the fuel in the packing (9). These changes resulted in limited success and combustion of the fuel in the packing was difficult to sustain.

Figure 7. Rotating-Bed Combustor and Modular Test Rig.

4.4 Results of Task C. Design of a Dry, Ultra-Fine, Coal Combustion System

As part of the three year objectives, the design of a dry, ultra-fine coal combustion system was begun. A separate combustion device was not considered, as the stationary- and rotating-bed combustors were to be used. Because the dry, ultra-fine coal presented an explosion hazard if not handled properly, the main objective was to design a feed system that was both safe and reliable. Two feed system configurations were considered: The first was an extruder feeding a slightly dampened fuel, and the second was an entrained-coal feed system using nitrogen to convey the dry coal (10).

The extruding screw feeder would receive dampened coal fed from a hopper directly to the screw. The diameter of the screw shaft would increase along the length of the screw through a constant diameter pipe to slightly compact the fuel as it was conveyed. The slightly pelletized lumps would then fall onto the top of the packing of either the stationary- or rotating-bed combustor. The lump form of the coal was considered to aid in air and fuel distribution, while the slightly dampened coal would ensure complete safety of the fuel while in storage and in the feed system (10).

The use of nitrogen as a carrier gas for a dry, ultra-fine coal had two advantages. First, the very fine coal would require extremely low carrier velocities in the feeder pipe to remain fluidized. Thus, the relatively

inexpensive nitrogen would not represent a significant cost to the system because of the small amounts required to feed the dry fuel. Secondly, by keeping a constant nitrogen pressure in the storage tank (hopper) and in the feed line, the explosion hazard of the dry, ultra-fine fuel would be significantly reduced. Calculations made using a 1/4-inch, 20-gauge 304-SS tube indicated that between approximately 3 and 8 standard sized cylinders of nitrogen would be required to deliver 100 million BTUs of fuel, which is the average annual consumption on the residential scale (11).

To concentrate on the optimization of the stationary packed-bed combustor and on construction of the rotating-bed combustor, the design of the dry coal feed system was discontinued (8). Contract modifications were requested and granted, so no further development of the dry, ultra-fine combustion system was undertaken (9).

4.5 Results of Task D - Rheological Evaluation of Low-Rank CWF

A quantity of Kemmerer subbituminous coal was pulverized to 80% minus 200 mesh and processed in the pilot-scale, continuous process development unit (PDU) at UNDEMRC. The PDU uses a hydrothermal process that produces CWF at 625°F and 2200 psi with a five-minute residence time. The hydrothermal treatment (also called hot-water drying) forces inherent moisture out of the coal structure using carbon dioxide formed during the decarboxylation of the coal and increases the heating value of the product fuel. Tars are also exuded from the coal structure during treatment, sealing the micropore structure, reducing the surface area, and increasing the hydrophobicity of the coal. The CWF product slurry was concentrated using a solid-bowl centrifuge. A portion of the centrifuge cake was then processed in an attritor mill and blended to 80% coarse grind (39-micron average) and 20% fine grind (10-micron average). Xanthan gum was then added at the 0.2-wt% level to provide both dynamic and static stability to the fuel. In addition, D319-2, a ligno-sulfonate anionic dispersant, was added at the 1.0-wt% level. The dispersant typically contains 3000 ppm formaldehyde, which prevents biodegradation of the CWF and its additives (9).

To illustrate the effectiveness of the hot-water drying process, a curve showing apparent viscosity of treated and untreated CWFs over a range of solids loadings is shown in Figure 8. Prior to hydrothermal treatment, the maximum solids loading achievable at a given viscosity was 50 wt%, while after treatment the solids loading achieved was above 58 wt% at the same viscosity. When blended at 80% coarse/20% fine grind, a further increase to 60-wt% solids was noted at the given viscosity (9).

Two fuels were produced utilizing Kemmerer coal and UNDEMRC's hydrothermal treatment for combustion in the stationary and rotating packed-bed combustion systems. The first fuel produced had an ash content of 4.67 wt%, while the second fuel was cleaned with dilute nitric acid for 45 minutes to reduce the ash content from 4.67% to 2.8% prior to hydrothermal processing. A sample of the 4.67%-ash Kemmerer CWF was submitted for proximate, ultimate, and heating value analyses and is presented in Table 4. The rheological evaluation of the Kemmerer CWFs described above was completed and the results

Figure 8. Apparent Viscosity of Treated and Untreated CWFs.

tabulated in Table 5. The chemical cleaning of the fuel decreased the yield stress of the product fuel, changing the flow behavior to that of a more Newtonian fluid. This was the result of a decrease in cation content during the acid-washing of the fuel. The yield stress and viscosity of each fuel were plotted versus solids loading and are presented in Figures 9 and 10, respectively. Chemical cleaning did not appear to affect the viscosity of the fuel (9).

The rheological behavior, especially the Newtonian or non-Newtonian nature of the slurries, is a primary concern for combustion purposes. The behavior of a slurry at low, intermediate, and high shear rates essentially dictates its behavior during transportation, pumping, and atomization (12). Rheological properties of the hot-water-dried fuels were investigated using a concentric-cylinder Haake RV100 viscometer equipped with an MVII-p profiled rotor and sample cup. Shear stress-versus-shear rate rheograms were recorded over the shear rate range of 0 to 440 sec^{-1} .

The study involved optimization of particle size and investigation of additives to improve fuel rheological performance and stability, in comparison to the performance of fuels produced by directly mixing clean, hot-water-dried, combustion-grind centrifuge cake with water and no additives. A portion of the centrifuge cake was processed in the attritor mill and blended

TABLE 4
PROPERTIES OF KEMMERER CWF

Date Sampled	1/17/89	
Sample Number	89-0031	
	<u>As-received</u>	<u>Moisture-free</u>
Proximate Analysis, wt%		
Moisture	45.80	---
Volatile Matter	20.82	38.45
Fixed Carbon	30.84	56.88
Ash	2.52	4.67
Ultimate Analysis, wt%		
Hydrogen	7.78	4.96
Carbon	39.99	73.84
Nitrogen	0.71	1.31
Sulfur	0.18	0.33
Oxygen	48.79	14.86
Ash	2.52	4.67
Heating Value, BTU/lb	6,956	12,842

TABLE 5
RHEOLOGICAL EVALUATION RESULTS FOR KEMMERER CWFs

	<u>Wt% Solids</u>	<u>Viscosity (cP)</u>	<u>Consistency Factor (cP)</u>	<u>Flow Factor (n)</u>	<u>Yield Stress (Pa)</u>
4.67 wt% ash	55.74	799	2235	0.753	15.04
Mean particle size	54.00	461	1256	0.761	7.90
33.5 microns	53.03	323	437	0.879	6.39
2.80 wt% ash	54.71	632	1201	0.816	6.02
Mean particle size	53.87	402	705	0.839	3.76
22.0 microns	51.82	237	520	0.801	3.01

Figure 9. Yield Stress of Hydrothermally Treated Kemmerer CWFs.

Figure 10. Viscosity of Hydrothermally Treated Kemmerer CWFs.

to yield an 80%-coarse/20%-fine-grind mixture and surfactants were added to lower the surface tension between the hydrophobic coal particle surfaces and the water, allowing the particles to be wetted and suspended. An anionic dispersant, D319-2, a lignosulfonate, and a non-ionic surfactant, T-Mulz, were added at the 1-wt% level. The anionic dispersant is adsorbed at particle surfaces and counteracts the Van der Waal forces present in the coal. The strength of the repulsive forces governs the degree of flocculation of the suspended particles. The non-ionic surfactant has a surface effect on the coal. Settling can be slowed through the use of polymeric additives that form gel structures with water. Xanthan gum was added at the 0.2-wt% level to provide aggregate stability to the coal/water fuel.

A summary of the power law flow behavior for the cleaned fuel at a viscosity of 500 cP and a shear rate of 100 sec^{-1} is shown in Table 6. The Kemmerer fuel tested showed no distinct differences between the anionic and non-ionic stabilizers. Both additive packages had a solids loading of greater than 55-wt% with an energy density of just over 7000 BTU/lb. The flow factor, which is the barometer of flow behavior for CWFs, for both additive packages was less than one, indicating a pseudoplastic (shear-thinning) fluid. This implies that as the fuel is pumped, its viscosity is lowered and the energy required to deliver the fuel to the combustor is reduced. This property is even more important for combustion systems utilizing atomization. As the fuel is delivered to the atomizer tip, its viscosity decreases allowing it to flow through the orifice more freely and with less chance of plugging than would be expected of a more Newtonian or dilatant fuel. A flow factor of one indicates a Newtonian fluid, while a flow factor greater than one indicates a dilatant (shear-thickening) fluid.

The Kemmerer fuel was also tested under high temperature and high pressure conditions to determine which additive package was better suited to combustion applications. The effect of temperature on the rheology of the CWF

TABLE 6
SUMMARY OF POWER LAW FLOW BEHAVIOR FOR KEMMERER CWFs
AT 25°C AND 500 cP

Additive Description	Solids Loading (wt% mf)	Energy Density (BTU/lb)	Consistency Factor (cP)	Flow Factor n
No additive	56.3	7250	2900	0.78
D319-2, anionic	55.3	7100	1300	0.80
T-Mulz, non-ionic	55.9	7150	850	0.85

depends on the type of interparticle interaction (whether electric double layer, solvation, or steric) and the degree of adsorption of the additive. The temperature of the fuel was varied from 30°C to 240°C, while the pressure of the system was increased from 14.7 psi to 800 psi to prevent the fuel from dewatering at the elevated temperatures. Results of the tests indicated that thermal breakdown of the non-ionic surfactant package caused the fuel to agglomerate and gel, increasing the viscosity of the fuel. No breakdown of the anionic package was observed and, therefore, this was considered the most desirable of the two additive packages for high temperature applications. The temperature/pressure effect on the viscosity of the fuel can be seen in Figure 11.

The Kemmerer coal/water fuel was also tested under freeze-thaw conditions in which each sample was frozen for one week and allowed to thaw for 3 days prior to testing. Results indicated a slight system loss of water; however, no change in rheology for the samples at a given solids loading was noted (9).

Figure 11. Viscosity Effect of High Temperature and High Pressure on Two CWFs Prepared with Different Additives.

5.0 SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS

Combustion of coal/water fuel on a packed-bed was studied at the bench and pilot scale and determined to be a promising method of providing space and water heat for residential and commercial applications. By eliminating the need for atomization, one of the most difficult problems in combustion of CWFs was circumvented. Bench-scale testing quantified the effects of air flow rate, packing size, and fuel density on the maximum temperature achieved in the packing and the overall combustion rate. The data was used to design two prototype packed-bed combustors and a modular test rig to study combustion characteristics such as ignition and combustion rate, fuel storage and delivery, particulate capture, and gaseous emissions control.

The nearly 60 pilot-scale combustion tests conducted on the stationary packed-bed combustor indicated that this mode of combustion for coal/water fuels has merit. Pilot-scale combustion test results include:

1. The stationary-bed combustor can be continuously cycled to study the effects of long-term operation on ash buildup, emissions control, catalyst efficiency and life, and particulate capture. Ash removal from the packing and conversion of gaseous emissions will ultimately determine the viability of this mode of combustion as an alternative to oil- and gas-fired combustion systems.
2. Uniform ceramic spheres are a good packing material on which coal/water fuels can be burned. The instability of various rock packings at the high temperatures achieved in the system made them incompatible with the combustion of CWF.
3. The coal/water fuel can be ignited safely and reliably with electric heaters located above the packing surface. Ignition of the fuel was typically observed within 15 minutes, using approximately 10.5 kW of electrical energy.
4. A standard platinum/palladium catalyst operated at 600°F and 5% excess air will effectively reduce carbon monoxide emissions from above 20,000 ppm (in a few tests, CO levels as high as 25,000 ppm were observed) to below 40 ppm.
5. Vibration of the packing at the end of each combustion cycle can reduce the amount of ash retained in the packing from 84% with no vibration, to below 30% with vibration.
6. The coal/water fuel can be delivered to the combustor reliably with the use of a peristaltic pump.

Rheological evaluation of two low-rank CWF additive packages indicated that D319-2, an anionic lignosulfonate dispersant, and T-Mulz, a non-ionic surfactant, can both be used in conjunction with xanthan gum to provide stability and improve flow behaviors of the fuel. Rheological analysis of the additive packages indicated relatively little difference between the anionic

and non-ionic additives, as each had a pseudoplastic or shear-thinning effect on the fuel. No significant differences were noted under freeze/thaw conditions; however, when tested under high temperature/high pressure conditions, the non-ionic surfactant tended to agglomerate and gel at higher temperatures ($>180^{\circ}\text{C}$), increasing the viscosity of the fuel. No breakdown of the anionic package was observed and, therefore, this was considered the most desirable of the two additive packages for high temperature applications.

This concludes all testing on the residential- and commercial-scale combustion systems. Should the need to investigate this method of combustion arise in the future, it is recommended that a compact design for the stationary-bed combustor incorporate all modules -- including heat exchange equipment -- in the test rig. The design should include a method for the conversion of the hydrocarbon emissions, whether it be a reburner or a catalyst system. Limited testing in this area indicated that the platinum/palladium catalyst was effective for conversion of lower-order linear and aromatic hydrocarbons in the range from C_1 to C_7 . However, further testing is required to determine the level of conversion for higher-order hydrocarbons and the effect of residence time and increased surface area on the conversion efficiency of the platinum/palladium catalyst, or whether another catalyst system would be appropriate. Further study of fuel distribution across the packing surface was also deemed warranted, as a more effective method of distribution could broaden the range of fuel properties compatible for combustion in the packed-bed system. Testing on the rotating-bed concept is also recommended, as the inherent advantages of low CO , NO_x , and SO_x production during combustion of the fuel, and increased ash removal from the rotating chamber could make this a viable alternative to present small-scale combustion systems.

Future work under the Cooperative Agreement will focus on combustion characteristics such as flame stability, carbon burnout, ash fouling, and ESP performance, and are outlined in the annual project plan for this year.

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FEDERAL ASSISTANCE MANAGEMENT SUMMARY REPORT

Page ____ of ____

1. Program/Project Identification No.	2. Program/Project Title Combustion Characterization of LRC Fuels	3. Reporting Period 4/1/88 through 3/31/89
4. Name and Address University of North Dakota Energy & Mineral Research Center Box 8213, University Station, Grand Forks, ND 58202		5. Program/Project Start Date 4/1/86
		6. Completion Date 3/31/92

11. Major Milestone Status	Units Planned	
	Units Complete	
Testing of Stationary Packed Bed Combustor	P	1 2 3
	C	
	P	
	C	
Testing of Rotating Packed Bed Combustor	P	1 2 3
	C	
	P	
	C	
Construction of Ultra Fine Dry-Coal Based System	P	1 2 3 4 *
	C	
	P	
	C	
Slurry Fuels Development	P	1 2 3
	C	
	P	
	C	

* Task Deleted

12. Remarks

13. Signature of Recipient and Date

Michael D. Mann

5/10/89

14. Signature of DOE Reviewing Representative and Date

U.S. DEPARTMENT OF ENERGY
FEDERAL ASSISTANCE MANAGEMENT SUMMARY REPORT

1. Program/Project Identification No. DE-FC21-86MC10637	2. Program/Project Title Combustion Characterization of LRC Fuels	3. Reporting Period 4/1/89 through 6/30/89
4. Name and Address University of North Dakota Energy & Mineral Research Center Box 8213, University Station, Grand Forks, ND 58202		5. Program/Project Start Date 4/01/89
		6. Completion Date 3/31/92

Milestone ID No.	Description	Planned Completion Date	Actual Completion Date	Comments
TASK A	Testing of Stationary Packed-bed Combustor			
a.1	Preliminary ignition and cycling studies completed	6/30/88	6/30/88	
a.2	Catalyst optimization studies completed	11/30/88	9/30/88	
a.3	Heat exchange and cycling studies completed	3/31/89	6/30/89	
a.4	Complete design and assessment	6/30/89	6/30/89	
TASK B	Testing of Rotating Packed-Bed Combustor			
b.1	Complete system construction	9/30/88	12/30/88	
b.2	System shakedown completed	11/31/88	6/30/89	
b.3	Complete cycling and emission studies	3/01/89	*	
b.4	Complete design and assessment	6/30/89	*	
TASK C	Task Deleted			
TASK D	Slurry Fuels Development			
d.1	Develop acceptable additive package	5/01/88	5/01/88	
d.2	Identify temperature and pressure effects on storage and handling	2/05/89	6/30/89	
d.3	Resolve additive degradation and CWF dilatory problems	3/15/89	6/30/89	
* Unit was not successfully operated to allow completion of these tests.				

4.4 Diesel Utilization of Low-Rank Coals

DIESEL UTILIZATION OF LOW-RANK COALS

Final Technical Report for the Period April 1, 1988 - June 30, 1989
Including the Quarterly Technical Progress Report
for the Period April through June 1989

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Work Performed Under Cooperative Agreement No. DE-FC21-86MC10637

TABLE OF CONTENTS

	<u>Page</u>
List of Figures.....	iii
List of Tables.....	v
1.0 Introduction.....	1
2.0 Goals and Objectives.....	2
2.1 Three-Year Objectives.....	2
2.2 Third-Year Objectives.....	3
3.0 Reactivity of Fuel in Diesel Systems.....	4
3.1 Constant-Volume Combustion Bomb.....	6
3.1.1 Results and Discussion.....	9
3.2 Single-Stroke Diesel Simulator.....	18
3.2.1 Results and Discussion.....	18
3.3 Demonstration Diesel Engine.....	24
3.3.1 Preliminary Testing of 30-hp Ajax Diesel.....	27
3.3.2 Diesel Testing of GPGP Tar Oil.....	29
3.3.3 Engine Modifications and Preliminary Slurry Testing....	32
4.0 References.....	35

LIST OF FIGURES

<u>Figure</u>		<u>Page</u>
1	Photograph of the constant-volume combustion bomb.....	8
2	Detailed schematic of the constant-volume combustion bomb.....	8
3	Combustion bomb pressure traces using No. 2 diesel fuel.....	12
4	Combustion bomb pressure traces highlighting fuel injection and combustion events for No. 2 diesel fuel.....	12
5	Sum-of-squares error versus pressure recovery time (To).....	13
6	Ignition delay as a function of pressure and temperature for diesel fuel.....	16
7	Ignition delay as a function of pressure and temperature for Beulah CWS.....	16
8	Ignition delay as a function of pressure and temperature for Kemmerer CWS.....	17
9	Ignition delay as a function of pressure and temperature for Otisca CWS.....	17
10	Detailed schematic of modified diesel engine used as base engine for UNDEMRC's single combustion cycle diesel simulator...	19
11	Detailed schematic of test fuel combustion chamber on UNDEMRC's single combustion cycle diesel simulator.....	19
12	Measured versus predicted ignition delay values.....	22
13	Chamber pressure versus crank angle for diesel fuel and GPGP Tar Oil.....	25
14	Heat release versus crank angle for diesel fuel and GPGP tar oil.....	26
15	Demonstration diesel high-pressure coal liquid fuel feed system.....	27
16	Particle size distributions for diesel exhaust emissions.....	29
17	Diesel engine performance data for firing diesel fuel and GPGP coal tars under center point conditions.....	31
18	Exhaust port temperatures and gaseous emissions for diesel engine tests firing diesel fuel and GPGP tars under center point conditions.....	33

LIST OF FIGURES (Continued)

<u>Figure</u>		<u>Page</u>
19	Cross-sectional view of the piston and head for the Ajax 30-hp diesel engine.....	34
20	Photograph of New Bosch multi-hole diesel injector.....	36
21	Photograph of Bosch multi-hole diesel injector after one hour of fuel injection of Beulah CWS.....	36

LIST OF TABLES

<u>Table</u>	<u>Page</u>
1 Qualitative Analysis of Mild Gasification Coal Liquids.....	5
2 Composition and Calculated Heating Value of Coal Liquids.....	6
3 Distillation Data and Elemental Analyses for GPGP By-Product Streams and No. 2 Diesel Fuel (T-T).....	7
4 Constant-Volume Combustion Bomb Test Matrix.....	9
5 Ultimate Analysis of No. 2 Diesel Fuel.....	10
6 Properties of Coal/Water Slurries Used in Combustion Bomb Tests.....	11
7 Combustion Bomb Fuel Injection Conditions and Measured Ignition Delays.....	14
8 Statistical Highlights of Combustion Bomb Tests.....	15
9 Single Combustion Cycle Diesel Simulator Screening Test Matrix Variables.....	20
10 Variables and Measured Responses for the Two-Level Three-Variable Test Matrix.....	21
11 T-Test-Derived Confidence Levels for Main Effects of Experimental Variables.....	23
12 GC Analysis of Diesel Gaseous Emissions.....	28
13 Ultimate and Heating Value Analyses for Particulate Samples.....	28
14 Experimental Test Matrix Used to Compare Diesel No. 2 with GPGP Tar Oil.....	30

DIESEL UTILIZATION OF LOW-RANK COALS

1.0 INTRODUCTION

Lignite chars have a higher reactivity than chars of higher-rank coals, indicated by particle burning rates four to five times higher than observed for bituminous coals used in coal/water slurries investigated as potential heat engine fuels. A lignite slurry will therefore offer improved engine performance and, if ash concentrations are reduced to limit particulate emissions, may be used in higher-RPM diesel applications. In order to take advantage of low-cost coal as a fuel for heat engine systems, a major challenge is to produce a highly beneficiated fuel (with an ash content of less than 1 wt%, preferably less than 0.1 wt%).

The utilization of coal slurry fuels in medium-speed diesel engines offers the opportunity to replace premium petroleum-derived distillate fuels with fuels from more economical and abundant coal. Burning coal in diesel engines is not a new idea, but commercial success has yet to be achieved. Research into the coal-fueled compression-ignition engine began with Rudolph Diesel and continued with extensive work in Germany using a coal dust engine until 1945. These early diesel engine experiments with powdered coal were somewhat discouraging because of the deposits of unburned coal that formed between the piston and the cylinder. Therefore, the majority of further engine development concentrated on petroleum fuels. Since then several studies have been conducted in the United States involving the use of coal/oil slurry fuels in research engines. Additional attention was focused on the use of coal-fueled diesel engine technology after the oil embargo in the early 1970s. Much of the current research in the area was begun by the U.S. Department of Energy. The technical problems being addressed by this research include: 1) unsatisfactory carbon utilization because of incomplete burnout of the coal particles in the very limited combustion time, 2) corrosion and erosion of metal surfaces by ash constituents and particulates, and 3) excessive SO_x/NO_x and particulate exhaust gas emissions. Recent advances in coal technologies such as the ability to prepare satisfactory coal/water slurries, and the efforts to reduce the mineral content of parent coals in the clean coal program, suggest that coal-derived fuels with very low mineral contents soon may be technically feasible to produce and utilize in a cost-effective manner in diesel engines.

Until very recently, low-rank coals were not considered as parent coals for coal/water slurry fuels because of their high intrinsic moisture levels. It is extremely difficult to prepare a pumpable slurry of as-mined lignite with a dry solids loading of over 35 wt%. However, with the advent of UNDEMRC's hydrothermal drying process, lignite slurries have been produced with solids loadings of up to 62 wt% and heating values of 6800 Btu per pound of slurry. Subbituminous coals also respond very well to hydrothermal treatment and produce high-quality slurries. With the availability of a slurry with a high enough fuel value, it is now possible to take advantage of a main characteristic of low-rank coals; namely, the higher reactivity of their nonvolatile carbonaceous component. Consequently, a low-rank coal slurry should require less residence time in the cylinder of an engine to obtain complete combustion. Another advantage of low-rank coal slurries is their relatively nonagglomerating properties during atomization and

combustion. Consequently, micronization to extremely fine coal particle sizes and atomization to fine spray droplet sizes will be less critical than it is for bituminous coal slurries.

2.0 GOALS AND OBJECTIVES

The overall objective of this program is to develop a scientific and engineering data base on the utilization of subbituminous and lignite coals (LRCs) for emerging heat engine technologies, specifically diesel applications. Research will be directed toward understanding the characteristics of LRC fuels produced from existing and advanced beneficiation processes for diesel engine applications. Combustion studies will provide functional relationships between fuel properties and the subsequent products of combustion. The formation of nitrogen and sulfur oxides and other potential environmentally detrimental species along with methods to reduce their emission levels will be investigated. The impact of LRC fuels on diesel engine components, including injection systems and combustion chambers, will also be studied.

The investigation of diesel engine utilization of low-rank coals at UNDEMRC is a multi-year program. Three-year goals were established at the beginning of the program, but were modified at the start of the second program year in response to changes in direction and funding level for the project. The current emphasis of the project is to study the characteristics of diesel performance using low-rank coal-derived fuels, and to optimize the diesel system for use with these fuels. The modified three-year goals are discussed in the following text.

2.1 Three-Year Objectives

1. Technology Assessment -- To better understand the concerns and needs for the use of coal-derived fuel in diesel engine applications, a technology assessment will be made. This assessment will include a determination of which market segments will be the most likely to make use of this technology. The results of this assessment will be used to direct the program. This objective will be completed during the first year of the program.
2. Reactivity of Fuel in Diesel System -- The reactivities of low-rank coal-derived fuels will vary with coal properties and preparation methods. Fast, simple and inexpensive experiments in a constant-volume combustion bomb will provide basic information about the pressurized combustion behavior of these fuels. This information will be critical in determining the fuel specifications of coal-derived liquid fuels for use in heat engine applications. Data collected during these tests will include the heat of combustion (calorimetry) of the fuel, the burning-time/reactivity (from pressure sensors) of the fuel, and the products of combustion of the fuel under various conditions (subsequent gas analysis). Parameters to be investigated include fuel type, gas composition, and combustion bomb temperature and pressure at fuel injection and initial system pressure. This testing will provide semi-quantitative information in a fast and inexpensive manner.

3. Characteristics of Diesel Performance Using Low-Rank Coal-Derived Liquid Fuels -- This task will involve testing on a bench-scale, single-stroke diesel simulator to study fuel properties affecting injection, atomization, and heat release rates. Before testing of various fuels is initiated, baseline testing will establish the reliability of the system. Measurement methods include photography to examine particle size and distribution, and optical pyrometry to measure chamber temperatures and enable the high-speed acquisition of the operating pressures and temperatures.
4. Demonstrate the Feasibility of Using Low-Rank Coal-Derived Liquid Fuels in a Diesel Engine -- UNDEMRC has a 30-hp diesel engine capable of firing liquid fuels. Based on the findings in Tasks B and C, the low-rank coal-derived fuels possessing the fuel specifications most desirable for use in a reciprocating engine will be tested in this engine. Overall performance of this engine will be evaluated. Performance will be measured in terms of the particulate and gaseous emissions from the engine, deposition on internal surfaces, the engine's operational characteristics (i.e., overall thermal efficiency, load-following and RPM range), and the amount of corrosion/erosion experienced by the cylinder, rings, and fuel injectors.
5. Optimization of LRC Heat Engine Applications -- Although conventional diesel engines can sustain combustion of coal-derived liquid fuels, it is expected that several design modifications will be necessary before efficient operation can be expected. These changes will be required due to the inherently different properties of low-rank coal-derived fuels. To determine the impact and potential design changes for heat engine components, the information obtained from the previous four tasks will be evaluated. Some of the major systems that will be evaluated include the fuel injection system, combustion chambers, reciprocating surfaces, and the post-combustion and exhaust components to potentially allow burning fuels with higher levels of contaminant species.

2.2 Third-Year Objectives

Specific objectives of the Diesel Utilization of Low-Rank Coal Project for the third year include:

1. Perform reactivity tests in the constant-volume combustion bomb using various low-rank coal-derived liquid fuels. The heat of combustion, fuel reactivity and combustion products will be determined. Data will be compared to results obtained in Task 3 to document differences (where available) in diesel performance.
2. Perform shakedown and baseline testing of bench-scale single-stroke diesel simulator. Conventional diesel fuel will be used for shakedown testing. The fuel chosen for the baseline test will be one for which data from operation of a large-scale system exists.

3. Test low-rank coal-derived fuels and coal-based slurries in the diesel simulator and investigate the effects of the various fuel properties on the interactions that occur within the system. Effects on pumping, injection and atomization, ignition delay, total burn time and rate of heat release during combustion will be investigated for several potential fuels.
4. Test low-rank coal-derived liquid fuels in UNDEMRC's 30-hp diesel engine. Data to be evaluated will include gaseous and particulate emissions; deposition on, and corrosion and erosion of internal surfaces; operational characteristics; and ease of fuel handling and injection.
5. Evaluate information produced in Tasks 1, 2, and 3 to determine the impact and potential design changes necessary to optimize heat engine components. Conceptual designs of various components identified during the evaluation process will be developed.

3.0 REACTIVITY OF FUEL IN DIESEL SYSTEMS

Coal-derived liquids were extracted from the condensate water from the mild gasification process. This process is being investigated at UNDEMRC under sponsorship by the Department of Energy, which makes these liquids readily available for the diesel program. These liquids were recovered using a single methylene chloride batch extraction in a separatory funnel. The organics recovered constituted approximately 1% of the total volume of condensate, and were extracted at a neutral pH.

The qualitative characterization of the organics is presented in Table 1. Butylacetate is believed to have been solubilized from the sample container while in storage. The coal liquids were analyzed quantitatively for carbon, hydrogen, nitrogen, sulfur, ash, and moisture. These results and the calculated heating value are shown in Table 2.

In addition to the mild gasification coal liquids, UNDEMRC has access to the Great Plains Gasification Plant (GPGP) by-product coal liquid streams. This plant produces 150 million cubic feet per day of synthetic natural gas (SNG) and, as coal liquid by-products, produces nominally 880 barrels per day (BPD) of rectisol naphtha, 920 BPD of crude phenols, and 3450 BPD of tar oils. Under contract by the Department of Energy (DOE), extensive physical and chemical characterization of these streams were performed to determine their suitability as jet fuels (1).

Table 3 presents distillation data and elemental analyses for the various GPGP by-product streams and a typical diesel fuel found in the eastern United States. Data for by-product streams was reprinted from the report entitled "Production of Jet Fuels from Coal-Derived Liquids," by C.L. Knudson (1). The rectisol naphtha stream is much too light for use as a diesel fuel. Because of its high content of benzene (30%), toluene (10%), and xylene (3%), this stream would be better utilized as a chemical feedstock.

TABLE 1
QUALITATIVE ANALYSIS OF MILD GASIFICATION COAL LIQUIDS

<u>Carbon-13 NMR:</u>	<u>Carbon, %</u>
Aromatics	64.1
Ether/Alcohols	2.6
Methylene Chloride	1.9
Aliphatics	31.4

<u>GC-MS Elution Order</u>	<u>Chemical Species</u>
1	Methylene Chloride (Solvent)
2	Toluene
3	Butylacetate
4	C2-Benzene
5	C3-Benzene
6	Phenol
7	C3-Benzene
8	Indene
9	o,m,p-Cresol
10	C1-Indene
11	C2-Phenol
12	Naphthalene
13	C2-Phenol
14	C2-Phenol
15	C3-Phenol
16	C3-Phenol
17	C1-Naphthalene
18	C14-Olefin
19	C14
20	C2-Naphthalene
21	C2-Naphthalene
22	C15-Olefin
23	C15
24	C3-Naphthalene
25	C16-Olefin
26	C16
27	C17-Olefin
28	C17
29	Phytene
30-38	C18-Olefin, C18 to C22-Olefin, C22
39-44	C23 to C28

TABLE 2
COMPOSITION AND CALCULATED HEATING
VALUE OF MILD GASIFICATION COAL LIQUIDS

	<u>Weight %</u>
Carbon	77.30
Hydrogen	8.29
Nitrogen	0.77
Oxygen (by diff)	13.23
Sulfur	0.22
Ash	0.07
Moisture	0.12
Calculated Heating Value, Btu/lb	15,200 ^a

^a Calculated from equation for coal liquids (3).

The crude phenol stream also exhibits much lower distillation temperatures than a typical diesel blend. In addition, the quantities of carbon and hydrogen in this stream are lower, being replaced mainly by the oxygen associated with phenolics. This stream may also be of value as a chemical feedstock for phenol and benzene. From the data in Table 3, the tar oil stream appears to be most suited for use as a diesel fuel, although the presence of nitrogen compounds and residual insolubles would have to be addressed.

The preliminary testing with coal-derived liquids consisted of estimating ignition delay and indicated work output. It is expected that the final form of these coal liquids could be improved through a combination of hydrogenation, distillation, blending, or additive enhancement.

3.1 Constant-Volume Combustion Bomb

The constant-volume combustion bomb was constructed from a Parr 1108 oxygen combustion bomb. The bomb has an easily removable head that seals internally when pressurized and an internal volume of 345 ml. Figure 1 is a photograph of the complete combustion bomb. Figure 2 shows a cross-sectional view of the head and sealing rings in the combustion bomb. Also shown in this figure are the electrodes and the nickel alloy fuse used for igniting the lean mixtures of $H_2/O_2/N_2$ in the bomb. In addition, openings for a pressure transducer and thermocouple were machined in the head of the combustion bomb for monitoring the combustion behavior of the fuel. Another opening was machined in the head for feeding the $H_2/O_2/N_2$ mixture into the combustion bomb and for venting the combustion gas through the pressure relief valve if the bomb should over-pressurize. Combustion bomb and fuel injection pressures are obtained using Kistler Piezotron pressure transducers.

TABLE 3
DISTILLATION DATA AND ELEMENTAL ANALYSES FOR GPGP
BY-PRODUCT STREAMS AND NO. 2 DIESEL FUEL

	<u>Tar Oil</u>	<u>Crude Phenols</u>	<u>Rectisol Naphtha</u>	<u>Diesel (T-T)</u>
Barr. Press. (mm Hg)	756	742	731	-- ^a
Distill. Temp. (°F), Volume Recovered:				
IBP	199	206	109	462 ^b
5	275	208	145	--
10	338	365	156	493
20	383	374	168	--
30	410	379	174	--
40	437	379	181	--
50	482	384	186	536
60	505	393	192	--
70	545	410	201	--
80	566	444	215	--
90	577	505	246	571
95	--	--	269	--
Maximum Temp. (°F)	577	509	269	589
Sp.Gr. (60/60 F)	1.015	1.060	0.821	0.85
Elemental Analysis, wt% as-received				
Carbon	83.76	72.18	87.65	85.04
Hydrogen	8.83	7.49	10.12	13.19
Nitrogen	0.52	0.28	0.00	0.01
Sulfur	0.39	0.04	0.00	0.22
Water	1.20	4.48	--	--
Oxygen (by diff)	5.30	15.53	2.23	1.54
HHV (Btu/lb) ^c	17000	14000	18200	19900

^a Values unknown.

^b Source for diesel fuel data:
Internal Combustion Engines, Colin R. Ferguson, 1986 (2).

^c Values calculated from empirical equation for coal liquids (3).

Figure 1. Photograph of the constant-volume combustion bomb.

Figure 2. Detailed schematic of the constant-volume bomb.

A gas mixing system that allows various concentrations of gases to be accurately mixed and fed to the combustion bomb was constructed. This system mixes gases to the desired partial pressures in an evacuated pressure vessel before feeding this gas to the combustion bomb or allowing a gas sample to be obtained for analysis. A Bosch KCA 18 S 48 nozzleholder and DNOS225 pintle nozzle are used for the injection of the test fuels into the combustion bomb. This fuel injector has a screw-in seal and is capable of injecting fuels at pressures of up to 8700 psia while the PFR1K diesel fuel pump is capable of pumping approximately 0.2 gm of fuel/stroke at pressures of up to 7250 psia. Three Delco-Remy 1115556 starter solenoids supply the force needed to push the diesel fuel pump plunger against the injection pressure.

Testing with this solenoid has shown that reproducible response times of 27 milliseconds can be obtained with this injection system. This response time is fast enough to allow the computer to control the fuel injection timing so that the fuel can be injected at preselected temperatures or pressures. The data acquisition was accomplished using a Metrabyte Dash 16 board capable of sampling its eight input channels at 25,000 conversions per second. This board also has four digital inputs and outputs for triggering events. The software for the Metrabyte Dash 16 analog/digital board will allow various timing sequences to be tested.

3.1.1 Results and Discussion

Table 4 shows the test matrix used to evaluate fuels in the combustion bomb. This two-level, three-variable full factorial matrix examines the effects of solids loading, and bomb pressure and temperature at the time of injection. The combustion bomb temperature is varied by changing the number of loops performed by the software before it triggers the solenoids on the fuel injection system. Bomb pressure is varied by changes in the initial pressure of the $H_2/O_2/N_2$ gas mixture loaded into the bomb.

TABLE 4
CONSTANT-VOLUME COMBUSTION BOMB TEST MATRIX

Run	Bomb Temperature (K)	Bomb Pressure (psig)	Solids Loading (wt%)
1	900	400	45
2	1300	400	45
3	900	800	45
4	1300	800	45
5	900	400	55
6	1300	400	55
7	900	800	55
8	1300	800	55
9	1100	600	50
10	1100	600	50

Table 5 lists the ultimate analysis of the No. 2 diesel fuel used for the baseline diesel testing. The analyzed sample of this fuel contained no detectable moisture, fixed carbon or ash. Table 6 lists the properties of the hot-water-dried coal slurries used in the combustion bomb testing to date. These included Beulah and Velva (North Dakota) lignites, Kemmerer (Wyoming) subbituminous, and Otisca (Virginia) high-volatile bituminous.

Figure 3 shows the pressure traces of the injection and ignition of a No. 2 diesel fuel in the combustion bomb after an $H_2/O_2/N_2$ mixture was ignited in the bomb. This figure indicates that approximately 51 msec into the start of the data acquisition program, the $H_2/O_2/N_2$ mixture (with mole fractions of 0.1605/0.2775/0.5620) was ignited. This mixture burned within 15 msec, followed by a period of approximately 473 msec before the diesel fuel was injected at 5500 psia, resulting in the second pressure rise in the combustion bomb. Figure 4 highlights the pressure traces from Figure 3 in the vicinity of the diesel fuel injection. This figure indicates that this pressure rise (pressure recovery delay) started within 1.3 milliseconds of the diesel fuel injection, indicating a high reactivity of diesel fuel under these injection conditions.

Figure 4 also highlights how the ignition delay is determined from the combustion bomb and fuel injection pressure traces. The start of the ignition delay period is defined as the point where the fuel injection pressure trace first decreases after the injector has been pressurized with the fuel pump. A best-fit straight line is drawn through the declining portion of the combustion bomb pressure trace. Likewise, a quadratic equation is used to fit the rising combustion bomb pressure trace. The transition data point between the straight line and the curve is varied until the sum of the errors for the two lines is minimized. This point constitutes the end of the ignition delay period and the beginning of combustion. Figure 5 shows a graphical representation of this process. In this figure, T_o is the point of transition from the linear to quadratic curve fit, while the horizontal line denotes the 95% confidence interval.

TABLE 5

ULTIMATE ANALYSIS OF NO. 2 DIESEL FUEL USED
IN COMBUSTION BOMB BASELINE TESTING

	<u>Wt% Moisture-Free</u>
Hydrogen	13.19
Carbon	85.04
Nitrogen	0.01
Sulfur	0.22
Oxygen (by diff)	1.54
Ash	0.00
Heating Value (Btu/lb)	19,900

TABLE 6
PROPERTIES OF HYDROTHERMALLY TREATED SLURRIES

	<u>Velva Lignite</u>	<u>Otisca Bituminous</u>	<u>Beulah Lignite</u>	<u>Kemmerer Subbituminous</u>
Proximate (wt%, mf):				
Moisture	NA	NA	NA	NA
Volatile Matter	41.94	36.50	38.18	41.10
Fixed Carbon (by diff)	56.12	62.42	59.52	56.62
Ash	1.94	1.08	2.20	2.28
Ultimate (wt%, mf):				
Hydrogen	4.85	5.66	3.95	5.03
Carbon	71.61	84.35	71.72	75.72
Nitrogen	1.15	1.48	1.21	1.30
Sulfur	0.38	0.52	0.47	0.26
Oxygen (by diff)	20.06	6.89	20.54	15.40
Ash	1.94	1.08	2.20	2.28
HHV (Btu/lb)	12154	15401	11907	12925
Particle Size:				
Mean (μm)	8.0	4.6	13.9	10.1
Top Size (μm)	50.0	17.4	76.0	56.6
Ash Composition (wt% as oxides, SO_3 free):				
SiO_2	49.6	35.0	42.5	49.0
Al_2O_3	19.9	35.3	14.6	22.0
Fe_2O_3	21.7	18.8	35.4	14.5
TiO_2	2.1	3.8	2.9	1.2
P_2O_5	0.2	0.4	0.0	0.4
CaO	3.4	11.8	3.3	9.1
MgO	1.6	2.5	0.6	3.5
Na_2O	0.7	0.8	0.0	0.0
K_2O	0.7	1.6	0.6	0.2

Figure 3. Combustion bomb pressure traces using No. 2 diesel fuel.

Figure 4. Combustion bomb pressure traces highlighting fuel injection and combustion events for No. 2 diesel fuel.

Figure 5. Sum-of-squares error versus pressure recovery time (T_o).

Table 7 contains the pressure of the bomb at fuel injection, the calculated temperature at injection, the solids loading when applicable, and the calculated ignition delay for several combustion tests. These tests were run in accordance to the matrix shown in Table 4 and were accumulated over the course of the year. Due to problems of high viscosity and instability, the Beulah lignite slurry was run only at a single solids loading of 40%.

The highlights of the statistical analyses performed on the various fuels are shown in Table 8. The results expressed in this table are valid only over the experimental range of the variables shown in Table 4. The values expressed in this table are the probabilities (confidence levels) of an effect occurring merely by chance; i.e., 0.0001 means that data producing a certain effect will occur randomly once in 10,000 observations. Usually, a probability value of 0.05 is deemed significant for decision making purposes. Also contained in the table are the R-square values for the linear models used to fit data. An R-square value of one represents a perfect fit, which means all data can be expressed by the model.

Several generalizations can be made about the effects of temperature, pressure, and solids loading on the ignition delays of various fuels:

1. Within the bounds of the experimental model, the ignition delay for diesel fuel was found to be independent of temperature and pressure.
2. The temperature at the time of injection had a very significant effect on all coal/water slurry ignition delays, i.e., increasing temperature decreased ignition delays.

TABLE 7
COMBUSTION BOMB FUEL INJECTION CONDITIONS
AND MEASURED IGNITION DELAY

Test Fuel	Solids Loading (wt%)	Operating Pressure (psia)	Operating Temperature (K)	Ignition Delay (ms)
Diesel Fuel	NA	413	1415	1.1
Diesel Fuel	NA	702	873	1.1
Diesel Fuel	NA	862	1369	1.6
Diesel Fuel	NA	398	878	1.3
Diesel Fuel	NA	377	1283	0.38
Diesel Fuel	NA	381	865	0.38
Diesel Fuel	NA	775	1368	0.82
Diesel Fuel	NA	720	864	0.82
Otisca Slurry	45.0	823	1353	4.6
Otisca Slurry	45.0	404	1326	2.6
Otisca Slurry	45.0	406	891	9.5
Otisca Slurry	45.0	436	1365	2.9
Otisca Slurry	45.0	762	908	10.7
Otisca Slurry	45.0	727	944	8.0
Otisca Slurry	50.0	646	1181	2.8
Otisca Slurry	50.0	637	1137	5.2
Otisca Slurry	52.7	452	992	8.9
Otisca Slurry	52.7	843	1210	4.6
Otisca Slurry	52.7	427	1126	3.8
Otisca Slurry	52.7	710	961	7.6
Beulah Slurry	40.0	411	1303	2.9
Beulah Slurry	40.0	397	1195	4.9
Beulah Slurry	40.0	751	894	7.4
Beulah Slurry	40.0	814	1339	2.9
Beulah Slurry	40.0	384	886	8.8
Beulah Slurry	40.0	414	855	9.5
Beulah Slurry	40.0	374	1172	5.2
Kemmerer Slurry	45.0	410	1237	0.68
Kemmerer Slurry	45.0	661	838	8.0
Kemmerer Slurry	45.0	840	1294	2.9
Kemmerer Slurry	45.0	390	856	7.4
Kemmerer Slurry	48.0	718	1266	1.9
Kemmerer Slurry	48.0	682	1203	2.0
Kemmerer Slurry	48.0	543	1057	2.6
Kemmerer Slurry	48.0	599	1132	2.9
Kemmerer Slurry	51.0	407	1262	1.6
Kemmerer Slurry	51.0	877	1350	3.4
Kemmerer Slurry	51.0	775	941	6.1
Kemmerer Slurry	51.0	416	894	9.7
Kemmerer Slurry	51.0	431	954	7.9

TABLE 8
STATISTICAL HIGHLIGHTS OF COMBUSTION BOMB TEST

Probability of Parameter Estimate ≤ 0				
	<u>Diesel</u>	<u>Beulah</u>	<u>Otisca</u>	<u>Kemmerer</u>
Variable				
Solids (S)	--	--	0.5964	0.0690
Pressure (P)	0.3995	0.0521	0.5860	0.2097
Temperature (T)	0.8136	0.0002	0.0111	0.0001
PxT ^a	0.8143	0.0383	0.4239	0.0104
SxP	--	--	0.8098	0.1329
SxT	--	--	0.4681	0.9614
R-square ^b	0.2592	0.9947	0.8747	0.9742

^a Designates 2-way interaction of variables.

^b Calculated for complete model including interactions.

3. The effect of pressure alone was not significant, although its interaction with temperature at times was.
4. Solids loading was not significant for Otisca slurry, but was marginally significant for Kemmerer.

In the cases of the Beulah and Kemmerer slurries, there were significant temperature-pressure interactions, although none existed with Otisca. Because of the intimate relationship between temperature and pressure on water vapor formation, one might expect an interaction, although the reason Otisca (bituminous) remained unaffected is unclear. This is possibly the result of the solids loading being lower and/or the reactivity being higher for the former slurries. Alternate explanations may involve differences among physical properties such as viscosity, pore structure, and particle size after atomization, or simply too much variability in data to discern effects.

Figures 6 through 9 show graphically the relationship between pressure, temperature, and ignition delay for each of the fuels used in combustion bomb testing. Each figure displays the actual value of ignition delay used to calculate the surfaces as well as a grid consisting of lines of constant pressure and temperature. It should be noted that the scaling of the ignition delay axis is approximately equal for all figures so that relative comparisons can be made. The distortions in the grids, such as with Otisca, show the experimental error of measurement, since one would expect a relatively smooth response surface.

Among the slurries, only small differences in ignition delay are seen under these experimental conditions. However, all tests with Beulah slurry were conducted at only 40% solids, and solids loadings for Kemmerer slurries were again appreciably lower than those used in the Otisca tests.

KEMMERER CWF

Figure 8. Ignition delay as a function of pressure and temperature for Kemmerer CWS.

OTISCA CWF

Figure 9. Ignition delay as a function of pressure and temperature for Otisca CWS.

3.2 Single-Stroke Diesel Simulator

Figure 10 is a schematic drawing of the Cooper-Ajax AE-22 diesel engine used to supply the base engine and flywheel along with the supporting frame for mounting the test cylinder. The diesel simulator system uses a 7.5-horsepower electric motor to bring the system up to speed before injecting a single shot of fuel during a test.

Figure 11 shows the ported two-cycle test cylinder with a bore of 2.375" and an 8" stroke. The test cylinder is lined with standard hydraulic cylinder tubing with a 2.375" ID and 0.25" wall thickness. The cylinder head in this figure has since been modified to a flat-head design to allow for higher compression ratios. The current head has both the fuel injector and the optical access port directed parallel to the axis of the bore.

A major consideration in designing this diesel simulator was the need for a variable compression ratio. Variation of the compression ratio is achieved by varying the length of the rod connecting the original piston and the test cylinder piston, thus changing the proportion of the 8" stroke that is actually doing useful compression of the intake air.

The fuel injection system consists of an American Bosch APF1A fuel pump and two KB95SA pintle type injectors. The dummy fuel injector will be set at a lower injection pressure than the injector in the test cylinder head so that as the engine is coming up to speed, conventional diesel fuel only is being circulated. At the start of the test cycle, a fast-acting, high-pressure solenoid valve closes the fuel line to the dummy injector, thereby forcing the diesel fuel into the small hydraulic accumulator prefilled with the desired test fuel. The ability to feed preheated and compressed air was added to simulate the effects of turbocharging the intake air.

Instrumentation was included in the system to determine piston position and engine speed, pressures in the fuel lines and combustion chamber, and temperatures of the intake and exhaust gases, cylinder wall, piston surface, and combustion chamber.

3.2.1 Results and Discussion

The detailed test plan for the diesel simulator involves testing low-rank coal-derived fuels (i.e., mild gasification liquids, GPGA gasification tars, etc.) and some of the same coal-based slurries used in the combustion bomb studies. In addition to fuel type tests, the effect of variables such as intake air temperature, cylinder wall temperatures, cylinder compression ratio and fuel injection pressure were examined.

Preliminary work was initiated using coal/water slurries as the test fuels. With wall temperatures of 100°F and a compression ratio of approximately 14, little or no combustion occurred as evidenced by pressure traces and detectable noise. It should be noted that No. 2 diesel fuel easily ignites under these conditions. The combination of small clearance volume associated with the test cylinder and the low volatility of this fuel resulted in piston and wall impingement and, consequently, poor combustion. Further testing with slurry fuel was impossible with the current setup and, therefore, testing was terminated.

Figure 10. Detailed schematic of modified diesel engine used as a base engine for UNDEMRC'S single combustion cycle diesel simulator.

Figure 11. Detailed schematic of test fuel combustion chamber on UNDEMRC'S single combustion cycle diesel simulator.

Table 9 shows the test matrix used to evaluate the combustion behavior of GPGP tar oil relative to diesel fuel in the single combustion cycle diesel simulator. When running this matrix, the fuel quantity, engine speed, temperature, and compression ratio were held constant to reduce the number of variables. The measured responses included ignition delay (chamber pressure definition), peak heat release rate and angle, peak chamber pressure and angle, piston temperature, and work (i.e., integral of the PV curve). The matrix is an eight-run full-factorial for three variables, designed to resolve the main effects and their interactions using a linear model.

TABLE 9
SINGLE COMBUSTION CYCLE DIESEL SIMULATOR TEST MATRIX VARIABLES

Variables	(+)	(-)
Engine RPM	200	200
Injection Timing	12 BTDC	6 BTDC
Compression Ratio	17	17
Quantity Fuel Injected	35 mm	35 mm
Injection Pressure	5500 psig	3500 psig
Inlet Air Temperature	22°C	22°C
Wall Temperature	120°C	120°C

The variables and measured responses for the test matrix are presented in Table 10. Piston temperature and dynamic timing were added as variables after the matrix was completed. Dynamic timing is defined in the table as the time elapsed from the start of fuel injection to the top-dead-center (TDC) mark. This variable was later defined because it accurately defines the true start-of-injection point. Dynamic timing was found to correlate closely to static timing and, for the purposes of analysis, these variables are interchangeable. Piston temperature was added as a variable since there were slight run-to-run differences in temperatures that could not be avoided. Most of the values presented in the table are averages of at least three separate tests, with the corresponding standard deviation listed after the mean.

The most obvious effect shown in the Table 10 is the effect of fuel injection pressure on ignition delay. From the data it can be seen that the ignition delay varied directly with injection pressure. This result is contrary to the expected result of shorter ignition delays with higher injection pressures. Two explanations, mechanical overload and/or spray impingement, could yield this result. Under higher pressure the atomizing spray, with more penetrating energy, impinged upon the piston crown. This is somewhat substantiated by the fact that the piston temperature had a significant effect on ignition delay.

TABLE 10
VARIABLES AND MEASURED RESPONSES FOR THE TWO-LEVEL THREE-VARIABLE TEST MATRIX

Variables					Responses					
Fuel	Injection Pressure (psig)	Static Timing (°BIDC)	Dynamic ^a Timing (ms)	Piston Temp. (°C)	Ignition Delay (ms)	Work (Joules)	Peak Pressure (psia)	Peak Pressure Angle (°ATDC)	Peak Heat Release (Joules/°CA)	Peak Heat Angle (°ATDC)
Diesel	3500	12	5.48	136	1.47±0.00 ^b n=3	102±18.3 n=3	1045±60.9 n=3	-2.8±0.29 n=3	93.8±18 n=3	-5.0±0.5 n=3
Diesel	3500	6	0.542	140	1.56±0.18	124±12.8 n=3	1035±8.66 n=4	2.4±0.25 n=4	105±4.1 n=4	1.2±0.29 n=4
Diesel	5500	6	0.105	142	4.80±0.20	153±6.03 n=3	1043±15.5 n=4	6.5±0.00 n=4	174±19 n=4	5.9±0.25 n=4
Diesel	5500	12	5.53	141	4.62±0.00	110±5.69 n=3	1208±11.0 n=4	0.62±0.63 n=4	162±19 n=4	-0.88±0.25 n=4
GGPP Tar	3500	12	5.7	139	2.34±0.45	69.7±0.14 n=2	1036±20.7 n=4	-2.5±0.71 n=4	70.0±11 n=4	-4.0±0.41 n=4
GGPP Tar	3500	6	0.688	140	3.32±0.45	73.9 n=1	944±30.4 n=3	4.3±0.76 n=3	74.8±6.5 n=3	3.3±0.29 n=3
GGPP Tar	5500	6	0.338	129	4.85±0.53	69.3 n=1	1012±24.8 n=3	7.8±0.76 n=3	104±10 n=3	6.7±0.58 n=3
GGPP Tar	5500	12	5.36	129	4.80±0.20	126±4.50 n=3	1233±23.3 n=4	0.88±0.25 n=4	134±20 n=4	-0.25±0.29 n=4

^a Dynamic timing defined as the time from start of injection to when "piston" reaches the TDC timing mark.

^b All values expressed as ±1 standard deviation from the mean of "n" observations.

The complete statistical analysis of the test matrix is presented in Table 11. The values expressed in this table are the probabilities of the effect occurring by chance. Also contained in the table are the R-square values for the linear models used to fit data. The values in the table marked with an asterisk are those values that remained significant after systematic removal of least significant variables. Only the variables that were significant to the 0.10-level remained after this "backward" elimination procedure. In analyzing the data, all interactions were ignored for simplicity. Inclusion of the interactions could potentially produce a better model.

From the data in Table 11, it is interesting to note that injection pressure and fuel type were significant variables in almost every response, and that dynamic and static timing variables were similarly correlated, except for the case of the peak heat release angle. In addition, it should be noted that the responses in the table are not necessarily independent and are, to some extent, measurements of the same parameter; e.g., angles of peak pressure and heat release.

Figure 12 shows a plot of predicted versus measured values for ignition delay. The figure shows a good correlation of the reduced mathematical model with the measured data. Because the resolution of determining ignition delay is 0.35 ms, the data on the graph appears at distinct intervals along the x-axis. The correlation could actually be much stronger (or weaker) if the data points were measured with more resolution.

Figure 12. Measured versus predicted ignition delay values.

TABLE 11
T-TEST-DERIVED CONFIDENCE LEVELS FOR MAIN EFFECTS OF EXPERIMENTAL VARIABLES

Variable	Responses				
	Ignition Delay	Work	Peak Pressure	Peak Pressure Angle	Peak Heat Release Angle
Fuel	* 0.0002	* 0.0926	* 0.1925	* 0.0829	* 0.0241 * 0.0001
Injection Pressure	* 0.0001	* 0.1531	* 0.0001	* 0.0004	* 0.0001 * 0.0001
Static Timing	0.8726	0.6763	0.0296	* 0.7203	0.9825 0.6777
Dynamic Timing	0.8030	0.6187	* 0.0164	0.7758	0.9914 * 0.0555
Piston Temperature	* 0.0361	0.9250	0.2566	0.6695	* 0.1022 * 0.2024
Full Model R ² Value	0.9834	0.5346	0.8103	0.9194	0.8847 0.9941
Reduced Model R ² Value ^a	0.9808	0.5208	0.7805	0.9183	0.8845 0.9940

* Variables that remained in model after "backward" elimination procedure.

^a Reduced model contained variables that were significant to the 0.1000 level.

A comparison of GPGP tar oil and diesel fuel pressure traces is shown in Figure 13 for each of the test conditions. From these traces the effects of timing and injection pressure are readily observed. The preignition TDC pressure is higher for the GPGP tar oil traces in all cases. This effect was due to slight variances in compression ratio and not to a difference in fuels. Although the GPGP tar pressure trace started out at a higher pressure, the overall peak pressure and the descending pressures were lower in general for the GPGP fuel. This is most likely due to the lower heating value of GPGP tar, since all tests were conducted using volumetrically equivalent fuel injections. In one case, at 5500 psig injection pressure and 12° BTDC timing, the overall peak pressure exceeded that of diesel fuel. This is probably due to the fact that the combined effect of ignition delay and injection timing created an optimum condition for peak pressure.

Heat release rates were calculated using the First Law for a simple closed system and neglecting heat losses. This one-zone model assumes that the thermodynamic state (variables) of the combustion chamber is represented by average values between the burning and unburning zones. Because of the simplicity of this heat release model, only qualitative comparisons can be made between different fuels combusted in the same engine. The plots of heat release as a function of crank angle are shown in Figure 14. The slightly longer ignition delays and the characteristic broader peak for GPGP tar oil can be easily recognized. The majority of both fuels were burned in the premixed combustion state as evidenced by the single narrow band of heat release. This is due to the rapid injection of small quantities of fuel and long ignition delays.

3.3 Demonstration Diesel Engine

UNDEMRC has a Cooper-Ajax AE-30 ported 2-cycle diesel engine that was originally designed to fire on natural gas. This particular engine has a 7.25" bore with an 8" stroke and was originally rated at 30 hp. A new head was made to convert the engine to fire liquid fuels and allow both the test fuel and a diesel fuel pilot to be injected into the precombustion chamber. This head also has an opening for a glow plug for starting the engine with diesel fuel and openings for inserting a thermocouple and a pressure transducer for monitoring the combustion chamber temperature and pressure. The fuel injection pressure, the head cooling water, and exhaust gas temperatures can also be monitored during a test.

Two American Bosch (now United Technologies Diesel Systems) APF1B fuel pumps and two KB95SA fuel injectors are used in both the test fuel and pilot diesel fuel feed systems. A cambox is run off the layshaft to provide control of both the fuel injection timing in relation to TDC and between the pilot fuel injection and the test fuel injection.

Figure 13. Chamber pressure versus crank angle for diesel fuel and GPGP tar oil.

Figure 14. Heat release versus crank angle for diesel fuel and GPGP tar oil.

The injection system used for injecting coal liquid fuels is shown in Figure 15. This simple system has been used successfully for testing with both coal slurries and coal-derived liquids. A conventional diesel fuel jerk-pump with its check valve removed supplies the pressure to the free-moving piston. The pressurized slurry feed fills the cylinder and restores the piston to the delivery position. A check valve in the slurry line prevents the slurry from being forced back into the supply vessel. The obvious shortcoming to this design is the check valve, but small leakages hopefully can be tolerated with the fast-acting jerk-pump.

Figure 15. Demonstration diesel high-pressure coal liquid fuel feed system.

3.3.1 Preliminary Testing of 30-hp Ajax Diesel

Openings in the exhaust gas piping allow gas and particulate sampling probes to be inserted for evaluating emissions and determining the combustion efficiency of the test fuel. Table 12 shows the analyses of gaseous emissions while the diesel was operated under no-load and full-load conditions. The decrease in combustion efficiency with increasing load can easily be seen from this data. The relatively high concentration of oxygen is believed to be partly the result of intake air short-circuiting through the exhaust port.

TABLE 12
GC ANALYSIS OF DIESEL GASEOUS EMISSIONS

<u>Component</u>	<u>Concentration, No-Load</u>	<u>Mole % Full-Load</u>
H ₂	0.13	1.28
CO ₂	3.30	5.20
CO	0.32	2.16
CH ₄	0.00	0.72
C ₂ H ₄	0.02	0.28
C ₄	0.00	0.14
O ₂	14.3	9.93
N ₂	81.9	80.3

Particulate sampling was performed using a high-volume sampler located approximately 12" from the exhaust ports. The particulate was captured by a borosilicate glass filter supported by wire mesh. Particulate samples were drawn from the exhaust pipe while burning diesel fuel and while burning a 50/50 blend of Otisca bituminous slurry and diesel fuel. The diesel and slurry were injected through separate injectors and combined within the precombustion chamber. Table 13 presents the ultimate and heating value analyses for these two samples.

TABLE 13
ULTIMATE AND HEATING VALUE ANALYSES FOR PARTICULATE SAMPLES

<u>Ultimate Analysis, wt%</u>	<u>Diesel Fuel</u>	<u>Diesel/Slurry</u>
Hydrogen	1.15	2.54
Carbon	91.79	90.27
Nitrogen	0.31	1.23
Sulfur	0.12	0.50
Oxygen (by diff)	4.69	3.86
Ash	1.94	1.60
Heating Value, Btu/lb HHV	14413	14585

Particle size distributions were determined for the exhaust particulate samples analyzed in Table 13. When running the analyses on a Malvern flow-cell particle sizer, the distributions slowly shifted from a bimodal distribution to the smaller distributions shown in Figure 16, suggesting that the captured particulates were agglomerates of smaller particles. The equilibrium distributions shown are those obtained from the flow-cell when stirred and sonicated simultaneously. The mean particle size diameters for the diesel fuel and diesel/slurry tests were 27.3 and 22.1 microns, respectively. The slight difference between these values is probably within experimental error.

Figure 16. Particle size distributions for diesel exhaust emissions.

3.3.2 Diesel Testing of GPGP Tar Oil

The GPGP coal tars were pumped to the fuel injection system at 300 psig via a Moyno pump. An isolation piston pump was operated from the action of the standard diesel jerk pump to inject fuel through the multi-hole nozzle. A system of valves was installed to facilitate switching between diesel fuel and GPGP tars while the engine was running and using a single injector. This allowed the engine to be preheated and tested on diesel fuel, followed by a smooth transition to GPGP tars.

The effect of fuel-type, injection pressure, and injection timing were determined by monitoring performance characteristics and exhaust emissions at various loads. A typical test would consist of bringing the engine up to full load at 600 rpm, at which point the power output would be measured and used to calculate the power output at the partial loads of 10%, 25%, 50%, 75%, and 90% used for test conditions. At each test condition, the engine was allowed to equilibrate before recording engine temperatures, air and cooling water flow

rates, torque, rpm, fuel consumption, and exhaust emissions. Table 14 shows the experimental test matrix used to compare diesel fuel and GPGP tar oil. Prior to designing this test matrix both diesel fuel and GPGP tar oil were run through the engine to determine the optimum engine timing with respect to power output. These values were then used as the center points of the matrix.

TABLE 14
EXPERIMENTAL TEST MATRIX USED TO COMPARE DIESEL NO. 2 AND GPGP TAR OIL

<u>Fuel Type</u>	<u>Injection Pressure (psig)</u>	<u>Injection Timing (BTDC)</u>
Diesel	2000	22
Diesel	2000	14
Diesel	4000	22
Diesel	4000	14
GPGP	2000	26
GPGP	2000	18
GPGP	4000	26
GPGP	4000	18
<u>Center Points</u>		
Diesel	3000	18
GPGP	3000	22

The results from the regression analysis of the factorial test matrix showed that injection timing, injection pressure, load, and fuel type had significant effects on engine power output. Decreased injection pressure and advanced timing relative to the respective center points of the two fuels produced more power. Diesel fuel produced more power than GPGP tars due to the lower energy density of the tars. It was also found that timing and load had a significant effect on the brake-specific fuel consumption (BSFC). The more advanced timing showed better fuel economy.

Figure 17 presents the performance characteristics of the Ajax 30-hp diesel firing GPGP tar oil and diesel No. 2. These tests represent the center points for the respective fuels as defined in Table 14. The performance curves for the two fuels are nearly identical with the exception of power output. The difference in power output is directly proportional to the difference in energy density of the two fuels as seen in Table 3. Since the fuel was delivered on a constant-volume basis and the fuel pump was run to its maximum output, fewer Btus could be delivered per stroke. The overall performance of the engine was poor when compared to modern multi-cylinder 4-cycle diesel engines, which can have thermal efficiencies of 40%.

Figure 17. Diesel engine performance data firing diesel fuel and GPGP coal tars under center point conditions.

Gaseous emissions were measured at two positions: immediately after the exhaust port, and approximately 7 feet downstream at the muffler. Figure 18 presents gas emission data for the corresponding center point tests shown in Figure 17, and also the exhaust port temperature where the gases were sampled. The diesel fuel gas emissions were sampled only at the port. It was found later that combustion was occurring in the exhaust pipe downstream of the port at high loads, and therefore provisions were made for gas sampling near the muffler. The exhaust port temperature was found to vary with load as expected. At high loads, it was found that the exhaust pipe temperature exceeded the port temperature, indicating further combustion downstream.

The SO_x emissions at the exhaust port for the two fuels were low, near the detection limit, showing that the formation of these compounds occurred further downstream as indicated by the readings recorded near the muffler. The concentration of SO_x also increased with relation to load (or fuel input) as would be expected since GPGP tar oil contains 0.39% sulfur.

On the other hand, NO_x emissions from GPGP tar oil showed a nearly constant level of formation that was dependent only on the location at which the emissions were measured. The reason for this is unclear. The formation of thermal NO_x may be suppressed under fuel-rich conditions. The diesel fuel NO_x emissions were considerably lower and are probably indicative of thermal NO_x production.

The CO emissions for both diesel fuel and GPGP tar oil show nearly the same trends. The emissions remain low until about the 75% load condition. This appears to be the transition point where normal combustion can not be completed in the cylinder, and continues into the exhaust pipe. This problem is probably related to poor fuel-air mixing in the combustion chamber and the short-circuiting tendencies of a ported 2-cycle engine.

Although ignition delay was not explicitly measured during the diesel engine testing, it is interesting to note that the difference in injection timing between Diesel No. 2 and GPGP tar oil at optimal conditions was approximately 4 degrees. At 600 rpm, this difference translates into 1.1 ms in ignition delay. Diesel simulator data showed the ignition delay to be 1.56 ms for diesel fuel at an injection pressure of 3500 psig when injected at 6 degrees BTDC at 200 rpm. Comparable run data for GPGP tar oil (12 degrees BTDC) showed an ignition delay of 2.34 ms. The difference in the delay between the two fuels under simulation conditions was 0.78 ms, showing the similarity of this data with actual engine performance. In addition, combustion bomb data displays the same trend with an ignition delay of 1.12 ms for diesel fuel and 2.6 ms for GPGP tar oil at 750 psia and 1700°F (5).

3.3.3 Engine Modifications and Preliminary Slurry Testing

The Ajax 30-hp diesel engine has evolved during the past year through numerous modifications. Originally, the engine was of a prechamber design, producing only 5-8 hp, or 27% of the rated brake output power. Later, the prechamber was enlarged and the cylinder head was contoured to the piston to reduce volume. This effort resulted in a net power output of 16 hp, or 53% of the rated output. The preliminary testing of the engine reported in Section 3.3.1 was performed under the prechamber operating conditions (5-16 hp). The

Figure 18. Exhaust port temperatures and gaseous emissions for diesel engine tests firing diesel fuel and GPGP tars under center point conditions.

engine was then further modified to a direct-injection design using multi-hole injection nozzles to align our program with the mainstream research effort. In this configuration the engine produced 20 hp, and was used to perform the tests using GPGP coal tars.

Presently, the engine is producing 25 hp, or 83% of the rated power output, with the head and piston design shown in Figure 19. This design is approaching the practical limit for further improvement in power. The torroidal cup was added to the piston to allow extra clearance for injection and enhance turbulence. The central core of the head containing the injectors is removable to facilitate using other injection systems or configurations as required in future testing.

Figure 19. Cross-sectional view of the piston and head for the Ajax 30-hp diesel engine.

Using this final configuration, slurry was successfully burned when using a diesel pilot fuel. When running this test, Beulah lignite slurry at 49% solids loading was injected while using a minimal amount of diesel fuel. The extra power output from the slurry was absorbed using the dynamometer, producing about 8 hp at 600 rpm. The maximum power output was governed by the size of the fuel pump, since it was sized for diesel fuel. About one-third of the maximum power output should be expected under this configuration due to the lower energy density of the slurry.

Approximately one hour of slurry testing in three separate runs was performed using a single multi-hole nozzle. Figures 20 and 21 show scanning electron microscope (SEM) pictures of a new nozzle and one used for an hour of testing, respectively. The diameter of the measured hole increased from 0.378 mm to 0.448 mm in this short period. This translates into a 40% increase in the cross-sectional area for fluid flow.

An automated engine analyzer consisting of a data acquisition system, gas analyzers, and temperature, engine speed, air and water flow rate, and torque monitors was constructed and tested and is currently available for future testing. In addition, a high-speed data acquisition system is being assembled to collect and average engine pressure-cycle data.

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Figure 20. Photograph of New Bosch multi-hole diesel injector.

Figure 21. Photograph of Bosch multi-hole diesel injector after one hour of fuel injection of Beulah CWS.

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4. Name and Address University of North Dakota Energy & Mineral Research Center Box 8213, University Station, Grand Forks, ND 58202		5. Program/Project Start Date 4-01-86
		6. Completion Date 3-31-92

11. Major Milestone Status	Units Planned	
	Units Complete	
A. Technology & Market Assessment	P	
	C	Work has been completed in Year 1.
	P	
	C	
B. Reactivity of Fuel	P	▼3,4
	C	
	P	
	C	
C. Diesel Engine Simulation	P	3,4 ▼ ▼5,6
	C	
	P	
	C	
D. Diesel Demonstration	P	4 ▼ ▼5
	C	
	P	
	C	
E. Optimization of LRC Engines	P	▼1,2
	C	
	P	
	C	
	P	
	C	
	P	
	C	
	P	
	C	
	P	
	C	
	P	
	C	

12. Remarks	
13. Signature of Recipient and Date	14. Signature of DOE Reviewing Representative and Date

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	Units Complete	
A. Technology & Market Assessment	P	
	C	Work has been completed in Year 1.
	P	
	C	
B. Reactivity of Fuel	P	
	C	
	P	
	C	
C. Diesel Engine Simulation	P	
	C	
	P	
	C	
D. Diesel Demonstration	P	
	C	
	P	
	C	
E. Optimization of LRC Engines	P	
	C	
	P	
	C	
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		6. Completion Date 3-31-92

Milestone ID. No.	Description	Planned Completion Date	Actual Completion Date	Comments
Task B	Reactivity of Fuel:			
b.1	Reactivity tests of coal-derived liquid fuels in combustion bombs.	10/87		
b.2	Reactivity tests of LRC slurries in combustion bomb.	02/89	05/89	
b.3	Correlate results from reactivity tests to single-stroke diesel simulator performance.	03/89		
b.4	Correlate results from reactivity tests to fuel properties.	03/89	*	*Unable to complete due to inability to combust CWF in diesel simulator.
Task C	Diesel Engine Simulator:			
c.1	Screening tests on baseline coal-derived liquid fuel using fractional factorial test plan.	07/88		
c.2	Screening tests on baseline LRC slurry fuel using fractional factorial test plan.	01/89	*	*Unsuccessful combustion of CWF due to spray impingement problems.
c.3	Test remaining liquid on single-stroke diesel simulator to investigate important parameters.	10/31/88	02/89	
c.4	Test LRC slurries on single-stroke diesel simulator to investigate important parameters.	04/89	*02/89	*Unsuccessful combustion of LRC in simulator.
c.5	Correlate single-stroke diesel simulator data with 30-hp diesel engine performance.	03/15/89	*03/89	*For coal-derived liquid fuel only.
c.6	Correlate single-stroke diesel simulator data with fuel properties.	03/31/89		

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Page ____ of ____

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		6. Completion Date 3-31-92

Milestone ID. No.	Description	Planned Completion Date	Actual Completion Date	Comments
Task D	Diesel Demonstration:			
d.1	Construction of 30-hp diesel engine.	04/30/88	06/88	
d.2	Baseline diesel fuel testing with 30-hp diesel.	11/88	12/89	
d.3	Testing with selected coal-derived liquid fuels.	01/89	03/89	
d.4	Testing with selected micronized, cleaned LRC slurries.	03/89	06/89	
d.5	Long-term DEC test with 30-hp engine.	02/28/89	*	*Unable to complete due to nozzle life & poor engine performance.
Task E	Optimization of LRC Engines:			
e.1	Determine impact of coal-derived fuels and design changes needed to optimize a diesel engine.	05/89	07/89	
e.2	Prepare conceptual design of components for optimized diesel engine.	05/89		

5.0 LIQUEFACTION RESEARCH

5.1 Low-Rank Coal Direct Liquefaction

DIRECT LIQUEFACTION OF LOW-RANK COALS

Annual Technical Report for the Period April 1, 1988 - June 30, 1989
including the
Quarterly Technical Progress Report for the Period April through June 1989

by

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TABLE OF CONTENTS

	<u>Page</u>
LIST OF TABLES.....	iii
LIST OF FIGURES.....	v
EXECUTIVE SUMMARY.....	1
1.0 INTRODUCTION.....	3
2.0 GOALS AND OBJECTIVES.....	3
2.1 Proposed Work for the Third Year (4/88-3/89).....	3
2.1.1 Task A - ChemCoal Process Verification.....	3
2.1.2 Task B - Utilization Testing.....	4
2.1.3 Task C - ChemCoal Economics Update.....	4
2.1.4 Task D - LRC Agglomeration.....	4
2.1.5 Tasks E and F - Determination of Co-Processing Yield Structures.....	4
2.1.6 Task G - Comparison of LRC-Derived Solvent and Co-Processing Tests.....	5
2.1.7 Task H - CPU Analytical Support.....	5
2.1.8 Task I - Hydrogen Transfer in the ChemCoal Process.....	5
2.2 Change of Scope.....	5
3.0 ACCOMPLISHMENTS.....	6
3.1 Results of Task A - ChemCoal Process Verification.....	6
3.1.1 Chemical Properties.....	6
3.1.1.1 Solubility and Elemental Analyses.....	6
3.1.1.2 NMR Analyses.....	7
3.1.1.3 Thermogravimetric Analysis.....	7
3.1.1.4 Molecular Weight Determination.....	7
3.1.1.5 Derivatization.....	10
3.1.2 Testing Performed on the CPU.....	15
3.1.2.1 Shakedown Runs.....	17
3.1.2.2 ChemCoal Production Runs.....	19
3.1.3 Results of the ChemCoal Production Runs.....	21
3.1.3.1 Analyses of Product Samples.....	21
3.1.3.2 Development of an Interactive Flowsheet for the Application of the ChemCoal Process to Wyodak Subbituminous Coal.....	26
3.1.3.3 Discussion of the Results of the Statistical Analysis.....	38
3.1.3.4 Effects of the Independent Variables on the System.....	40
3.1.3.5 Validity of the Model.....	51
3.1.3.6 Runs Using Pittsburgh No. 8 Bituminous Coal...	51
3.1.3.7 Indian Head Recycle Verification Run.....	51
3.1.4 ChemCoal Precipitation Tests.....	51

TABLE OF CONTENTS (CONT.)

	<u>Page</u>
3.2 Results of Task B - Utilization Testing.....	53
3.2.1 As a Diesel Fuel Extender.....	53
3.2.2 As a Fuel for Gas-Fired Turbines.....	55
3.3 Results of Task C - ChemCoal Economics.....	55
3.4 Results of Task D - LRC Agglomeration.....	61
3.5 Results of Tasks E and F - CPU Co-Processing Tests.....	65
3.6 Results of Task G - Comparison of LRC-Derived Solvent and Co-Processing Tests.....	65
3.7 Results of Task H - CPU Support.....	65
3.8 Results of Task I - Hydrogen Transfer in the ChemCoal Process.....	66
3.8.1 Hydrogenation Tests.....	66
3.8.2 Analytical Scheme.....	68
3.8.3 Analytical Results.....	68
3.9 Results of Task K - Low-Severity Direct Liquefaction.....	81
3.10 Papers/Presentations Made Based upon the Year Three Work.....	84
3.11 Conclusions.....	84
4.0 FUTURE OBJECTIVES.....	86
5.0 ACKNOWLEDGMENTS.....	86
6.0 REFERENCES.....	86
APPENDIX--RESULTS OF STATISTICAL ANALYSES.....	A-1

LIST OF TABLES

<u>Table</u>	<u>Page</u>
1 Results of Solubility and Elemental Analyses of ChemCoal Process Solid Products.....	6
2 C-13 NMR Data for ChemCoal Solid Product and Its Fractions.....	8
3 TGA Proximate Data for ChemCoal Process Solid Product Factions...	9
4 Solubility Data for ChemCoal Process Solid Product Derivatives...	11
5 Summary of ChemCoal CPU Shakedown Runs.....	15
6 Box-Behnken Statistical Experimental Design for Three Factors....	20
7 Independent Variables and Their Ranges Included in the Wyodak ChemCoal Experimental Matrix.....	20
8 Run Conditions of Abbreviated Matrix for Pittsburgh No. 8 Bituminous Coal.....	21
9 Methanol and THF Solubilities of Product Slurries.....	22
10 Peak Data from HPLC Molecular Weight Studies.....	26
11 Summary of Data Collected During Runs C152-C153.....	28
12 C152 and C153 Data Entered into the SAS Program.....	34
13 Definitions of Z Functions Used.....	36
14 Response Variables for the Wyodak ChemCoal Experimental Matrix...	36
15 Intercepts and Coefficients of the Model Equations.....	37
16 Center Point Conditions for Independent Variables.....	40
17 Results of ChemCoal Process Solid Product Admixture Tests.....	52
18 Relationship between Acid Concentration and Final Ash Content for Run N-403.....	54
19 Results of Agglomeration Experiments Performed in a Ball Mill....	62
20 Results of TGA Proximate Analysis of Agglomerates of 50 wt% Indian Head and 50 wt% GPGP Phenols.....	64
21 ChemCoal Solids Hydrogenation Tests.....	66

LIST OF TABLES (CONT.)

<u>Table</u>		<u>Page</u>
22	Catalyst Screening during ChemCoal Solid Hydrogenation Testing...	67
23	Summary of ChemCoal Solid Hydrotreatment.....	69
24	Analysis Scheme for Hydrogenated ChemCoal Solids Samples.....	70
25	Results of Elemental Analysis of Distillate and Bottoms Fractions of Hydrogenated ChemCoal Solids.....	71
26	Hydrogenated ChemCoal Filtrate ASTM D86 Distillation Data.....	71
27	Results of TGA of Hydrogenated ChemCoal Filter Cake and Distillation Bottoms.....	72
28	Solubility of ChemCoal Solid in Various Solvents.....	73
29	Results of Analysis of Fractionated Product Slurry.....	73
30	Summary of the Batch Staged Liquefaction Tests Performed During June.....	82
31	Analytical Results of N-441 and N-442.....	83

LIST OF FIGURES

<u>Figure</u>		<u>Page</u>
1	Molecular weight distribution of the THF-, base-, and MeCl ₂ -soluble fractions of ChemCoal Process solid product.....	10
2	Solid C-13 NMR spectra of (a) ChemCoal Process solid product and (b) acetylated ChemCoal Process solid product.....	11
3	Solid C-13 NMR spectra of THF-soluble fraction of (a) ChemCoal Process solid product and (b) alkylated ChemCoal Process solid product.....	12
4	Solid C-13 NMR spectra of (a) ChemCoal Process solid product and (b) addition spectra of THF-soluble and insoluble fractions of solid product methylated with dimethyl sulfate.....	13
5	Solid C-13 NMR spectrum of (a) ChemCoal Process solid product and (b) addition spectrum of THF-soluble and insoluble spectra of ChemCoal Process solid product methylated with diazomethane..	13
6	[Top] NMR spectra of (a) ChemCoal Process solid product and (b) solid product photolyzed at 254 nm. [Bottom] NMR spectra of (a) ChemCoal Process solid product and (b) solid product photolyzed at 350 nm.....	14
7	Typical proton NMR spectrum of the methanol-soluble fraction of ChemCoal product made during Runs C152 and C153. (Sample C153-9).....	23
8	Molecular weight distribution obtained for Sample C152-1 prior to evaporation.....	24
9	Molecular weight distribution obtained for Sample C152-1 after evaporation.....	25
10	Molecular weight distribution obtained for Sample C153-11.....	25
11	Effect of temperature on conversion and yield of coal-derived liquids.....	41
12	Effect of temperature on hydrocarbon gas yield.....	41
13	Effect of temperature on hydrogen utilization.....	42
14	Effect of temperature on carbon monoxide utilization.....	42
15	Effect of pressure on conversion and yield of coal-derived liquids.....	43

LIST OF FIGURES (CONT.)

<u>Figure</u>		<u>Page</u>
16	Effect of pressure on hydrocarbon gas yield.....	44
17	Effect of pressure on hydrogen utilization.....	44
18	Effect of pressure on carbon monoxide utilization.....	45
19	Effect of MAF coal loading rate on conversion and yield of coal-derived liquids.....	46
20	Effect of MAF coal loading rate on hydrocarbon gas yield.....	46
21	Effect of MAF coal loading rate on hydrogen utilization.....	47
22	Effect of MAF coal loading rate on carbon monoxide utilization..	47
23	Effect of gas flow rate on hydrogen utilization.....	48
24	Effect of caustic loading on conversion and yield of coal-derived liquids.....	49
25	Effect of caustic loading on shift gases.....	49
26	Effect of caustic loading on hydrogen utilization.....	50
27	Effect of caustic loading on carbon monoxide utilization.....	50
28	Comparison of admix procedures for methanol-only case.....	54
29	Interactive flowsheet for the ChemCoal Process at 80% conversion.....	56
30	Interactive flowsheet for the ChemCoal Process at 85% conversion and 3-hour residence time.....	57
31	Interactive flowsheet for the ChemCoal Process at 85% conversion and 0.6-hour residence time.....	58
32	Interactive flowsheet for the ChemCoal Process at 85% conversion and 9% caustic loading.....	59
33	Agglomerates formed from Indian Head lignite, Triton X-100, and GPGP crude phenol.....	63
34	Moisture and ash contents (on a moisture- and oil-free basis) as a function of air drying time for agglomerates of a mixture of 50 wt% Indian Head and 50 wt% GPGP phenols with Triton X-100 added as 3 wt% of the coal present.....	65

LIST OF FIGURES (CONT.)

<u>Figure</u>	<u>Page</u>
35 Molecular weight profiles of the hexane-, methylene chloride-, and THF-soluble fractions of the distillation bottoms of hydrogenated ChemCoal solids.....	75
36 Molecular weight profiles of hydrogenated ChemCoal solids distillation bottoms and filtrate.....	76
37 Proton NMR spectrum of hydrogenated ChemCoal solids distillate..	77
38 Proton NMR spectrum of hydrogenated ChemCoal solids distillation bottoms.....	78
39 Proton NMR spectra of the short-column fractions of hydrogenated ChemCoal solids distillation bottoms.....	79
40 Proton NMR spectra of [Top] THF-soluble fraction of ChemCoal solids and [Bottom] hydrotreated ChemCoal solids aromatic material.....	80

DIRECT LIQUEFACTION OF LOW-RANK COALS

EXECUTIVE SUMMARY

The primary objective of the Direct Liquefaction project at the Energy and Mineral Research Center (EMRC) is to expand the scientific and engineering data base of liquefaction of low-rank coals (LRCs) by investigating direct liquefaction processes that will produce the most competitive feedstocks or liquid fuels. During the 1988-89 program year (4/88-6/89), work was performed in four areas: the ChemCoal Process, LRC agglomeration, co-processing, and staged direct liquefaction of LRCs.

Extensive analytical work was performed to determine the chemical properties of the ChemCoal Process solid product. The analyses were performed on ChemCoal solids prepared from Indian Head lignite. To better study the solids, they were separated into base-, tetrahydrofuran (THF)-, and methylene chloride-soluble and insoluble fractions and each fraction was analyzed. Elemental analysis, nuclear magnetic resonance (NMR) spectroscopy, thermogravimetric analysis (TGA), and gel permeation chromatography (GPC) were performed on the resulting fractions. The ChemCoal solid product was subsequently derivatized by acetylation, alkylation, and methylation and the derivatives were analyzed. Photolysis was also examined as a method of determining if the ChemCoal solids could be hydrogenated.

Twenty-two runs were performed on the continuous process unit (CPU) during the program year. Some of the runs were performed as shakedown and/or operator-training runs, while others were performed to produce ChemCoal either for analysis or end-use studies. During these runs, it was found that the changes that had been made in the reactor, downstream processing, and control panel areas improved system operability, reliability, and safety. Mass balances of $\pm 2\%$ were easily obtained with the redesigned CPU.

Two runs were performed to produce ChemCoal solids from Wyodak subbituminous coal and to obtain data that could be used to mathematically model the system. Run pass conditions were set as per a statistical experimental matrix, and the engineering data gathered were entered into a pc-based SAS program. The resulting mathematical equations were combined with the mass- and material-balanced flowsheet to produce an interactive flowsheet that can be used to predict conversion and product yield structures as a function of temperature, pressure, residence time, gas flow rate, and caustic loading. Temperature, pressure, and caustic loading were found to significantly affect the conversion and product slate. Surprisingly, it was found that residence time had very little effect on conversion or product slate. Although the flowsheet can be used as a tool to understand reaction mechanisms and to predict the run conditions necessary to obtain a given product slate and conversion, its real value will be as the cornerstone of an upcoming engineering economics evaluation of the ChemCoal Process. Two sets of ChemCoal operating conditions were recommended from an engineering economics point of view: 1) temperature of 350°C, pressure of 1750 psi, residence time of 3 hours, gas flow rate of 12 scfh, and caustic loading of 8 wt% of the moisture- and ash-free (MAF) coal loading; and 2) temperature of 350°C, pressure of 2000 psi, residence time of 0.6 hours, gas flow rate of

12 scfh, and caustic loading of 8 wt% of the MAF coal loading. Both sets of conditions result in an approximately 85% conversion; selection of one would be made based upon the capital costs of the pressure and the residence time.

The results of the original Indian Head lignite recycle run were successfully verified. A conversion of approximately 75% was achieved. Product gas made up 1.5%, coal-derived distillate comprised 30%, and solid ChemCoal product made up 43.5% of the exit stream. Hydrogen consumption was low, and sodium recovery during the run was 85%-88%. Due to the new reactor configuration, the residence time was reduced by a factor of 8 over the residence time of the original recycle run.

During studies of the precipitation of the ChemCoal solid from the product slurry, it was found that it is easier to recover the ash/sodium if the methanol partitioning solvent has been acidified.

ChemCoal solids were produced for possible end-use testing as a diesel fuel extender. The testing met with many delays, primarily due to contractual difficulties with the testing subcontractor, Southwest Research Institute (SwRI). It is anticipated that it will take place at some point during the 1989-90 program year.

Indian Head lignite was successfully agglomerated in the crude phenol stream of the Great Plains Gasification Plant by the addition of Triton X-100 surfactant. An addition of 3 wt% Triton X-100 appears to be the most effective.

Co-processing studies had been scheduled to take place on the CPU. Due to facilities repair and improvement in the control panel area, the CPU was not available for use during part of the year and the CPU co-processing runs were not performed. These studies are important to the co-processing data base, and the runs will be rescheduled for performance during the 1989-90 program year.

Studies of the hydrotreatment of ChemCoal solids were performed to determine hydrogen transfer mechanisms and to determine if the ChemCoal Process could produce a product suitable for the liquid fuels market. The fact that the hydrogenation required a catalyst that is used in other catalytic upgrading processes indicates that the transfer of hydrogen to the ChemCoal solid occurs by a reaction mechanism that is at least similar to that of other upgrading processes. The ChemCoal solids were successfully upgraded to a product with three distinct distillate regions: a gasoline fraction, a recycle phenolic fraction, and a heavy oil bottoms fraction.

Further investigations of staged liquefaction were performed on a batch scale using CO as the first-stage reductant and H₂S as a reaction promoter. Indian Head Lignite and a phenolic solvent served as the feedstocks for the first-stage tests. Two second-stage tests were performed using hydrogen as the reductant and products of two of the first-stage tests as feedstock. Analytical results were not available for all of the tests, but preliminary results indicate that the addition of H₂S results in higher conversions and a more homogeneous product.

1.0 INTRODUCTION

Co-processing of low-rank coals (LRCs) with petroleum residual under mild conditions may produce a product that extends petroleum refinery feeds with a partially coal-derived material. These co-processing products may also provide a lower-cost way to introduce coal-derived materials into the commercial market. In this staged process, the petroleum residual acts as a solvent, aiding in the solubilization of the coal during the first stage, and both the dissolved coals and the residual are upgraded during a second-stage catalytic hydrogenation.

Another method of upgrading coal in a liquefaction process is the ChemCoal Process. The process uses chemical methods to transform coal into clean solid and liquid products. It features low-severity conversion of coal in a phenolic solvent, using an alkali promoter and carbon monoxide as the reductant.

Oil agglomeration has been used to reduce the ash and mineral matter in bituminous coals to obtain a product with increased heating value, reduced moisture, and lower sulfur content. This method can be used to produce a clean coal feedstock for LRC liquefaction. During agglomeration, an oil is used to preferentially wet the organic phases of the coal, and water is used to wet the minerals, resulting in a separation of ash and water from the coal.

2.0 GOALS AND OBJECTIVES

The primary objective of this project is to expand the scientific and engineering data base of LRC liquefaction by investigating direct liquefaction processes that will produce the most competitive feedstocks or liquid fuels. Work scheduled for the 1988-1989 program year (4/88-3/89) dealt with the ChemCoal Process, LRC agglomeration, and co-processing of LRCs with petroleum resid.

2.1 Proposed Work for the Third Year (4/88-3/89)

2.1.1 Task A - ChemCoal Process Verification

This task included further verification of the ChemCoal Process using higher-rank coals. The testing was scheduled for the Energy and Mineral Research Center (EMRC) Continuous Process Unit (CPU) and included:

1. The performance of a statistically based parametric study to determine solvation step sensitivity as a function of various system parameters including pressure, residence time, catalyst loading, and reducing gas composition. This study was aimed at determining the optimum operating conditions for a select Powder River subbituminous coal, as well as the effect of solvation step variability on the downstream processing loop.
2. The performance of a similar matrix on a select midwestern bituminous coal. This test series was scheduled to verify the early processing testing, which suggested that bituminous coals produced yields of ChemCoal solids that were at least as good as those

produced by LRCs when processed in the sodium/phenol system. Based on this earlier work by Carbon Resources, Inc. (CRI), it was expected that the change in feed coals would result in a significantly different yield structure during the solvation step. Since improvements in downstream processing had not been tested with any higher-rank coals, operation of the solvent recovery system/downstream processing loop required verification. The secondary matrix was aimed at producing the largest variation in feed to the downstream processing loop to develop enough information to evaluate the success of the ChemCoal Process on higher-rank coals.

2.1.2 Task B - Utilization Testing

This task was directed at producing samples of both liquid and slurry ChemCoal product for testing as diesel fuel extenders and in gas turbines. Testing of the product was to be performed by laboratories known for their reputation in diesel or gas turbine testing, as appropriate.

2.1.3 Task C - ChemCoal Economics Update

The performance of an economics update for the ChemCoal Process is a key element in its further development. To be effective, this evaluation should be performed by a reputable, nationally known engineering firm. An evaluation by such a firm will provide the necessary credibility to generate the private-sector funding needed to commercialize the process. Gathering the process information required for the performance of the update was the objective of this task.

2.1.4 Task D - LRC Agglomeration

Testing continued to determine how to produce an easily handled, dry, low-ash LRC product using oil agglomeration techniques. Various solvents were tested to improve upon previously attained ash and moisture content reduction of LRCs. The use of additives to neutralize the oleophobic properties of the surface functional groups on coal was to be investigated.

2.1.5 Tasks E and F - Determination of Co-Processing Yield Structures

The goal of this task was to determine the variability of the product slate during LRC/resid co-processing. The results of batch testing performed during the 1987-88 program year were to be used to define the ranges for the parametric variables (temperature, pressure, reducing gas composition, residence time, relative concentrations of coal/solvent, and catalyst systems). It was planned that the independent variables would be evaluated on the CPU as part of a statistically designed test matrix. The data obtained during the CPU runs were to be statistically analyzed to formulate mathematical models for predicting yield structures. Key variables that emerged in the models were to be used to select run samples for detailed chemical analyses.

A particular co-processing yield structure was to be selected and a long-term CPU run made at the corresponding conditions determined by the mathematical model. The test was to be performed to determine the effects of long-term operation on the catalyst system and to validate the predictive model.

2.1.6 Task 6 - Comparison of LRC-Derived Solvent and Co-Processing Tests

Results of the experimental matrix of Task G were to be compared to equivalent test points obtained using an LRC-derived solvent produced during earlier activities. In essence, this task added an additional variable to the experimental matrix of Task E.

2.1.7 Task H - CPU Analytical Support

Samples produced during CPU co-processing operations were to be analyzed to determine yields of distillate, solubles, and solids. The chemical nature of these fractions was to be determined and compared to material produced previously.

2.1.8 Task I - Hydrogen Transfer in the ChemCoal Process

To determine hydrogen transfer mechanisms that occur during the ChemCoal Process, coal was to be reacted with and without deuterated solvent and water in microreactor tests. Yields were to be determined and the product reactions analyzed to determine changes in the chemical composition as well as locations of hydrogen transfer between the reactants and the coal.

2.2 Change of Scope

The CPU co-processing runs from Tasks E, F, and G were not performed due to scheduling difficulties that followed facilities repair. These are important tests with respect to the co-processing data base; therefore, they will be performed when they can be scheduled during the Year 4 work effort.

A transition quarter was added to Year 3 as part of the change of the Cooperative Agreement program year to a start date of July 1. The work scheduled for the transition quarter (4/89-6/89) dealt with staged direct liquefaction of LRCs. This work was incorporated into the Year 3 Program Plan as Task K, Low-Severity Direct Liquefaction. Testing took place in a time-sampled batch autoclave system, where the first stage was a low-severity stage and the second stage was performed at higher-severity conditions. Phenolic solvent, H_2S , and HA061 were investigated as additives. Solid, liquid, and gas samples were collected and analyzed to determine their chemical characteristics and the product yield structure. The batch testing was to be followed by a CPU run to confirm the batch data and to obtain information on process performance. Due to the fact that the analytical data were incomplete at the end of the transition quarter, the CPU run was postponed until Year 4.

Other analytical work scheduled during the transition quarter involved the characterization of various fractions of the ChemCoal Process and co-processing product slates to enable their comparison to the products of conventional direct liquefaction processes.

3.0 ACCOMPLISHMENTS

3.1 Results of Task A - ChemCoal Process Verification

3.1.1 Chemical Properties

Extensive analytical work was performed during the July through September quarter to determine the chemical properties of ChemCoal Process solid product. Details of this work were presented in the July through September Quarterly Technical Progress Report (1). A condensed version of the results is presented in the following subsections.

The analyses were performed on ChemCoal solids prepared previously from Indian Head lignite. To better study the solids, they were separated into base-, tetrahydrofuran (THF)-, and methylene chloride-soluble and insoluble fractions and each fraction was analyzed. Elemental analysis, nuclear magnetic resonance (NMR) spectroscopy, thermogravimetric (TGA) analysis, and gel permeation chromatography (GPC) were performed on the resulting fractions. The ChemCoal solid product was subsequently derivatized by acetylation, alkylation, and methylation and the derivatives were analyzed. Photolysis was also examined as a method of determining if the ChemCoal solids could be hydrogenated.

3.1.1.1 Solubility and Elemental Analyses

Solubility data and results of elemental analyses are presented in Table 1. As the table shows, the ChemCoal solid product was the most soluble in THF and the least soluble in methylene chloride (MeCl_2). The fact that

TABLE 1
RESULTS OF SOLUBILITY AND ELEMENTAL ANALYSES OF
CHEMCOAL PROCESS SOLID PRODUCTS

Fraction	Solubility (wt%)	C	H	N	S	O+Ash ^a
ChemCoal Process Solid Product		80.66	6.31	0.97	0.19	11.87
Base-Soluble	36.8	78.61	7.02	0.93	0.31	13.13
Base-Insoluble	62.7	75.99	5.24	0.94	0.13	17.70
Mass Balance %	99.5					
MeCl_2 -Soluble	18.9	85.51	13.38	0.00	0.24	0.87
MeCl_2 -Insoluble	76.0	79.59	5.27	1.02	0.23	13.89
Mass Balance %	94.9					
THF-Soluble	60.8	81.47	7.15	0.85	0.20	10.33
THF-Insoluble	38.9	75.87	5.01	1.08	0.31	14.73
Mass Balance %	99.7					

^a Determined by difference.

38.9 wt% of the original ChemCoal Process solid products were insoluble in THF indicates that they are heavier than preasphaltenes and that the phenolic solvent used during the processing cut deep into the coal to extract very heavy material. The table also shows that, as solubility increased, the hydrogen content of the insolubles decreased. The insoluble fractions were all higher in oxygen and, to a certain extent, nitrogen content than the soluble fractions.

3.1.1.2 NMR Analyses

The results of the solid-state C-13 NMR analyses of the soluble and insoluble fractions are given in Table 2. The insoluble fractions consistently contained more carboxyl, phenolic, and methoxyl functionalities (accounting for their higher oxygen content) and were more aromatic than the soluble fractions. This indicates how polar, aromatic materials are solubilized during the ChemCoal Process, which makes use of a very polar, aromatic solvent.

Proton NMR analysis indicated that the soluble fractions may contain larger aromatic systems which have few protons attached directly to the aromatic carbon structure. The fractions do not appear to have been heavily substituted, as indicated by the low alpha and beta aromatic regions of the proton spectrum and the fairly narrow aromatic region of the carbon spectrum. The main protonated species present were the aliphatic methyl and methylenes, which contained over 70% of the protons in the methylene chloride-soluble fraction. Compared to the MeCl₂-soluble fraction, the THF- and base-soluble fractions had a little larger aromatic region and more alpha and beta aromatic protons, which would indicate that they were substituted to a greater extent. However, the methyl and methylene protons still accounted for the majority of the protons in these samples.

3.1.1.3 Thermogravimetric Analysis

Thermogravimetric analyses were performed on each fraction to obtain proximate data. These data are presented in Table 3. The insoluble fractions had fairly similar proximate analyses, whereas the soluble fractions had a wider range of volatile matter and fixed carbon values. In general, the insoluble fractions were lower in volatile matter and higher in fixed carbon than the soluble fractions. The temperatures at which the volatile matter and fixed carbon were determined were higher for the insoluble fractions than for the soluble fractions.

3.1.1.4 Molecular Weight Determination

Molecular weight distributions were determined for the soluble fractions using GPC and are shown in Figure 1. The ChemCoal solid was found to be more soluble in THF (60.8 wt%) than the other solvents; this fraction also contained the heaviest material. As the figure shows, the molecular weight of the material that was solubilized increased with solubility.

TABLE 2

C-13 NMR DATA FOR CHEMCOAL PROCESS SOLID PRODUCT AND ITS FRACTIONS

Functionality	NMR Region (ppm)	Solid Product (% of C)	THF Soluble (% of C)	THF Insoluble (% of C)	Base Soluble (% of C)	Base Insoluble (% of C)	MeCl ₂ Soluble (% of C)	MeCl ₂ Insoluble (% of C)
Carbonyl	205-168	3.6	3.9	2.7	4.5	6.8	not	2.2
Phenolic	168-147	11.8	10.9	12.0	10.7	11.3	solid	11.1
Aromatic	147-92	59.9	55.3	67.9	56.0	61.1		68.5
Methoxy/Ether	92-52	0.6	0.0	1.3	1.4	1.6		0.3
Aliphatic:								
-CH-, -C-	52-37	3.7	2.5	1.9	5.6	2.9		2.2
-CH ₂ -	37-25	6.7	10.1	3.8	8.7	5.9		4.4
-CH ₃ -	25-0	13.8	18.0	10.3	13.2	10.5		11.4
Total		100.0	100.0	100.0	100.0	100.0		100.0
Fractional wt%		100.0	60.8	38.9	36.8	62.7	18.9	76.0

TABLE 3

TGA PROXIMATE DATA FOR CHEMCOAL PROCESS SOLID PRODUCT FRACTIONS

Fraction	Moisture Temp. (°C)	VM ^a Temp. (°C)	FC ^b Temp. (°C)	Moisture (solvent) (wt%)	VM (wt%)	FC (wt%)	Residue (ash) (wt%)	Total (wt%)
ChemCoal Process Solid Product	73.0	497.7	946.5	1.74	47.22	50.79	0.06	99.81
MeCl ₂ -Soluble	130.7	408.5	763.8	1.13	78.77	19.39	0.50	99.79
MeCl ₂ -Insoluble	77.1	499.3	906.3	1.09	38.71	59.09	1.09	99.98
Base-Soluble	28.9	467.9	898.1	0.27	54.15	44.89	0.63	99.94
Base-Insoluble	82.4	491.9	911.1	1.98	36.18	58.13	3.60	99.89
THF-Soluble	27.4	478.0	897.8	0.07	52.97	46.75	0.18	99.97
THF-Insoluble	85.8	501.2	900.7	1.05	34.07	62.80	2.06	99.95

^a Volatile matter.^b Fixed carbon.

Figure 1. Molecular weight distribution of THF-, base-, and MeCl_2 -soluble fractions of ChemCoal Process solid product.

3.1.1.5 Derivatization

The C-13 NMR spectrum of ChemCoal solids was compared with the spectrum obtained from ChemCoal solids following acetylation. The spectrum of the original ChemCoal solid indicates the presence of oxygen-substituted aromatic carbons, specifically phenolics or aromatic ethers. The oxygen-substituted aromatic carbon peak found in the acetylated spectrum is shifted upfield. Data indicate that the addition of the acetyl group occurred at a phenolic site. The spectra of the ChemCoal solids and the acetylated ChemCoal solids are compared in Figure 2. The solubility of the ChemCoal solids in hexane increased from 2 to 10 wt% after acetylation, as shown in Table 4. This change in solubility indicates that the polarity of the acetylated surface was somewhat reduced. The solubility of the acetylated product in THF was not determined.

Alkylation of the ChemCoal solids increased their solubility in hexane from 2 to 10 wt% and in THF from 70 to 80 wt%. Figure 3 compares the solid C-13 NMR spectra of the THF-soluble fraction of ChemCoal solids and alkylated ChemCoal solids. The NMR data indicates that two additional isopropyl groups per 100 carbon atoms were added to the THF-soluble fraction of the alkylated product. The larger aromatic area in the spectrum of the alkylated material is probably due to the increased solubility of the product.

Figure 2. Solid C-13 NMR spectra of (a) ChemCoal Process solid product and (b) acetylated ChemCoal Process solid product.

TABLE 4
SOLUBILITY DATA FOR CHEMICAL PROCESS SOLID PRODUCT DERIVATIVES

	Hexane (%)	THF (%)
ChemCoal Process Solid Product	2	70
Acetylated	10	-- ^a
Alkylated	10	80
Methylated [(CH ₃) ₂ SO ₄]	10	55
Methylated [CH ₂ N ₂]	0	70

^a Not determined.

Figure 3. Solid C-13 NMR spectra of THF-soluble fraction of (a) ChemCoal Process solid product and (b) alkylated ChemCoal Process solid product.

ChemCoal solids were methylated by two methods, the first using dimethyl sulfate and the second using diazomethane. The solid C-13 spectra for the THF-soluble fractions of the methylated products are compared to the C-13 spectrum for ChemCoal solids in Figures 4 and 5. The spectra indicate that the methylation took place on hydroxyls, resulting in the formation of methoxyl attachments. Diazomethane-methylated ChemCoal solids showed no increase in solubility. ChemCoal solids methylated with dimethyl sulfate did exhibit some changes in solubility, although the changes were not as significant as those shown in the alkylated products. This information suggests that large alkyl groups on the aromatic ring can increase solubility, while aliphatic methyl groups have little or no ability to increase solubility.

The NMR spectra of ChemCoal solids and photolyzed ChemCoal solids are compared in Figure 6. The data indicate that photoreduction had little effect on the ChemCoal solids.

Figure 4. Solid C-13 NMR spectra of (a) ChemCoal Process solid product and (b) addition spectra of THF-soluble and insoluble spectra of ChemCoal Process solid product methylated with diazomethane.

Figure 5. Solid C-13 NMR spectrum of (a) ChemCoal Process solid product and (b) addition spectrum of THF-soluble and insoluble spectra of ChemCoal Process solid product methylated with diazomethane.

Figure 6. [Top] NMR spectra of (a) ChemCoal Process solid product and (b) solid product photolyzed at 254 nm. [Bottom] NMR spectra of (a) ChemCoal Process solid product and (b) solid product photolyzed at 350 nm.

3.1.2 Testing Performed on the CPU

Twenty-two CPU runs were performed during the 1988-1989 program year. Some of the runs were performed as shakedown runs, while others were performed to produce ChemCoal product either for analysis or end-use studies. A brief synopsis of each run is included in the following paragraphs, and a summary of the 22 runs is presented as Table 5.

TABLE 5
SUMMARY OF CHEMCOAL CPU SHAKEDOWN RUNS

Run	Date	Conditions/Comments
C136	4/04/88	Distillation column shakedown at 100°C.
C137	4/22/88	Distillation column shakedown at 200°C; mass overheads:mass bottoms = 0.10.
C138	4/24/88	Pot temp. = 260°C, overheads temp. = 210°C; mass overheads:mass bottoms = 0.27.
C139	5/13/88	Ash/IOM-removal centrifuge shakedown; centrifuged ~4.5 gallons.
C140	5/19/88 and 5/23/88	Centrifuged 15-20 gallons; initial testing of homogenizer.
C141	6/07/88 and 6/14/88	Final level indicator check; operator training run. Liquid flow rate = 3 lbs/hr, gas flow rate = 15 scfh. Air lines flooded twice. Conversion = 75%.
C142	6/21/88	Operator training run. House air failed. Conversion = 75%.
C143	6/28/88	Liquid flow rate = 1.8 lbs/hr, gas flow rate = 8 scfh. (Extension of residence time was an attempt to attain higher conversion.)
C144	7/06/88	Excess water in house air. Difficulties with high-voltage wiring.
C145	7/27/88	Final shakedown of large distillation unit.

Continued ...

TABLE 5 (CONT.)
SUMMARY OF CHEMCOAL CPU SHAKEDOWN RUNS

<u>RUN</u>	<u>Date</u>	<u>Conditions/Comments</u>
C146	7/31/88	Run to verify Indian Head recycle run conversions of 79%-80%. Conversion on this run $\approx$ 75%. Liquid flow rate = 1.8 lbs/hr, gas flow rate >15 scfh.
C147	8/09/88	Investigation of polish filter as part of the downstream processing. Processed approximately 15 gal of material produced during Run C146.
C148	8/14/88	Primary compressor failed during heatup.
C149	8/22/88	Indian Head run with liquid flow rate varied from 3 to 3.5 lbs/hr, gas flow rate = 17.5 scfh. Reactor temperatures were varied from zone to zone within reactor. Reached conversion of 70%. Difficulties found with coal pulverizer.
C150	9/12/88- 9/14/88	Indian Head verification recycle run. Difficulties encountered with peristaltic slurry pump.
C151	9/26/88- 10/07/88	Downstream shakedown run using methanol. ChemCoal solids precipitated, phenolic solvent cleaned for recycle.
C152	10/16/88- 10/24/88	Wyodak subbituminous coal run at matrix-determined conditions. Run terminated by flash tower plug.
C153	10/25/88- 10/31/88	Completion of Wyodak matrix run.
C154	--	Distillation tower heater burned out during start-up.
C155	11/29/88- 11/30/88; 12/05/88	Pittsburgh No. 8 bituminous coal run at matrix-determined conditions.
C156	12/10/88	Continuation of Pittsburgh No. 8 matrix run.
C157	12/14/88- 1/12/89	Indian Head recycle verification run.

3.1.2.1 Shakedown Runs

At the end of FY87-88, a glass distillation column was installed to facilitate easier solvent recovery. The reboiler cracked during its initial shakedown run and was replaced by a stainless steel reboiler. Run C136 (4/4/88) was performed to shake down the repaired distillation column. The system was heated to 100°C and the column operated as expected.

Run C137 (4/22/88) was also performed as a distillation column shakedown run. The column was insulated and the system was heated to 200°C. The target mass ratio of overheads to bottoms for shakedown runs was 0.30; the ratio for this run was determined to be 0.10.

Run C138 (4/24/88) was performed with a liquid temperature of 260°C and an overheads temperature of 210°C. The mass ratio of overheads to bottoms was determined to be 0.27.

Run C139 (5/13/88) was performed as the initial shakedown run of the ash/IOM-removal centrifuge. Approximately 4.5 gallons of slurry were pumped through the system. The filtered liquid was sampled and analyzed for THF insolubles. No change was observed in the THF insoluble content of the samples with time during the operation of the centrifuge. The accumulated filter cake was left in the centrifuge bowl and allowed to spin down for visual observation. Inspection of the filter cake showed that a coal-like solid/paste had developed. The filter cake was approximately 1 inch thick, or half of the volume of the centrifuge bowl. This filter cake was removed manually.

Run C140 (5/19/88) was the first long-term run performed with the ash/IOM-removal centrifuge. The goal of this run was to determine if it would be possible to operate the centrifuge without manually removing the filter cake. Approximately 15 gallons of product slurry were pumped into the centrifuge at a constant rate, producing 11 gallons of clarified liquid and 4 gallons of concentrated solids. The filter cake was successfully removed using the removal tube supplied with the unit, making automatic operation of the downstream loop possible. In general, the centrifuge worked better than had been anticipated.

Run C140 continued four days later (5/23/88) when the clarified stream (deashed product slurry) that had been obtained during earlier CPU operation was used to shake down the homogenizer. Equal amounts of methanol and deashed product slurry were homogenized as a test batch. The homogenizer worked very well during the testing. However, the quality of the resulting ChemCoal solid indicated that a greater quantity of methanol should have been used during the mixing step.

Run C141 (6/7/88) was performed as the final check on the level indicator, which was integrated into the computer control system prior to the run. However, flooded air lines forced a shutdown of the CPU. The run was attempted again one week later (6/14/88), at which time the air lines again had to be drained and the valves purged. The system was operated at a 3-lb/hr slurry feed rate and a gas flow rate of 15 scfh. A 75% conversion of the coal was obtained. The level indicator functioned consistently throughout the run.

Run C142 (6/21/88) was performed as an operator training run. The system ran well until the house air failed. This situation exhibited the intrinsic safety of the unit, as it handled the air shutoff without dangerous consequences. A 75% conversion was attained during this run.

A target conversion rate of 85%-90% had been set for Run C143 (6/28/88). Previous slurry and gas feed rates of 5 lbs/hr and 15 scfh, respectively, resulted in a coal conversion of 55%. For Run C143, the pumps were set so that the slurry feed rate was 1.8 lbs/hr and the gas feed rate was 8 scfh. The resulting increase in residence time should have increased the conversion, but approximately the same level was attained. The fact that the conversion did not increase indicated that the reaction is gas-limited rather than residence time-limited and that not enough gas was present during this run.

CPU Run C144 was initiated on 7/6/88, but was terminated during startup due to excess water in the house air. Additional problems developed with the high-voltage wiring due to faulty initial wiring. These problems had to be resolved prior to further operation of the high-pressure portion of the system.

CPU Run C145 began on 7/27/88 as a final shakedown of the large distillation unit. The bottoms pump had been added earlier in the month, and the control loop was added during the run. The unit functioned well, duplicating ASTM distillation data. A distillation of the feed material under the ASTM distillation procedure indicated that a pot temperature of 260°C would produce an overheads temperature of 230° to 240°C and a separation of 30% by volume. During the CPU test, a pot temperature of 260°C produced an overhead rate of approximately 28% by weight. Taking into account the difference in specific gravity between the overheads and the bottoms, 28 wt% is very close to the 30 vol% observed during the ASTM procedure.

CPU Run C146 was initiated on 7/31/88. Indian Head lignite slurry was fed at a rate of 1.8 lbs/hr, producing a residence time of approximately 90 minutes. The gas flow rate was in excess of 15 scfh. The resulting THF insolubles content of the product was 9.43 wt%, which is equivalent to a coal conversion of approximately 75%. This conversion level is reasonably close to the 79%-80% required to duplicate the Indian Head recycle test results.

Run C147 was initiated on 8/9/88 and was performed to investigate the effectiveness of a polish filter on the downstream processing. The smallest polish filter that could be conveniently added to the loop for the test was a 7-micron filter, but it actively collected a fraction of the solid particles in the product slurry prior to precipitation of the solid product. Approximately 15 gallons of material that had been produced during Run C146 were processed during this run to train operators on the use of the downstream processing loop.

Run C148 began on 8/14/88 as a run to finalize operator training, to add a new shift, and to obtain a conversion closer to the 80% required to verify the recycle run. During heatup, the primary compressor failed and the system was shut down. The compressor was replaced, the level indicator was updated, and the balance of the week was spent performing additional downstream processing.

Run C149 was initiated on 8/22/88. Indian Head slurry was pumped in at a rate of 3.5 lbs/hr. The gas flow rate was 17.5 scfh. During previous runs, the reactor temperature had been set at a constant 330°C. During this run, the entrance zone (i.e., the top 30% of the reactor) was set at a temperature of 280°C, and the balance of the reactor was set at 330°C. At these conditions, the THF insolubles content was approximately 12.5 wt%. The entrance zone temperature was increased to 330°C, with the balance of the reactor reset at 340°C. These changes lowered the product THF insolubles content to approximately 11.5 wt%. The slurry feed rate was lowered to 3.0 lbs/hr and the temperature increased to 350°C, which lowered the THF insolubles content further to approximately 10.5 wt%. This THF insolubles content is approximately equivalent to a 70% conversion of the feed coal. At a flow rate of 3 lbs/hr, the total liquid volumetric flow rate is equivalent to a residence time of 0.9 hrs. With the gas volume throughput remaining the same, the equivalent liquid residence time is between 25 and 45 minutes. The unconverted particles appeared to be quite large, indicating that a problem existed with the pulverizer. Further investigation of the pulverizer found this to be the case. Because the coal must be ground very close to the time of use, it is unlikely that problems with the pulverizer would show up until during or after a run.

The Indian Head recycle verification run, C150, was initiated on 9/12/88. The run was terminated on 9/14/88 when difficulties were encountered with the peristaltic slurry pump.

Run C151 was performed as a downstream shakedown run using methanol. ChemCoal solids were precipitated and the phenolic solvent cleaned for recycle.

3.1.2.2 ChemCoal Production Runs

Two runs (C152 and C153) were performed to produce ChemCoal solids from Wyodak subbituminous coal and to obtain data that could be used to mathematically model the system. Run conditions were determined using a statistical experimental design. The experimental matrix was built around what were thought to be the most important three variables: residence time, pressure, and temperature. The effects of caustic loading and gas flow rate were also determined based upon the results of four tests performed in addition to the matrix tests.

It was assumed that the effects of residence time, pressure, and temperature on the conversion of coal to ChemCoal products would not be linear and a full response surface estimation would be necessary. A Box-Behnken design was chosen because this design is fairly sparing in its use of runs. In addition, Box-Behnken designs are three-level designs, making the actual running of the experimental program fairly easy. Both simple and interactive relationships between the independent, or x, variables and the dependent, or y, variables can be determined with this design. A Box-Behnken design for three factors is presented in Table 6, while the actual run matrix is given in Table 7. Table 7 also shows the four runs made to determine the effects of gas flow rate and caustic loading.

TABLE 6
BOX-BEHNKEN STATISTICAL EXPERIMENTAL DESIGN FOR THREE FACTORS

Run	X_1	X_2	X_3
1	-1	-1	0
2	1	-1	0
3	-1	1	0
4	1	1	0
5	-1	0	-1
6	1	0	-1
7	-1	0	1
8	1	0	1
9	0	-1	-1
10	0	1	-1
11	0	-1	1
12	0	1	1
13,14,15	0	0	0

TABLE 7
INDEPENDENT VARIABLES AND THEIR RANGES INCLUDED IN THE
WYODAK CHEMCOAL EXPERIMENTAL MATRIX

Run/ Run Pass	Avg. Temp. (°C)	Avg. Pressure (psig)	MAF ^a Coal In (gm/hr)	NaOH In (% MAF)	Gas Flow (scfh)
Run C152					
1	351.3	1756	315.0	3	16.4
2	350.2	1759	306.1	5	16.4
3	309.4	2495	288.2	5	17.6
4	345.1	2504	148.6	5	17.6
Run C153					
1	343.6	2521	471.0	5	17.6
2	375.4	2499	209.5	5	17.6
3	307.4	1746	469.7	5	16.4
4	307.6	1739	123.4	5	16.4
5	346.2	1741	298.8	5	16.4
6	347.2	1739	298.8	5	12.6
7	346.4	1765	299.9	5	20.4
8	343.7	1744	298.8	5	16.4
9	378.9	1741	441.3	5	16.4
10	383.0	1750	123.4	5	16.4
11	376.8	1017	343.6	5	16.0
12	344.8	1019	507.5	5	16.0
13	344.9	985	101.5	5	16.0
14	308.9	986	321.8	5	16.0
15	344.4	1757	311.0	8	16.4

^a Moisture- and ash-free.

The first run, C152, was initiated on 10/16/88. During additional operator training on 10/24/88, the flash tower plugged. Following cleanup, Run C153 was begun on 10/25/88. The experimental matrix was completed on 10/31/88. During these tests, the CPU was operated in a single-pass mode with consistent recycle solvent (i.e., solvent that had been through the process at least two times.) With the exception of the flash tower plug that occurred due to operator error, the system ran flawlessly during the two runs.

An experimental design identical to that used for the Wyodak testing was planned using Pittsburgh No. 8 bituminous coal to provide a comparison of the results of the two tests. Run C154 was slated as the bituminous coal run; however, the distillation tower heater burned out during run start-up. A new heater was fabricated and Run C155 was begun on 11/29/88. Difficulties with coking and plugging of the system were experienced, and the system had to be shut down for cleaning. Due to these difficulties, an abbreviated matrix was planned incorporating data from Run C155 in an effort to obtain some information about the performance of the Pittsburgh No. 8 coal in the ChemCoal Process. Run C156 was performed on 12/10/88 to obtain data from two additional run passes. Run pass conditions for this matrix are presented in Table 8.

TABLE 8

RUN CONDITIONS OF ABBREVIATED MATRIX FOR PITTSBURGH NO. 8 BITUMINOUS COAL

Run Pass	Temp. (°C)	Press. (psig)	Slurry Flow (lb/hr)	CO Flow (scfh)	Caustic (fr. maf) ^a
C155-1	345	1750	3	15	0.02
C155-2	345	1750	3	15	0.05
C155-3	310	2500	3	15	0.05
C156-1	310	1750	3	15	0.05
C156-2	380	1750	3	15	0.05

^a Fraction of the moisture- and ash-free coal loaded.

The recycle verification test using Indian Head lignite, Run C157, was initiated on 12/14/88 and continued through 1/12/89. The run was performed to verify the results obtained during the original ChemCoal recycle run using Indian Head lignite and to provide data for a detailed mass balance of the solvent and sodium streams.

3.1.3 Results of the ChemCoal Production Runs

3.1.3.1 Analyses of Product Samples

During the April through June quarter, the product samples from the end of each pass of Runs C152 and C153 were analyzed with respect to structure, molecular weight distribution, and solubility in methanol.

Methanol solubility data is used in the calculation of product yields in the ChemCoal Process. The yield of ChemCoal solid product is determined by subtracting the weight percent of the product slurry that is soluble in hot phenolic solvent (POH) and tetrahydrofuran (THF) from the weight percent of product slurry that is soluble in methanol. (Solubility in POH also provides an indication of the ease with which the product can be put in a liquid form. This information could be of value when designing processes capable of achieving ultra-high conversions using LRCs.) Liquid product (distillate) yield is determined by subtracting the quantity of the starting solvent that is present in the product slurry from the methanol-soluble fraction of the product. The methanol solubilities of the product slurry samples are listed in Table 9.

TABLE 9
METHANOL AND THF SOLUBILITIES OF PRODUCT SLURRIES

Run Pass ID	MeOH Sol. (wt%)	MeOH Insol. (wt%)	THF Sol. of MeOH Insol. ^a (wt%)	Additional THF Sol. ^b (wt%)	Calc. Total THF sol. ^c (wt%)
C152-1	80.07	19.93	7.18	1.43	81.50
-2	79.10	20.90	7.58	1.58	80.68
-3	81.61	18.39	3.54	0.65	82.26
-4	79.72	20.28	6.86	1.39	81.11
C153-1	81.18	18.82	5.74	1.08	82.26
-2	82.25	17.75	14.48	2.57	84.82
-3	78.18	21.82	4.19	0.91	79.09
-4	76.17	23.83	1.22	0.29	76.46
-5	81.61	18.39	3.87	0.71	82.32
-6	80.32	19.68	4.92	0.97	81.29
-7	80.90	19.10	8.28	1.58	82.48
-8	79.49	20.51	10.54	2.16	81.65
-9	82.63	17.37	8.04	1.40	84.03
-10	78.64	21.36	20.92	4.47	83.11
-11	80.10	19.90	8.49	1.69	81.79
-12	80.45	19.55	4.49	0.88	81.33
-13	79.19	20.81	12.63	2.63	81.82
-14	80.36	19.64	4.49	0.88	81.24
-15	83.27	16.73	12.47	2.09	85.36

^a Portion of MeOH-insoluble fraction that is soluble in THF.

^b Portion of product slurry that is insoluble in MeOH but soluble in THF = (MeOH Insolubles)(THF-soluble MeOH Insolubles)/100.

^c Calculated THF-soluble fraction of product slurry = MeOH solubles + THF solubles from footnote b.

To obtain information about ChemCoal product structure, proton NMR analysis of the methanol-soluble fraction of the product slurries was attempted. Each sample was dissolved in deuterated methylene chloride that contained an internal reference standard (TMS). The samples exhibited a poor solubility in the NMR solvent, even with the aid of sonication. The spectra obtained were all very similar and showed very poor resolution. Figure 7 is a typical spectrum, and it shows the cresol resonance pattern with aromatic resonances from 6.5 to 7.2 ppm and alpha-to-aromatic resonances from 2 to 2.5 ppm. Some aliphatic resonances occurred within the 0.9- to 1.5-ppm region. Due to severe line broadening and the solubility problems, these spectra were found to be of little use and further proton NMR analysis of the samples was abandoned.

Gel permeation chromatography (GPC) was performed using high-pressure liquid chromatography equipment (HPLC) and size distribution columns. This analysis provided molecular weight information about the nonvolatile aromatic products. The methanol-soluble fraction of each product slurry sample was evaporated to remove methanol and much of the cresol processing solvent, which otherwise masked the higher-molecular-weight material. A known weight of the material was solubilized in THF and chromatographed. The separation obtained was dependent on the molecular weight and polarity of the different compounds present in the sample and was referenced to a series of polyglycol standards of known molecular weights.

Figure 7. Typical proton NMR spectrum of the methanol-soluble fraction of ChemCoal product made during Runs C152 and C153 (Sample C153-9).

The molecular weight distribution (MWD) obtained for sample C152-1 prior to evaporation is shown in Figure 8. Figure 9 shows the MWD of the same sample after evaporation. Figure 9 also shows the MWD for the methanol insoluble-THF soluble fraction of the Sample C152-1 product slurry. Figure 10 shows the MWD for Sample C153-11. Comparison of Figures 9 and 10 illustrates the changes in MWD that occur due to a change in CPU operating conditions.

Figure 10 shows the positions in the profile that were measured and compared to evaluate the effects of changes in the processing conditions. The cresol solvent peak is marked, as is the position of toluene (if present). To put the data on a common base, calculations using internal ratios were performed on the data. The Peak 1 region was designated as the base region. The height of Peak 1 and the ratios of Peaks 2 through 6 to Peak 1 are presented in Table 10. The ratio of the cresol peak to Peak 1 would have been proportional to its concentration in the mixture if the evaporation step had not been required to reduce solvent masking.

Figure 8. Molecular weight distribution obtained for Sample C152-1 prior to evaporation.

Figure 9. Molecular weight distribution obtained for Sample C152-1 after evaporation.

Figure 10. Molecular weight distribution obtained for Sample C153-11.

TABLE 10
PEAK DATA FROM HPLC MOLECULAR WEIGHT STUDIES

Run Pass I.D.	Peak 1 Height (in.)	Height Ratios				
		Peak 2/ Peak 1	Peak 3/ Peak 1	Peak 4/ Peak 1	Peak 5/ Peak 1	Peak 6/ Peak 1
C152-1	1.53	0.90	1.02	0.59	1.26	0.37
-2	0.62	0.97	0.90	0.50	5.84	0.32
-3	1.15	0.87	0.80	0.50	0.77	0.17
-4	2.05	0.94	0.95	0.61	1.00	0.40
C153-1	1.35	0.88	0.84	0.55	1.87	0.24
-2	1.69	1.00	1.03	0.70	1.16	0.50
-3	0.95	0.79	0.83	0.49	1.79	0.24
-4	1.07	0.82	0.77	0.43	1.13	0.23
-5	1.33	0.95	0.99	0.63	1.47	0.35
-6	1.27	0.91	0.93	0.61	2.05	0.33
-7	1.16	0.89	0.97	0.58	2.16	0.43
-8	1.20	0.92	0.96	0.60	1.92	0.36
-9	1.48	1.05	0.47	0.67	1.86	0.49
-10	1.39	1.50	2.44	0.65	1.02	1.45
-11	1.62	1.09	1.85	0.65	1.25	1.38
-12	1.04	0.91	1.13	0.55	1.72	0.54
-13	1.59	1.21	1.03	0.57	1.38	0.40
-14	1.06	0.89	1.01	0.55	1.55	0.34
-15	1.42	0.90	0.93	0.61	1.51	0.35

The most obvious change in the data was noted in the higher ratios of Peaks 2, 3, and 6 for run passes C153-2, -9, -10, and -11. During these run passes, the operating temperature was over 360°C. The magnitude of the changes in MWD suggests that the solvent polymerizes at more severe operating conditions. A less polar aryl ether dimer formed from cresol solvent would be much less polar than cresol and would probably account for Peak 6. Dimers or polymers formed from solvent that retain the polar hydroxide functional group would have a higher molecular weight than cresol and would elute after cresol, as Peak 3 does. The presence of different isomers could account for the other peaks. The base peak, Peak 1, probably represents a region where the higher-molecular-weight coal-derived material is relatively free of the polymerized solvent.

3.1.3.2 Development of an Interactive Flowsheet for the Application of the ChemCoal Process to Wyodak Subbituminous Coal

An interactive process flowsheet was developed to provide a basis for a comparison of the ChemCoal Process to the existing data bank within the current DOE liquefaction program. The flowsheet generates data concerning the effects of changes in operating conditions and feedstocks on the product slate and yield. It is set up in such a manner that individuals not familiar with the Chemcoal Process can review process variables and their effects on the

product yield structures. Because its major use will be as a tool during the upcoming engineering economics evaluation, the flowsheet itself will be illustrated and explained in detail in Section 3.3, ChemCoal Economics Update. The following paragraphs summarize the procedures used in the development of the flowsheet.

Mass and material balances were performed based on the results of analyses of samples taken at the end of each run period. The data from Runs C152 and C153 are summarized in Table 11. Stream samples were also taken one hour prior to the end of each run period for comparison to the end-of-run samples to be certain that steady-state conditions were achieved. In most cases, functional lineout was achieved prior to the intermediate time sampling.

The mass balance was within 2.0% closure in most instances. For improved accuracy of the material balance based upon the mass-balanced model, all lost or excess material was assumed to be liquid product and was added or subtracted as appropriate from the liquid product flow rate.

The data were entered into a pc-based SAS program for the purpose of formulating model equations describing the system. The data entered into the computer program are listed in Table 12. The program used independent variables, their squares, and cross-product terms (Ax_i , Ax_i^2 , and $Ax_i x_q$, respectively). These values were incorporated by the computer into Z functions that were defined in such a manner that the computer read the variables as approximately -1, 0, or 1. The eleven Z functions that were input into the computer are listed in Table 13. The computer performed a stepwise regression of variables based upon an 85% confidence level. Subsequent manual selection or exclusion of specific steps was based upon a 95% confidence level.

Table 14 summarizes the response variables that were calculated. The complete results of the regression analysis are contained in the Appendix.

The general formula of the equation for each response variable is given by Equation 1.

$$Y = \text{intercept} + (\text{coefficient} * Z) \quad [1]$$

where the y, intercept, coefficient, and Z values are defined as in Table 15. If a coefficient is not listed for a given variable, the variable was not considered to be statistically important in that instance.

The computer-formulated model equations describe the liquid and gas flow rates out, components of the product gas, product solubility in hot phenolic solvent (POH) and THF, conversion of MAF feed to desired product, liquid product water content, product insolubility in methanol, and molecular weight ratios of the product as functions of the gas flow rate in, residence time, caustic loading, temperature, and pressure. The equations were incorporated into the mass- and material-balanced flowsheet to make it interactive for use in predicting yield structure at a particular set of process conditions.

TABLE 11

SUMMARY OF DATA COLLECTED DURING RUNS C152 AND C153

Run Pass ID Number	Nominal Temp. (°C)	Average Temp. (°C)	Nominal Pressure (psig)	Average Pressure (psig)	AR Coal In ^a (gm)	POH In ^b (gm)
152-01-1	345	351.3	1750	1756	890	1810
152-01-2	345	351.3	1750	1756	890	1810
152-02-1	345	350.2	1750	1759	890	1810
152-02-2	345	350.2	1750	1759	890	1810
152-03-1	310	309.4	2500	2495	890	1810
152-03-2	310	309.4	2500	2495	890	1810
152-04-1	345	345.1	2500	2504	890	1810
152-04-2	345	345.1	2500	2504	890	1810
153-01-1	345	343.6	2500	2521	890	1810
153-01-2	345	343.6	2500	2521	890	1810
153-02-1	380	375.4	2500	2499	890	1810
153-02-2	380	375.4	2500	2499	890	1810
153-03-1	310	307.4	1750	1746	890	1810
153-03-2	310	307.4	1750	1746	890	1810
153-04-1	310	307.6	1750	1739	890	1810
153-04-2	310	307.6	1750	1739	890	1810
153-05-1	345	346.2	1750	1741	890	1810
153-05-2	345	346.2	1750	1741	890	1810
153-06-2	345	347.2	1750	1739	890	1810
153-07-1	345	346.4	1750	1765	895	1810
153-07-1	345	346.4	1750	1765	895	1810
153-07-2	345	346.4	1750	1765	890	1810
153-08-2	345	343.7	1750	1744	890	1810
153-09-1	380	378.9	1750	1741	890	1810
153-09-2	380	378.9	1750	1741	890	1810
153-10-1	380	383.0	1750	1750	890	1810
153-10-2	380	383.0	1750	1750	890	1810
153-11-1	380	376.8	1000	1017	890	1810
153-11-2	380	376.8	1000	1017	890	1810
153-12-1	345	344.8	1000	1019	890	1810
153-12-2	345	344.8	1000	1019	890	1810
153-13-1	345	344.9	1000	985	890	1810
153-13-2	345	308.9	1000	986	890	1810
153-14-2	310	308.9	1000	986	890	1810
153-15-1	345	344.4	1750	1757	895	1810
153-15-2	345	344.4	1750	1757	895	1810

^a As-received coal in feed slurry.^b Phenolic solvent in feed slurry.

Continued

TABLE 11 (CONT.)

SUMMARY OF DATA COLLECTED DURING RUNS C152 AND C153

NaOH In ^a (gm)	Added H ₂ O In ^b (gm)	Ash (wt.fr. ^c coal)	NaOH In (fr. MAF Coal)	Coal Moisture (wt.fr.)	Nom. Liq. Flow In (lb/hr)	Act. Liq. Flow In (lb/hr)
15.5	100	0.0653	0.02	0.2405	3	3.162
15.5	100	0.0653	0.02	0.2405	3	3.162
39.0	100	0.0653	0.05	0.2405	3	3.099
39.0	100	0.0653	0.05	0.2405	3	3.099
39.0	100	0.0653	0.05	0.2405	3	2.917
39.0	100	0.0653	0.05	0.2405	3	2.917
39.0	100	0.0653	0.05	0.2405	1	1.504
39.0	100	0.0653	0.05	0.2405	1	1.504
39.0	100	0.0653	0.05	0.2405	5	4.768
39.0	100	0.0653	0.05	0.2405	5	4.768
39.0	100	0.0653	0.05	0.2405	3	2.120
39.0	100	0.0653	0.05	0.2405	3	2.120
39.0	100	0.0653	0.05	0.2405	5	4.754
39.0	100	0.0653	0.05	0.2405	5	4.754
39.0	100	0.0653	0.05	0.2405	1	1.249
39.0	100	0.0653	0.05	0.2405	1	1.249
39.0	100	0.0653	0.05	0.2405	3	3.024
39.0	100	0.0653	0.05	0.2405	3	3.024
39.0	100	0.0653	0.05	0.2405	3	3.024
39.0	100	0.0653	0.05	0.2405	3	3.024
39.0	100	0.0653	0.05	0.2405	3	3.024
39.0	100	0.0653	0.05	0.2405	3	3.024
39.0	100	0.0653	0.05	0.2405	5	4.466
39.0	100	0.0653	0.05	0.2405	5	4.466
39.0	100	0.0653	0.05	0.2405	1	1.249
39.0	100	0.0653	0.05	0.2405	1	1.249
39.0	100	0.0653	0.05	0.2405	3	3.478
39.0	100	0.0653	0.05	0.2405	3	3.478
39.0	100	0.0653	0.05	0.2405	5	5.136
39.0	100	0.0653	0.05	0.2405	5	5.136
39.0	100	0.0653	0.05	0.2405	1	1.027
39.0	100	0.0653	0.05	0.2405	1	1.027
39.0	100	0.0653	0.05	0.2405	3	3.257
39.0	100	0.0653	0.05	0.2405	3	3.257
62.5	100	0.0653	0.08	0.2405	3	3.162
62.5	100	0.0653	0.08	0.2405	3	3.162

^a NaOH in feed slurry.^b Added H₂O in feed slurry.^c Weight fraction.

Continued ...

TABLE 11 (CONT.)

SUMMARY OF DATA COLLECTED DURING RUNS C152 AND C153

MAF Coal In (gm/hr)	Ash In (gm/hr)	H ₂ O In (gm/hr)	POH In (gm/hr)	Act. Liquid Flow Out (lb/hr)	Nom. Gas Flow In (scfh)
315.0	37.5	160.1	922.9	3.04	15
315.0	37.5	160.1	922.9	3.02	15
306.1	48.1	155.6	896.9	2.97	15
306.1	48.1	155.6	896.9	2.97	15
288.2	45.3	146.5	844.3	2.82	15
288.2	45.3	146.5	844.3	2.82	15
148.6	23.4	75.5	435.4	1.42	15
148.6	23.4	75.5	435.4	1.42	15
471.0	74.0	239.4	1380.0	4.56	15
471.0	74.0	239.4	1380.0	4.56	15
209.5	32.9	106.5	613.7	1.96	15
209.5	32.9	106.5	613.7	1.96	15
469.7	73.8	238.7	1375.9	4.63	15
469.7	73.8	238.7	1375.9	4.63	15
123.4	19.4	62.7	361.6	1.22	15
123.4	19.4	62.7	361.6	1.22	15
298.8	47.0	151.9	875.3	2.90	15
298.8	47.0	151.9	875.3	2.89	15
298.8	47.0	151.9	875.3	2.94	10
299.9	47.0	152.2	873.8	2.94	20
299.9	47.0	152.2	873.8	2.94	20
298.8	47.0	151.9	875.3	2.94	20
298.8	47.0	151.9	875.3	2.86	15
441.3	69.4	224.3	1292.8	4.22	15
441.3	69.4	224.3	1292.8	4.22	15
123.4	19.4	62.7	361.6	1.07	15
123.4	19.4	62.7	361.6	1.07	15
343.6	54.0	174.7	1006.6	3.46	15
343.6	54.0	174.7	1006.6	3.46	15
507.5	79.8	258.0	1486.7	5.06	15
507.5	79.8	258.0	1486.7	5.06	15
101.5	16.0	51.6	297.3	0.98	15
101.5	16.0	51.6	297.3	0.97	15
321.8	50.6	163.6	942.8	3.30	15
321.8	50.6	163.6	942.8	3.29	15
311.0	60.5	157.8	906.1	2.96	15
311.0	60.5	157.8	906.1	2.96	15

Continued ...

TABLE 11 (CONT.)

SUMMARY OF DATA COLLECTED DURING RUNS C152 AND C153

<u>Act. Gas Flow In (scfh)</u>	<u>Gas In (gm)</u>	<u>Gas Out (scfh)</u>	<u>Gas Out (gm/hr)</u>	<u>Gas Out -Gas In (gm/hr)</u>
16.408	581.0	17.60	638.4	57.4
16.408	581.0	17.60	643.3	62.3
16.408	581.0	17.28	639.8	58.8
16.408	581.0	17.28	639.3	58.3
17.562	621.8	18.24	664.4	42.5
17.562	621.8	18.24	666.4	44.6
17.562	621.8	18.34	660.8	39.0
17.562	621.8	18.34	660.8	39.0
17.562	621.8	19.26	716.2	94.4
17.562	621.8	19.26	716.7	94.9
17.562	621.8	18.91	695.1	73.3
17.562	621.8	18.91	696.1	74.3
16.408	581.0	17.30	637.0	56.0
16.408	581.0	17.30	636.8	55.8
16.408	581.0	16.48	594.1	13.2
16.408	581.0	16.48	593.5	12.5
16.408	581.0	17.31	638.2	57.2
16.408	581.0	17.31	639.9	58.9
12.622	446.9	13.02	485.7	38.7
20.406	722.6	20.83	758.5	35.9
20.406	722.6	20.83	762.9	40.3
20.406	722.6	20.83	761.9	39.3
16.408	581.0	17.92	657.1	76.1
16.408	581.0	18.44	693.7	112.7
16.408	581.0	18.44	693.0	112.0
16.408	581.0	18.34	662.1	81.1
16.408	581.0	18.34	662.8	81.9
15.994	566.3	15.59	573.2	6.9
15.994	566.3	15.59	573.7	7.4
15.994	566.3	16.17	600.6	34.3
15.994	566.3	16.17	599.4	33.1
15.994	566.3	16.32	589.5	23.2
15.994	566.3	16.32	590.1	23.7
15.994	566.3	15.11	547.2	-19.1
15.994	566.3	15.11	550.9	-15.4
16.408	581.0	18.31	674.6	93.6
16.408	581.0	18.31	672.2	91.2

Continued ...

TABLE 11. (CONT.)
SUMMARY OF DATA COLLECTED DURING RUNS C152 AND C153

----- Normalized ----->					
<u>H₂</u> (mol% Gas Out)	<u>CO₂</u> (mol% Gas Out)	<u>H₂S</u> (mol% Gas Out)	<u>C2</u> (mol% Gas Out)	<u>C1</u> (mol% Gas Out)	<u>CO</u> (mol% Gas Out)
0.578	5.204	0.000	0.000	0.000	94.217
0.613	6.637	0.000	0.000	0.000	92.750
2.097	11.445	0.000	0.000	0.065	86.393
2.155	11.406	0.000	0.021	0.062	86.357
1.226	7.012	0.000	0.000	0.000	91.762
1.603	8.188	0.000	0.000	0.000	90.209
1.770	6.005	0.000	0.011	0.063	92.151
1.444	5.455	0.000	0.000	0.042	93.059
2.525	12.935	0.000	0.000	0.041	84.499
2.497	13.022	0.000	0.000	0.041	84.440
2.829	11.370	0.000	0.022	0.131	85.649
2.911	11.779	0.000	0.031	0.135	85.144
0.950	8.539	0.000	0.000	0.000	90.511
0.968	8.503	0.000	0.000	0.000	90.529
0.515	4.022	0.000	0.000	0.000	95.463
0.539	3.859	0.000	0.000	0.000	95.602
1.497	9.691	0.000	0.000	0.053	88.759
1.410	10.046	0.000	0.000	0.051	88.492
2.334	13.210	0.000	0.021	0.064	84.371
0.911	6.453	0.000	0.000	0.000	92.636
0.904	7.480	0.000	0.000	0.000	91.616
0.672	6.873	0.000	0.000	0.000	92.455
1.389	8.523	0.000	0.000	0.052	90.036
2.184	14.630	0.000	0.043	0.195	82.948
2.295	14.618	0.033	0.049	0.211	82.794
2.032	6.850	0.000	0.051	0.184	90.883
1.730	6.570	0.030	0.048	0.198	91.425
0.801	8.173	0.027	0.048	0.204	90.747
0.734	8.204	0.036	0.047	0.206	90.773
0.572	9.553	0.033	0.000	0.064	89.779
0.627	9.285	0.000	0.000	0.060	90.028
0.669	4.612	0.000	0.000	0.000	94.719
0.741	4.899	0.000	0.000	0.000	94.360
0.399	4.624	0.000	0.000	0.000	94.978
0.473	5.969	0.000	0.000	0.000	93.558
2.846	11.774	0.000	0.010	0.072	85.297
2.569	10.661	0.000	0.000	0.052	86.718

Continued ...

TABLE 11 (CONT.)
SUMMARY OF DATA COLLECTED DURING RUNS C152 AND C153

POHTHFI ^a (wt% Prod. Slurry)	Conv. (wt% MAF Coal In)	H ₂ O Out (wt% Prod. Slurry)	MeOH ^b (wt% Prod. Slurry)	Karl Fisher H ₂ O (wt% Prod. Slurry)	HPLC Mol. Wt. Ratio ^c
12.95	55.3	6.8	-- ^d	--	--
13.15	54.6	6.8	19.93	11.57	0.90
NA ^e	NA	5.7	--	--	--
11.34	65.8	5.7	20.90	11.34	0.97
18.07	35.4	10.8	--	--	--
17.00	40.2	10.8	18.24	15.54	0.87
10.62	69.7	4.5	--	--	--
9.98	72.5	4.5	20.28	9.09	0.94
NA	NA	5.4	--	--	--
10.35	70.2	5.4	18.82	11.68	0.88
9.21	76.6	4.1	--	--	--
10.15	72.7	4.1	17.75	11.04	1.00
15.77	45.2	7.5	--	--	--
15.28	47.3	7.5	21.82	12.89	0.79
14.66	49.9	4.9	--	--	--
15.93	44.1	4.9	23.83	12.09	0.82
12.27	61.7	6.9	--	--	--
12.40	61.2	6.9	18.39	12.63	0.95
11.31	65.2	5.8	19.68	12.23	0.91
NA	NA	7.1	--	--	--
11.16	66.1	7.1	--	--	--
12.48	60.0	7.1	19.03	12.97	0.89
11.91	64.0	6.5	20.51	11.97	0.92
12.14	63.1	8.7	--	--	--
10.65	69.5	8.7	17.37	13.97	1.05
10.37	74.9	6.9	--	--	--
10.92	72.8	6.9	21.36	11.99	1.50
13.27	55.0	9.8	--	--	--
13.61	53.5	9.8	19.55	13.65	1.09
14.99	47.9	8.4	--	--	--
14.45	50.3	8.4	20.81	11.10	0.91
12.83	59.7	5.5	--	--	--
12.57	60.9	5.5	19.64	13.95	1.21
15.17	45.1	8.9	--	--	--
15.44	44.0	8.9	16.73	12.06	0.89
11.01	72.0	5.4	--	--	--
10.05	76.0	5.4	19.90	14.23	0.90

^a Portion of product slurry that is insoluble in hot phenolic solvent and tetrahydrofuran.

^b Portion of product slurry that is insoluble in methanol.

^c Ratio of Peak 2 height to Peak 1 height, as determined during HPLC analyses.

^d Analysis performed for end-of-run samples only.

^e Data is unavailable.

TABLE 12

C152 AND C153 DATA ENTERED INTO THE SAS PROGRAM

Run ID	Temp. (°C)	Press (psig)	M&F In (gm/hr)	Liq. Out (lb/hr)	Gas In (scfh)	Caustic (fr. MAF) ^a	Gas Out (scfh)	H ₂ (mol%)	CO ₂ (mol%)	H ₂ S (mol%)	C2 (mol%)
152-03	309.4	2495	288.192	2.8186	17.5616	0.05	18.24	1.6033	8.1880	0.0000	0.0000
152-04	345.1	2504	148.608	1.4183	17.5616	0.05	18.34	1.443	5.4551	0.0000	0.0000
153-01	343.6	2521	471.043	4.5585	17.5616	0.05	19.26	2.4974	13.0215	0.0000	0.0000
153-02	375.4	2499	209.497	1.9567	17.5616	0.05	18.91	2.9109	11.7788	0.0000	0.0312
152-01	351.3	1756	315.019	3.0248	16.4080	0.02	17.60	0.6130	6.6371	0.0000	0.0000
152-02	350.2	1759	306.147	2.9701	16.4080	0.05	17.28	2.1548	11.4058	0.0000	0.0207
153-03	307.4	1746	469.669	4.6307	16.4080	0.05	17.30	0.9677	8.5032	0.0000	0.0000
153-04	307.6	1739	123.436	1.2218	16.4080	0.05	16.48	0.5392	3.8588	0.0000	0.0000
153-05	346.2	1741	298.787	2.8943	16.4080	0.05	17.31	1.4102	10.0463	0.0000	0.0000
153-06	347.2	1739	298.787	2.9388	12.6224	0.05	13.02	2.3342	13.2095	0.0000	0.0212
153-07	346.4	1765	298.787	2.9374	20.4064	0.05	20.83	0.6715	6.8734	0.0000	0.0000
153-08	343.7	1744	298.787	2.8565	16.4080	0.05	17.92	1.3892	8.5231	0.0000	0.0000
153-09	378.9	1741	441.292	4.2197	16.4080	0.05	18.44	2.2948	14.6185	0.0326	0.0489
153-10	383.0	1750	123.436	1.0690	16.4080	0.05	18.34	1.7299	6.5695	0.0300	0.0477
153-15	344.4	1757	311.044	2.9611	16.4080	0.08	18.31	2.5687	10.6610	0.0000	0.0000
153-11	376.8	1017	343.605	3.4615	15.9936	0.05	15.59	0.7344	8.2040	0.0361	0.0467
153-12	344.8	1019	507.486	5.0635	15.9936	0.05	16.17	0.6274	9.2849	0.0000	0.0000
153-13	344.9	985	101.494	0.9749	15.9936	0.05	16.32	0.7405	4.8994	0.0000	0.0000
153-14	308.9	986	321.811	3.2911	15.9936	0.05	15.11	0.4726	5.9694	0.0000	0.0000

^a Fraction of moisture- and ash-free coal.

Continued ...

TABLE 12 (CONT.)
C152 AND C153 DATA ENTERED INTO THE SAS PROGRAM

Run ID	C1 (mol%)	C0 (mol%)	POHTHF1 (fr. p.s.) ^a	Conv. (fr. MAE) ^b	Water (fr. p.s.)	MeOH1 (fr. p.s.)	KF Water ^c (fr. p.s.)	HPLC M.W. (ratio)
152-03	0.0000	90.2087	0.1700	0.4023	0.108	0.1824	0.1554	0.87
152-04	0.0416	93.0590	0.0998	0.7248	0.045	0.2028	0.0909	0.94
152-01	0.4011	84.4399	0.1035	0.7025	0.054	0.1882	0.1168	0.88
153-02	0.1351	85.1440	0.1015	0.7268	0.041	0.1775	0.1104	1.00
152-01	0.0000	92.7499	0.1315	0.5459	0.068	0.1993	0.1157	0.90
152-02	0.0622	86.3566	0.1134	0.6577	0.057	0.2090	0.1134	0.97
153-03	0.0000	90.5291	0.1528	0.4732	0.075	0.2182	0.1289	0.79
153-04	0.0600	95.6021	0.1593	0.4413	0.049	0.2383	0.1209	0.82
153-05	0.0515	88.4920	0.1240	0.6119	0.069	0.1839	0.1263	0.95
153-06	0.0637	84.3714	0.1131	0.6522	0.058	0.1968	0.1223	0.91
153-07	0.0000	92.4551	0.1248	0.6002	0.071	0.1903	0.1297	0.89
153-08	0.0522	90.0355	0.1191	0.6402	0.065	0.2051	0.1197	0.92
153-09	0.2108	82.7943	0.1065	0.6948	0.087	0.1737	0.1397	1.05
153-10	0.1979	91.4250	0.1092	0.7278	0.069	0.2136	0.1199	1.50
153-15	0.0522	86.7182	0.1005	0.7603	0.054	0.1990	0.1423	0.90
153-11	0.2059	90.7729	0.1361	0.5347	0.098	0.1995	0.1365	1.09
153-12	0.0597	90.0280	0.1445	0.5026	0.084	0.2081	0.1110	0.91
153-13	0.0000	94.3601	0.1257	0.6090	0.055	0.1964	0.1395	1.21
153-14	0.0000	93.5580	0.1544	0.4403	0.089	0.1673	0.1206	0.89

^a Fraction of product slurry.

^b Fraction of moisture- and ash-free coal.

^c Karl Fisher water analysis.

TABLE 13
DEFINITIONS OF Z FUNCTIONS USED

$Z1 = (X1 - 345)/35$
$Z2 = (X2 - 1750)/750$
$Z3 = (X3 - 300)/200$
$Z4 = (X4 - 15)/3$
$Z5 = (X5 - 5)/3$
$Z6 = Z1 * Z1$
$Z7 = Z2 * Z2$
$Z8 = Z3 * Z3$
$Z9 = Z1 * Z2$
$Z10 = Z1 * Z3$
$Z11 = Z2 * Z3$

TABLE 14
RESPONSE VARIABLES FOR THE WYODAK CHEMCOAL
EXPERIMENTAL MATRIX

Y	Description
Y1	Liquid Flow Out, lbs/hr
Y2	Gas Flow Out, scfh
Y3	H ₂ in Gas Out, wt%
Y4	CO ₂ in Gas Out, wt%
Y5	H ₂ S in Gas Out, wt%
Y6	C1 in Gas Out, wt%
Y7	C2 in Gas Out, wt%
Y8	CO in Gas Out, wt%
Y9	POHTHFI ^a , wt% product slurry
Y10	Conversion, wt% MAF coal
Y11	Water in product slurry, wt%
Y12	MeOH ^b , wt% product slurry
Y13	Karl Fisher water, wt% product slurry
Y14	HPLC molecular weight ratio

^a Portion of product slurry that is insoluble in hot phenolic solvent and tetrahydrofuran.

^b Portion of product slurry that is insoluble in methanol.

TABLE 15

INTERCEPTS AND COEFFICIENTS OF THE MODEL EQUATIONS

Variable	Intercept	Coefficient ^a										
		Z ₁	Z ₂	Z ₃	Z ₄	Z ₅	Z ₆	Z ₇	Z ₈	Z ₉	Z ₁₀	Z ₁₁
Liquid Out	2.8989	-0.0527	-0.0612	1.9804	--	--	--	0.0485	--	--	--	0.0391
Gas Out	16.0889	0.5002	0.6707	--	2.9887	--	--	-0.5902	--	--	--	--
H ₂	1.8115	0.5521	0.9512	0.2790	-0.6485	1.0347	--	--	--	0.3435	--	0.3285
CO ₂	10.1525	2.0075	2.2294	3.2888	-2.4925	2.2410	--	--	--	--	--	--
H ₂ S	-0.0007	0.0134	-0.0046	--	--	--	0.0136	--	--	-0.0088	--	--
C ₂	0.0070	0.0236	--	--	-0.0077	--	0.0196	--	--	--	--	--
C1	0.0457	0.0996	--	0.0173	-0.0214	0.0371	0.0638	--	--	--	--	--
CO	87.9519	-2.6556	-3.1533	-3.5205	3.1760	-3.3105	--	--	--	--	--	--
POHTHF1	0.1193	-0.0223	-0.0114	--	--	-0.0175	0.0145	--	--	-0.0144	--	-0.0070
Conversion	0.6302	0.1149	0.0617	--	--	0.1176	-0.0613	--	--	0.0665	--	0.0395
Water	0.0627	--	-0.0104	0.0122	--	--	0.0170	0.0082	-0.0152	-0.0178	--	--
MeOH1	0.1910	--	--	--	--	--	--	--	0.0182	--	--	--
KF Water	0.1242	--	--	--	--	--	--	--	--	-0.159	--	--
HPLC MW Ratio	0.9640	0.1461	-0.0688	-0.1202	--	--	--	--	--	--	-0.1163	--

^a $Z_1 = (\text{Temp}-345)/35$ $Z_2 = (\text{Pres}-1750)/750$ $Z_3 = (\text{MAF}-300)/200$ $Z_4 = (\text{Gas In}-15)/3$ $Z_5 = (\text{Caustic}-.05)/.03$ $Z_6 = Z_1 * Z_1$ $Z_7 = Z_2 * Z_2$ $Z_8 = Z_3 * Z_3$ $Z_9 = Z_1 * Z_2$ $Z_{10} = Z_1 * Z_3$ $Z_{11} = Z_2 * Z_3$

3.1.3.3 Discussion of the Results of the Statistical Analysis

The following discussion of the results of the statistical analysis of the CPU run data was originally contained in the January through March Quarterly Technical Progress Report. After the remaining analytical results became available during the April through June quarter, mathematical model equations were established to describe the results of Karl Fisher water, methanol solubility, and molecular weight analyses. New model equations were also developed describing the production of H_2S and $C1$ and $C2$ hydrocarbon gases. (Originally, several data points were missing for each of these product gas components, making the model equations preliminary at best.) The new H_2S , $C1$, and $C2$ model equations were incorporated into the interactive flowsheet. The printouts of the statistical development of the new model equations are contained in the Appendix.

Variable Y1 - Product Slurry Flow Rate (lbs/hr)

The product slurry flow rate was affected by temperature, pressure, feed slurry rate, and the cross-product of pressure and feed slurry rate. The relationship between product slurry flow rate and pressure was not a linear one. As expected, the feed slurry rate had the greatest effect on the product slurry flow rate.

Variable Y2 - Product Gas Flow Rate (scfh)

The product gas flow rate was affected by temperature, pressure, and feed gas flow rate. As expected, the feed gas flow rate greatly influenced the product gas flow rate. The relationship between product gas flow rate and pressure was not linear. The feed slurry rate, or residence time, did not significantly affect the product gas flow rate. This was unexpected, and it must be assumed that the effect of residence time is either too small to be of importance, or the increased production of gas due to longer exposure at reaction conditions is approximately equal to the amount of feed gas consumed.

Variables Y3, Y4, Y8, Y11 and Y13 - Water-Gas Shift Components (H_2 , CO_2 , CO , H_2O , and Karl Fisher H_2O)

The independent variables that affected the gas-phase water-gas shift components were temperature, pressure, residence time, gas flow rate, and caustic loading. The two CO_x gas-phase reactants in the water-gas shift reaction are essentially inverse functions of similar value. The H_2 model coefficients are of the same sign as the CO_2 model coefficients, indicating that the water-gas shift reaction dominates the gas-phase model. Additional influences on the hydrogen composition included interactions between temperature and pressure and between pressure and residence time.

The model equation for water is not in the same general format as the other water-gas shift reactants. It is not nearly as linear, and is not as directly linked to the other reactant species. It was determined that the differences could be due to either questionable analytical results or more complex reaction mechanisms. The water content values had been obtained during product slurry distillation analysis. To check the accuracy of the analytical results, product slurry water content was determined by Karl Fisher water analysis. The results of this analysis were input into the SAS

program. The resulting model equation indicated that only the cross-product of temperature and pressure affected the production of water. The results of the Karl Fisher water analyses appear to be even less reliable than the original product water content data; therefore, the model equation based upon the original data was left in the interactive flowsheet.

Variable Y5 - H_2S

The quantities of H_2S produced during the processing appear to have been below the sensitivities of the available analytical instrumentation. A model equation was developed which showed that temperature, pressure, the temperature/pressure cross-product, and the temperature-squared terms affected the production of H_2S . Temperature was shown to exert the greatest effect on the yield of H_2S in the product gas.

Variables Y6 and Y7 - Hydrocarbon Gas Composition

The newly calculated model equations showed that the C2 gas production was influenced by temperature, gas flow rate, and the square of the temperature. The C1 gas production was affected by more variables: temperature, feed slurry flow rate (i.e., residence time), gas flow rate, caustic loading, and the square of the temperature. In both instances, the temperature and the square of the temperature significantly affected the production of hydrocarbon gases.

Variables Y9 and Y10 - POHTHFI and Conversion

These are essentially functions of each other since conversion is calculated using the POHTHFI value (as well as mass flow rates). As a result, only conversion will be discussed. Conversion was most affected by the temperature, pressure, and caustic loading. The most surprising element of the model equation describing conversion was the fact that the residence time (feed slurry rate) appeared only in the interaction term of pressure and feed slurry rate and was not very significant.

Variable Y12 - Methanol Insolubles

The model equation indicated that only the square of the feed slurry flow rate influenced the production of methanol-insoluble material. It is difficult to tell if the process operating conditions actually have so little an effect on the product methanol solubility or if the analytical results are suspect.

Variable Y14 - HPLC Molecular Weight Ratio

The ratio of the second peak to the first peak of a spectrum obtained during HPLC of each product slurry sample was input into the SAS program. This ratio compares the height of the peak caused by the lighter, more volatile material present in the product to that of the heavy material. Depending upon the conversion of coal to ChemCoal product, a larger value may indicate that more light material (distillate, the preferred liquid product) is being produced at the expense of the production of heavy material. The model equation developed using the SAS program indicated that the ratio of

light to heavy molecular weight material in the product slurry was strongly influenced by the temperature as well as the MAF coal loading rate, the temperature/feed slurry rate cross-product, and the pressure.

3.1.3.4 Effects of the Independent Variables on the System

To determine the effect of each of the independent variables on the system, the others were held constant at the center point conditions listed in Table 16. Each variable under evaluation was input into the interactive mass flow sheet in incremental values from low to high test variance. The results were tabulated and plotted and are discussed in the following paragraphs.

TABLE 16
CENTER POINT CONDITIONS FOR INDEPENDENT VARIABLES

Variable	Center Point Value
X1	Temperature, 345°C
X2	Pressure, 1750 psig
X3	Slurry feed rate, 300 gm MAF coal/hr
X4	Gas treatment rate, 15 scfh
X5	Caustic loading, 5 wt% MAF coal

Temperature

Increases in temperature resulted in increases in overall conversion, as shown in Figures 11 through 14. As Figure 11 shows, the production of coal-derived liquids (CDLs) also increased as the temperature increased to 350°C; at higher temperatures, the additional conversion was lost to gas production. Figure 12, the plot of the production of C1 and C2 hydrocarbon gases, shows that the minimum production of hydrocarbon gas occurred at approximately 320°C. The C1 gas yield increased much more rapidly than the C2 gas yield as the temperature increased. Figures 13 and 14 show the efficiency of reductant utilization during the process as a function of temperature. The plot of Figure 13 shows that an increase in temperature resulted in a decrease in the utilization of the hydrogen charged to the system. As shown in Figure 14, CO utilization decreased as temperature increased, with a minimum utilization efficiency occurring at 360°C. The CO utilization efficiency was calculated as $CO_{eff} = (CO_{in} - CO_{out})/MAF\ coal_{in}$, while the hydrogen utilization efficiency was defined as $H_{2_{eff}} = 1 - (\text{moles } H_2 \text{ produced}/\text{moles CO consumed})$.

Figure 11. Effect of temperature on conversion and yield of coal-derived liquids.

Figure 12. Effect of temperature on hydrocarbon gas yield.

Efficiency of H₂ Utilization

Figure 13. Effect of temperature on hydrogen utilization.

Efficiency of CO Utilization

Figure 14. Effect of temperature on carbon monoxide utilization.

Pressure

The plots of Figures 15 through 18 show the effect of an increase in pressure on the yield structure. Figure 15 shows that both conversion and CDL production increased as the pressure increased. The CDL yield is derived from the unconverted insoluble organic matter (IOM) material balance, the water analysis equation, and the mass balance. The IOM material balance is based on the POHTHF1 and mass balance equations. As discussed previously, evidence exists which suggests that the water analysis equation may not be valid in certain regions of the model. In the region of pressures less than 1600 psig, the plot of Figure 15 indicates that more CDL was produced than coal converted. This is obviously not possible, and the result is probably due to the fact that the water analysis equation is not valid in this area.

Figure 16 plots the effect of pressure on hydrocarbon gas production and shows a slight increase in hydrocarbon gas production at pressures of less than 1800 psig. Further increases in pressure appear to have no effect on the hydrocarbon gas yields. This is fairly consistent with the upper region of the plot of CDL yield in Figure 15. The figure shows that, as pressure increased, the CDL yield increased slightly faster than the overall conversion. Taken together, Figures 15 and 16 indicate that increases in pressure do not result in increased gasification of CDLs. Figures 17 and 18 show that minimum H_2 and CO utilization efficiencies occurred at approximately 1800 and 2000 psig, respectively.

Figure 15. Effect of pressure on conversion and yield of coal-derived liquids.

Figure 16. Effect of pressure on hydrocarbon gas yield.

Figure 17. Effect of pressure on hydrogen utilization.

Figure 18. Effect of pressure on carbon monoxide utilization.

Residence Time Effects

Changes in the residence time were made by varying the liquid flow rate, i.e., the MAF coal charged, into the system. The effective residence times for the three primary set points of 100, 300, and 500 grams of MAF coal/hour were 2.9, 1.0, and 0.6 hours, respectively.

The effects on the product yield structure of increasing the residence time are shown in Figures 19 through 22. Figure 19, a plot of the effect of liquid flow rate on the conversion and production of CDLs, shows that conversion decreased slightly and the production of CDLs increased as the residence time decreased. The middle region of the CDL plot is a plateau with sharper changes at both short and long residence times. Once again, due to the dependence of the calculation of the CDL on the water analysis results, this plot may be affected by the water analysis equation. The yield of hydrocarbon gases increased as the MAF coal loading decreased (i.e., residence time increased), as shown in Figure 20. The increase was significant at the lowest MAF coal loading, but it should be noted that the hydrocarbon gases comprised only a very small portion of the product stream (approximately 0.135 mol% of the product gas). As these plots show, an increase in residence time did not have the large positive effect on conversion that was expected.

Figure 19. Effect of MAF coal loading rate on conversion and yield of coal-derived liquids.

Figure 20. Effect of MAF coal loading rate on hydrocarbon gas yield.

Figure 21. Effect of MAF coal loading rate on hydrogen utilization.

Figure 22. Effect of MAF coal loading rate on carbon monoxide utilization.

Figures 21 and 22 show that as the residence time decreased, the utilization of both CO and H₂ increased. The gas treatment rate was held constant as the residence time was decreased, which had the same effect as increasing the gas treatment rate. This would result in a less effective utilization for the same net conversion and was probably the major cause of the loss of reductant utilization efficiency in this case.

Gas Flow Rate

As mentioned earlier, the gas flow rate was a secondary variable and was varied during only four run periods. Results of mass and material balances based upon the model indicate that the gas flow rate affected only the H₂ utilization efficiency. Maximum efficiency occurred at approximately 15 scfh, as shown in Figure 23.

Caustic Loading

Caustic loading was also a secondary variable with a limited number of data points. Results indicate that as the caustic loading was increased, conversion and CDL production increased, as shown in Figure 24. This result was not expected, as earlier testing had indicated that increases in caustic loading had a detrimental effect on the process (2). Increased caustic loading also increased the shift from CO to H₂, as shown in Figure 25, and the efficiency of both H₂ and CO utilization, as shown in Figures 26 and 27, respectively.

Figure 23. Effect of gas flow rate on hydrogen utilization.

Figure 24. Effect of caustic loading on conversion and yield of coal-derived liquids.

Figure 25. Effect of caustic loading on shift gases.

Figure 26. Effect of caustic loading on hydrogen utilization.

Figure 27. Effect of caustic loading on carbon monoxide utilization.

3.1.3.5 Validity of the Model

A check on the validity of the system model involves the mass balance resulting from the calculated material balance derived from the model. If the model were not valid, the calculated mass balance from the model-derived material flowsheet would produce significant deviation from unity. Within the range over which the model was developed, no set of conditions was found that resulted in a calculated mass balance worse than $\pm 2\%$ closure. This is as good as the original data and serves as validation of the fit of the model.

3.1.3.6 Runs Using Pittsburgh No. 8 Bituminous Coal

As mentioned in Subsection 3.1.2.2, the runs using Pittsburgh No. 8 bituminous coal were very difficult to perform due to plugging and coking problems. Rather than attempting to perform the entire experimental matrix, an abbreviated matrix of five test points was performed. The analytical results are not available and preliminary conclusions regarding the use of Pittsburgh No. 8 bituminous coal in the ChemCoal Process system cannot be made at this time.

3.1.3.7 Indian Head Recycle Verification Run

This run was performed to verify the results obtained during the original ChemCoal recycle run using Indian Head lignite. During the first recycle run, the system remained operable for 40 passes, solvent balance was achieved, conversions of 80%-90% were attained, sodium recovery was 62%, and the reductant composition in hydrogen equivalents was approximately 1.5% MAF coal fed. The system was redesigned between the first recycle run and the verification run to include at least two rinses of the centrifuge cake to recover solvent and sodium, as well as a different reactor configuration and degree of solvent recycle. The target conversion of the recycle verification run was 80%; a conversion of approximately 75% was achieved. In addition, the gas make was only 1.5%, while coal-derived distillate comprised 30% and solid ChemCoal product made up 43.5% of the exit stream. Hydrogen consumption during the run was low. Due to the different reactor configuration, the residence time was reduced by a factor of 8. Sodium recovery during the run was 85%-88%.

3.1.4 Precipitation of ChemCoal Process Solid Product in the CPU

During the July through September quarter, an effort was made to adapt the laboratory-scale admix procedure that had been developed previously into the routine operation of the CPU. The laboratory-scale procedure was discussed in a previous Quarterly Technical Progress Report (3). Efforts to adapt this method to the CPU are summarized in the following paragraphs.

Various admixture procedures were evaluated under both laboratory-scale and continuous-process conditions. Table 17 summarizes the ash contents of ChemCoal solids produced during these tests. As the table shows, the best results were obtained during the laboratory-scale testing, with the lowest ash

TABLE 17
RESULTS OF CHEMCOAL PROCESS SOLID PRODUCT ADMIXTURE TESTS

Admixture	Constituents/Method	Ash (wt%)
1CC	2 parts MeOH added to 1 part PS. ^a	7.67
2CC	4 parts MeOH added to 1 part PS.	8.33
3CC	Stoichiometric amount ^b of formic acid added to H ₂ ; 2 parts MeOH added to 2 parts of the acid solution; 1 part PS added to the MeOH/H ₂ /acid.	2.98
4CC	Stoichiometric amount of formic acid added to H ₂ ; 1 part PS added to 2 parts of the acid solution; 2 parts MeOH added to the PS/H ₂ /acid.	3.38
5CC	Stoichiometric amount of formic acid added to MeOH; 1 part PS added to 4 parts MeOH/acid.	3.78
6CC	1 part MeOH added to 1 part PS.	7.67
7CC*	1 part PS added to 4 parts MeOH.	5.29
8CC*	1 part PS added to 4 parts MeOH.	8.09
9CC*	1 part Ps added to 4 parts MeOH; stoichiometric amount of formic acid added after precipitation step.	6.18
10CC*	1 part PS added to 2 parts MeOH and 2 parts water.	8.69
11CC*	1 part PS added to 2 parts MeOH and 2 parts water.	10.23
12CC*	1 part PS added to 2 parts MeOH and 2 parts water; stoichiometric amount of formic acid added after precipitation step.	8.43

^a Deashed product slurry.

^b Equal to the quantity of sodium initially present in the slurry.

* Continuous rather than laboratory-scale runs.

level of 2.98 wt% obtained using product slurry, water, methanol, and formic acid (3CC). Although this ash content is approximately three times lower than that obtained using the previous method of precipitation, it is not as low as the 1.4 wt% ash level obtained during earlier laboratory-scale testing using the same quantities of water, methanol, and formic acid with the product of Run N403. The results of this earlier testing are given in Table 18. Two explanations for the difference in final product ash contents were suggested: either the product slurry ash contents were different or the order in which the water, methanol, and formic acid were combined with the product slurry was important.

Examination of the data presented in Table 17 showed that the order in which the constituents were mixed significantly affected the ash content of the precipitated product. The results of three precipitations were examined: 1) 4 parts methanol added to 1 part product slurry; 2) 1 part product slurry added to 4 parts methanol, followed by the addition of a stoichiometric amount of formic acid; and 3) 1 part product slurry added to 4 parts methanol that had been acidified using a stoichiometric amount of formic acid. The best result, in terms of ash removal, was achieved by Combination 3, the acidified precipitation. These results are shown graphically in Figure 28. The least effective was the nonacidified precipitation, with the post-precipitation acidification intermediate in its ash removal. It is clear from these results that it is easier to recover the ash/sodium if the precipitating solvent has first been acidified.

3.2 Results of Task B - Utilization Testing

3.2.1 As a Diesel Fuel Extender

Planned tests of the use of ChemCoal Process solid product as a diesel fuel extender met with many delays. Initial delays were due to difficulties with the subcontract with Southwest Research Institute (SwRI). After the wording of the subcontract was changed to meet with the approval of all parties, a sample of ChemCoal Process solid product was prepared from Indian Head lignite and submitted for an in-house analytical workup to ascertain that the sample met SwRI requirements prior to shipment as a methanol/water slurry of suspended product.

Analysis of the sample indicated that the slurry had an unusually high ash content and low ChemCoal solid product content. Subsequent investigation showed that the temperature of the partitioning solvent is critical to the yield structure of the centrifuge streams. Earlier work at the laboratory scale suggested that product particle size can easily be controlled by the temperature of the precipitation solvent. The testing for this year was set up to utilize room-temperature partitioning solvent to produce a very fine particulate solid product suitable for utilization testing. These conditions produce very small particles but also, unfortunately, low concentrations of ChemCoal product. Because of the lower concentrations of solid product and the highly effective centrifuge system, all of the ash and the solid product were removed. This resulted in a good product from a particle-size point of view, but it had an unacceptable ash content of 5.29%.

TABLE 18
RELATIONSHIP BETWEEN ACID CONCENTRATION AND FINAL ASH CONTENT
FOR RUN N403^a

<u>Acid:Sodium</u>	<u>pH</u>	<u>Ash (wt%)</u>
1.23:1	5.2	1.4
0.5:1	5.8	4.1
0:1	7.9	8.1

^a Methanol:water:product slurry = 2:2:1.

Figure 28. Comparison of admix procedures for methanol-only case.

This development can offer significantly improved downstream operability. If the methanol/water partitioning solvent is kept at or slightly above room temperature, it can be added to the product slurry immediately after the letdown and prior to the first centrifuge. Since most of the solid product is soluble in warm partitioning solvent plus phenolic solvent, more of the solid product would pass through the first centrifuge and would not have to be rinsed out of the ash cake. Modification of the downstream processing loop in this manner could eliminate at least one rinse of the ash cake and, due to the low viscosity of the product slurry/partitioning solvent mix, improve the operability of the primary centrifuge.

3.2.2 As Fuel for Coal-Fired Gas Turbines

A letter was received from the Allison Gas Turbine Division of General Motors concerning a ChemCoal solid sample that had been prepared and shipped in March 1988. The letter stated that improvements had been made in fuel properties when compared to the samples submitted to Allison previously. The ash content was lower and the particle size was better controlled. The letter stated that researchers at Allison "... are impressed by the improved quality of the Chemcoal product and it appears that this process could produce an acceptable commercial coal-fired gas turbine fuel. ... With proper development, we feel that the Chemcoal product could become an acceptable ultraclean fuel." (4).

3.3 Results of Task C - ChemCoal Economics

Performance of an engineering economics evaluation of the ChemCoal Process will require information concerning the effects of changes in the feedstocks or the operating parameters on the product slate and system operation. An interactive flowsheet was developed based upon the results of more than 2000 hours of operation during 46 CPU runs over a 2-year period as well as the model formulated to describe the behavior of Wyodak subbituminous coal in the system.

The flowsheet is shown Figures 29 through 32. The feed slurry and feed gas enter the reactor. The operating conditions, conversion, hydrocarbon gas make, and residence time are listed to the right of the reactor. The liquid product is fed into Centrifuge 1, the first separation. The centrifuge efficiency and percent solids loading in the slurry out of the centrifuge are also noted. The centrifuge efficiency and effluent solids loading are based upon data gathered during approximately 500 hours of operation. The model was developed based on the single-pass efficiency of 95%, although it is possible to obtain an efficiency as high as 99% when a recycle is used. For this model, a 60 wt% solids loading was calculated for the effluent. The centrifuge is capable of producing virtually any effluent solids loading up to 70%-75%, although at solids loadings higher than 60 wt%, the effluent is essentially a solid paste. The effluent from Centrifuge 1 enters Centrifuge 2. The higher efficiency of this centrifuge, 99%, is due to the fact that the material entering the second centrifuge has a lower viscosity. Information concerning the efficiency of the second centrifuge is derived from approximately 1600 hours of operation. Again, the desired centrifuge efficiency and effluent solids loading are noted and could be changed. The methanol-to-water ratio in the partitioning solvent can also be set at this point.

		SLURRY IN		(-RECYCLE-)	
		maf	100.0		
		solv	293.0		
FEED		h2o	16.2	REACTOR	TEMP 350
MAF	100.0	NA	10.1		PRESS 1750
H2O	34.6	ash	9.4		MAF IN 100
ASH	9.4	mois	34.6	CONV	84.7% GAS IN 12
TOTAL	144.1	ar	144.1	HC	0.4% CAUST 9
		total	463.3	RES	3.0
		GAS OUT			
GAS IN				scfn	13.172
scfn	12.000			h2	1.1
h2		SLURRY OUT		co2	87.1
co2		maf	15.3	h2s	0.0
h2s		solv+cdl	358.0	c2	0.1
c2		h2o	14.7	c1	0.3
c1		ash	25.6	CD	394.6
CD	424.9	total	413.6	total	483.2
total	424.9	CNT EFF 95.0% CENT1			
CC	ASH	% SLDS 60%			
CAKE	CAKE	SOL+CDL	18.1	SOL+CDL	339.9
		MAF	14.6	MAF	0.8
V		ASH	8.9	ASH	0.5
CDL	24.7	40.0% H2O	0.7	H2O	14.0
POH	4.4	TOTAL	47.1	TOTAL	366.5
MAF	0.8	CENT2			
ASH	0.5	99%			
H2O	9.0	CDL	37.0	PRT FAC	
MEDH	8.7	POH	284.7	(MEDH)	1.5
TOTAL	50.9	MAF	0.01	RATIOS (H2O)	1.5
		ASH	0.00	MEDH	549.7
		H2O	554.7	H2O	543.7
		MEDH	541.0	POH	11.0
		TOTAL	1429	DIS 1	1110.4
H2O	173.6				
Na	5.0			DISTILLATION 1	
POH	17.4			TEMP 110 C	
				MAKEUP MEDH	
		MAF	0.00	8.7	
		CDL	11.1		
		NA	0.01		
		H2O	5.0053	H2O	3.5
CO2	19.2	MAF	0.01	MAF	0.01
(H2O)	173.6	PHEN	291.1	PHEN	203.8
		CDL	37.0	CDL	25.3
		Na	16.7	Na	11.7
		TOTAL	349.8	TOTAL	244.86
MAF	0.00	30%		DIS 2	TOT SOL
PHEN	17.4			SOL	69.9
CDL	11.1			H2O	1.5
Na	5.0			DISTILLATION 2	
(TOTAL)	33.5			TEMP 210.0 C	

Figure 30. Interactive flowsheet for the ChemCoal Process at 85% conversion and 3-hour residence time.

		SLURRY IN		(---RECYCLE---	
		maf	500.0		
FEED		solv	1464.8		
MAF	500.0	h2o	80.9	REACTOR	TEMP 350
H2O	173.2	NA	50.6		PRESS 2000
ASH	47.0	ash	47.0		MAF IN 500
TOTAL	720.3	mois	173.2	CONV	85.1% GAS IN 12
		ar	720.3	HC	0.1% CAUST 8
		total	2316.5	RES	0.6
				GAS OUT	
GAS IN				scfh	13.330
scfh	12.000			h2	1.5
h2		SLURRY OUT		co2	142.4
co2		maf	74.6	h2s	-0.0
h2s		solv+cdl	1872.0	c2	0.1
c2		h2o	124.5	c1	0.4
c1		ash	128.0	CO	361.1
CO	424.9	total	2199.1	total	505.5
total	424.9				
CC	ASH	CNT EFF 95.0% CENT1			
CAKE	CAKE	% SLDS 60%			
		SOL+CDL	87.1	SOL+CDL	1784.9
		MAF	70.9	MAF	3.7
		ASH	44.7	ASH	2.4 68.8
CDL	155.3	40.0% H2O	5.8	H2O	118.7
POH	25.4	TOTAL	232.2	TOTAL	1966.9
MAF	3.7	CENT2			
ASH	2.3	10.3			
H2O	55.9	CDL	233.0	PRT FAC	
MEDH	53.8	POH	1430.2	(MEDH)	1.5
TOTAL	312.1	MAF	0.04	RATIOS (H2O)	1.5
		ASH	0.02	MEDH	2950.3
		H2O	3013.2	H2O	2950.3
		MEDH	2896.6	POH	59.0
		TOTAL	7631	DIS 1	5959.7
H2O	875.2			DISTILLATION 1	
Na	25.0			TEMP 110 C	
POH	87.5				
				MAKEUP MEDH	
		MAF	0.01	53.8	
		CDL	69.9		
		NA	0.07		
		H2O	62.813	H2O	44.0
CO2	95.8	MAF	0.04	MAF	0.03
(+H2O	875.2	PHEN	1458.7	PHEN	1021.1
		CDL	233.0	CDL	163.1
		Na	83.4	Na	58.4
		TOTAL	1838.0		1286.5
MAF	0.01	30%		DIS 2	TOT SOL
PHEN	87.5			SOL	350.1 + 1655.5
CDL	69.9	80%		H2O	18.8
Na	25.0	0.01		DISTILLATION 2	
(-TOTAL	182.4			TEMP 210.0 C	

Figure 31. Interactive flowsheet for the ChemCoal Process at 85% conversion and 0.6-hour residence time.

		SLURRY IN		← RECYCLE	
		maf	100.0		
		solv	293.0		
FEED		h2o	16.2	REACTOR	TEMP 350
MAF	100.0	NA	11.4		PRESS 1200
H2O	34.6	ash	9.4		MAF IN 100
ASH	9.4	mois	34.6	CONV	85.3% GAS IN 12
TOTAL	144.1	ar	144.1	HC	0.4% CAUST 9
		total	464.6	RES	3.0
				GAS OUT	
GAS IN				scfh	12.362
scfh	12.000			h2	1.0
h2				co2	75.6
co2		SLURRY OUT		h2s	0.0
h2s		maf	14.7	c2	0.1
c2		solv+cdl	369.1	c1	0.3
c1		h2o	21.4	CO	375.6
CD	424.9	ash	27.6	total	452.7
total	424.9	total	432.8		
CC	ASH			CNT EFF	95.0% CENT1
CAKE	CAKE	% SLDS	60%		
		SOL+CDL	17.6	SOL+CDL	351.4
		MAF	14.0	MAF	0.7
		ASH	8.9	ASH	0.5
CDL	29.0	40.0% H2O	1.0	H2O	20.4
POH	4.9	TOTAL	46.6	TOTAL	386.2
MAF	0.7			CENT2	
ASH	0.5	2.3	99%		
H2O	10.5	CDL	43.5	PRT FAC	
MEDH	10.2	POH	285.7	(MEDH)	1.5
TOTAL	59.1	MAF	0.01	RATIOS (H2O)	1.5
		ASH	0.00	MEDH	579.3
		H2O	589.2	H2O	579.3
		MEDH	569.1	POH	11.6
		TOTAL	1501	DIS 1	1170.2
H2O	174.9				
Na	5.6			DISTILLATION 1	
POH	17.5			TEMP	110 C
				MAKEUP MEDH	
		MAF	0.00		10.2
		CDL	13.0		
		NA	0.01		
		H2O	9.8549	H2O	6.9
CO2	21.6	MAF	0.01	MAF	0.01
(H2O)	174.3	PHEN	291.6	PHEN	204.1
		CDL	43.5	CDL	30.4
		Na	18.8	Na	13.1
		TOTAL	363.7		254.58
MAF	0.00	30%		DIS 2	TOT SOL
PHEN	17.5				70.0 + 327.51
CDL	13.0			80%	H2O 3.0
Na	5.6	0.00		DISTILLATION 2	
(TOTAL)	36.2			TEMP	210.0 C

Figure 32. Interactive flowsheet for the ChemCoal Process at 85% conversion and 9% caustic loading.

The effluent from Centrifuge 2 enters the first distillation column. This distillation column has been operated continuously in a recycle mode as well as for bulk distillation and recovery of solvent in excess of 600 hours during the processing of over 6 barrels (330 gal) of material. The second distillation recovers the phenolic solvent and separates the liquids. In practice, this distillation column has processed over a barrel and a half of material, but not in the recycle loop. Its inclusion in this flowsheet is based upon the data derived during those operations.

The model is based on substantial quantities of real-world data with only two elements not verified by recycle: the aforementioned second distillation column and the water contact for CDL recovery. The stream in which the solvent is recycled to the front of the system was not integrated into the program since the nature of this recycle stream has not been verified by actual operation with respect to the second distillation.

It was assumed that the sodium in the system was converted from NaOH to an equal mixture of Na_2CO_3 and NaHCO_3 . When following the sodium through the reactor and material balance flowsheet, it can be noted that it gains weight. It can also be seen that more Na is recycled than was originally present. These apparent anomalies are due to the differences in molecular weight between the NaOH and the Na_2CO_3 and NaHCO_3 .

When the original economics study on the ChemCoal Process was performed by Bechtel, the lowest acceptable conversion rating was set at 80%. Figure 29 shows the total mass-balanced flowsheet at a conversion of approximately 80%. To achieve the 80% conversion, the temperature was set at 350°C, the pressure at 1200 psi, the residence time at 3 hours (based upon slurry feed rate), the gas flow rate at 12 scfh, and the caustic loading at 8 wt% of the MAF coal fed to the system. Depending upon capital and operating cost sensitivities, these generally low-pressure, moderate-temperature, and long-residence-time conditions will satisfy the 80% conversion rating. Should it be more appropriate to target an 85% conversion, the pressure would need to be increased from 1200 psi to 1750 psi. Figure 30 shows the flowsheet for this option.

If the capital cost of pressure is less than that associated with residence time, the residence time can be significantly reduced by increasing the pressure. Figure 31 shows the material balance for an 85% conversion at a residence time of 0.6 hours. This reduction in residence time would require an increase in pressure from 1750 psi to 2000 psi. The pressure increase would provide the additional benefit of a reduction in the hydrocarbon gas yield by a factor of 4, or 0.4 wt% MAF coal fed.

Either set of operating conditions (shown in Figures 30 and 31) and yield structures and would be acceptable as the basis for the engineering economics evaluation. The engineering company responsible for the evaluation should be able to select either of these conditions based on their in-field expertise with respect to relative capital costs between reactor volume and pressure design criteria.

An interesting speculation relative to the overall economics of this process may be seen in Figure 32. This figure shows what happens to the material balance as calculated by the model when the caustic loading is

increased from 8 wt% to 9 wt% of the MAF coal loading. While this supposition is not valid because it is outside of the range of the model and the actual testing, it does suggest that significant processing improvements could be made with small changes in the caustic loading level. According to the model, raising the caustic loading from 8 wt% to 9 wt% would result in a reduction of the pressure from 1750 psi (as shown in Figure 30) to 1200 psi. Additional research could verify this supposition.

3.4 Results of Task D - LRC Agglomeration

The agglomeration studies of LRCs continued during this program year using Indian Head lignite and two different binding oils.

Mixtures of p-xylene and Mandan Decant Oil from the Amoco Oil Refinery located in Mandan, North Dakota, served as the binding oil for the first tests. The viscosity obtained by mixing the two was more conducive to the formation of agglomerates than Mandan Decant Oil alone. The experiments were carried out using a 1.8-liter ceramic ball milling apparatus. The results are summarized in Table 19. The rollers turned at a maximum of approximately 200 rpm, resulting in a rotation of the jar of 88 rpm. Variations in mixing time and quantities of oil or water used produced a coal/oil slurry rather than agglomerated products.

Successful agglomeration tests were performed using Indian Head lignite, the crude phenol stream from the Great Plains Gasification Plant (GPGP) near Beulah, ND, and a surfactant, Triton X-100. Triton X-100 was added to four 50-gram samples of -200 mesh Indian Head lignite as either 1%, 5%, 10%, or 20% by weight of coal. Further details of the preparation of the agglomerates may be found in Reference (5). Each of the samples yielded agglomerates, and it was found that the particle size of the agglomerate formed was determined by the amount of surfactant present. The agglomerates are shown in Figure 33. Reductions in ash content of 15% to 25% were achieved in all cases. The results of proximate analysis performed on the agglomerates after washing and air drying for nonuniform time periods are shown in Table 20. As the table shows, an addition of 3 to 5 wt% surfactant was the most effective in producing agglomerates from the coal/oil mixture. An addition of 3 wt% Triton X-100 appears to have been the most effective.

Air drying was observed as a function of time for an agglomerated sample prepared with 3 wt% Triton X-100. Most of the moisture was removed during the first day. After 24 hours, agglomerated moisture content decreased from 29.5 wt% to 11.8 wt%. A substantial amount of volatiles was also lost during this time period due to the phenolic character of the oil used for the agglomeration. Volatile content decreased from 64 wt% to less than 60 wt% during the 24-hour period. Figure 34 shows both the moisture and ash contents as a function of time. The ash content is plotted on a moisture- and oil-free basis.

TABLE 19
RESULTS OF AGGLOMERATION EXPERIMENTS PERFORMED IN A BALL MILL

Test No.	Components ^a	Weight (g)	Time (hrs)		Agglomerates
			Crushing	Mixing	
1	Coal	50.03	0.16	1.0	None.
	Water	500.80			
	MDO	48.50			
2	Coal	50.01	0.16	1.0	Soft, oolitic, no binding strength.
	Water	100.16			
	MDO: PXY ^b =80:20	10.14			
3	Coal	50.32	0.25	30.0	Same as Test 2.
	Water	150.89			
	MDO: PXY=50:50 ^c	45.97			

^a Listed in the order in which they were charged.

^b p-Xylene.

^c Weight ratio.

1 wt% Surfactant

5 wt% Surfactant

10 wt% Surfactant

20 wt% Surfactant

Figure 33. Agglomerates formed from Indian Head lignite, Triton X-100, and GPGP crude phenol.

TABLE 20

RESULTS OF TGA PROXIMATE ANALYSIS OF AGGLOMERATES OF 50 WT%
INDIAN HEAD AND 50 WT% GPOP PHENOLS

	Indian Head	Phenols	With 20 wt% Iriton X-100		With 10 wt% Iriton X-100		With 5 wt% Iriton X-100		With 3 wt% Iriton X-100		With 1 wt% Iriton X-100	
With Moisture:												
Moisture	24.32	27.10	12.21		10.06		11.24	19.14	22.74	9.60	11.18	8.10
Volatiles	34.38	33.02	59.78		55.70		53.32	50.17	46.91	55.45	53.34	53.14
Fixed C	35.39	33.44	24.55		30.22		31.14	26.47	25.35	31.06	31.77	34.31
Ash	5.50	6.13	3.30		3.84		4.06	3.39	3.49	4.32	3.59	4.29
Moisture-Free:												
Volatiles	45.43	45.29	68.09		61.93		60.07	62.05	60.72	61.34	60.05	57.82
Fixed C	46.76	45.87	27.96		33.60		35.08	32.74	32.81	34.36	35.77	37.33
Ash	7.27	8.41	3.76		4.27		4.57	4.19	4.52	4.78	4.04	4.67
Moisture- and Oil-free:												
Volatiles			48.87		47.93		47.74	48.00	47.68	47.55	47.93	48.05
Fixed C			45.58		46.50		46.50	46.43	46.28	46.32	47.05	46.38
Ash	7.27	8.41	5.55		5.57		5.76	5.58	6.04	6.13	5.01	5.57
				1.06								

² Determined by Karl Fisher analysis.

Figure 34. Moisture and ash contents (on a moisture- and oil-free basis) as a function of air drying time for agglomerates of a mixture of 50 wt% Indian Head and 50 wt% GPGP phenols with Triton X-100 added as 3 wt% of the coal present.

3.5 Results of Tasks E and F - CPU Co-Processing Tests

The reconfiguration of the CPU in preparation for the co-processing screening tests was completed in May 1989. However, due to a lack of time caused by facilities repair of the CPU control area, the tests could not be performed as scheduled. These tests are important to the data base; therefore, they have been rescheduled to take place during the Year 4 program.

3.6 Results of Task G - Comparison of LRC-Derived Solvent and Co-Processing Tests

LRC-derived solvent was prepared in October 1988 for use in these studies. However, as mentioned previously, tests that involve the CPU have been rescheduled to take place during the Year 4 program.

3.7 Results of Task H - CPU Support

Because the CPU was not operated in a co-processing mode during Year 3, the analytical support for these runs could not take place. The CPU runs have been rescheduled for the Year 4 program.

3.8 Results of Task 1 - Hydrogen Transfer in the ChemCoal Process

To increase its viability, it is important that the products of the ChemCoal Process have access to various end-use markets. At this time, the liquid fuels market appears to be the most likely target. After determining if it is possible to upgrade the ChemCoal solids to a liquid fuel, it will be necessary to determine the effect of the catalyst on the phenolic solvent that may or may not be present in the hydrotreating stage. The upgrading scheme will need to be compared mechanistically to other catalytic upgrading processes to determine if the format of the coal-derived liquids from the ChemCoal Process is similar to those produced by other catalytic processes. In other words, it is necessary to determine if the ChemCoal Process operates under the same general mechanism as the other catalytic processes.

3.8.1 Hydrogenation Tests

During these studies, hydrogen transfer mechanisms during a second (i.e., hydrotreating) stage of the ChemCoal Process were investigated. The studies began with a microreactor screening of the conditions required to upgrade ChemCoal solids to liquids. Two microreactor runs were performed. The first run consisted of tests using (1) ChemCoal solids produced from Indian Head lignite, (2) ChemCoal solids with catalyst, (3) solvent only, and (4) ChemCoal solids, solvent, and catalyst. The initial hydrogen gas pressures varied from 400 to 1000 psi and the total reaction time for the run was 6 hours. The reactants and hydrogen pressures used in each of the microreactors during this run are listed in Table 21.

TABLE 21
CHEMCOAL SOLIDS HYDROGENATION TESTS

<u>Microreactor</u>	<u>Reactant^a</u>	<u>Pressure (psi)</u>
A	ChemCoal	400
B	ChemCoal	600
C	ChemCoal	800
D	ChemCoal	1000
E	ChemCoal + CoMoly ^b	400
F	ChemCoal + CoMoly	600
G	ChemCoal + CoMoly	800
H	ChemCoal + CoMoly	1000
I	Cresols ^c	600
J	ChemCoal + Cresols	600
K	ChemCoal + Cresols + CoMoly	600
L	ChemCoal + Cresols + CoMoly	1000

^a 1.0 g of each was used.

^b Catalyst.

^c m,p-Cresol solvent.

The results of the first microreactor run indicated that hydrogenation did not occur without a catalyst. Therefore, various catalysts were screened during the second microreactor run. Twelve catalysts were investigated, and the amount of hydrogen consumed was estimated for each of the reactions. This quantity was determined as follows. After loading the microreactors with ChemCoal solids, catalyst, and solvent, 2000 psi of hydrogen was added to each. The hydrogen gas was slowly removed from each reactor through a manometer and the volume of water displaced was measured and recorded. The reactors were repressurized to 2000 psi and reacted at 390°C for 2 hours. Following the reaction, the water displaced by the remaining hydrogen was measured, and the difference between the displacement prior to reaction and after reaction was calculated. Table 22 lists the reactants and quantity of hydrogen consumed per gram ChemCoal solids for each microreactor during the second run.

TABLE 22
CATALYST SCREENING DURING CHEMCOAL SOLID HYDROGENATION TESTING

Micro-reactor	Quantity of Reactants (g)			Catalyst	H ₂ Consumed at STP (ml/g ChemCoal)
	ChemCoal	Cresol	Catalyst		
A	0.91	4.05	1.01	Pyrrohtite	1060
B	0.99	3.92	1.08	NT-550	500
C	0.97	4.04	0.99	Trilobe HDN-60	908
D	0.94	3.91	1.14	Engelhard (Pt)	468
E	0.96	4.10	0.95	SiOAl ₂	390
F	0.96	4.03	1.01	Trilobe HDN-30	901
G	0.99	4.00	1.01	Co-Mo	529
H	0.99	4.02	0.99	ZnCl ₂	387
I	0.99	4.02	1.18	(NH ₄) ₂ MoO ₄	770
J	1.01	4.06	0.88	Pd on Carbon	427
K	1.02	4.00	0.98	Quinoline	344
L	1.06	4.02	0.95	NaOH	792

To produce enough product to complete the analytical work, it was necessary to perform an autoclave run. The test was performed in a 1-liter autoclave using one of the catalysts that performed well during the microreactor screening test, Trilobe HDN-60. Trilobe HDN-60 (SPS 0489-99) is an American Cyanamid Company catalyst. Rigorous reaction conditions were chosen for the autoclave run so that maximum product hydrogenation might take place.

Prior to the autoclave test, the catalyst was ground and sieved to -100 mesh and was activated by heating to 370°C for 1 hour. The feed materials (200 g finely divided ChemCoal solid product, 800 g commercial m,p-cresol, and 200 g Trilobe HDN-60) were charged at room temperature and a hydrogen gas pressure was maintained at 3500 psi throughout the test. The autoclave was heated to and held at 390°C for 3 hours, after which the reactor was allowed to cool to room temperature and the gas was metered out. Material collected in the cold trap was added to the bulk product.

3.8.2 Analytical Scheme

The product slurry was fractionated by filtration and distillation to provide four fractions for analysis, as shown in Table 23. Several analyses were performed on the feeds and product samples. Standard carbon, hydrogen, nitrogen, sulfur, Karl Fisher, and ash analyses were performed to provide elemental information. Thermogravimetric analysis was performed to provide a proximate analysis of volatiles, fixed carbon, and noncombustibles (ash). Proton NMR analysis was usually performed on the deuterated methylene chloride-soluble fraction to provide information about the product structures. Gas chromatography with flame ionization detection of volatiles was performed, usually followed by gas chromatography/mass spectroscopy for component identification. Gel permeation chromatography was performed to provide a molecular weight distribution of the THF-soluble fraction of the product. Short-column separation on activated silica gel produced four fractions: normal alkanes, branched alkanes, aromatics, and polar compounds. These fractions were analyzed further. Standard solubilities in excess hexane, methylene chloride, and THF were determined, and the soluble fractions were analyzed by GPC. Not all samples received the same analytical workups; the sample analysis scheme is given in Table 24.

3.8.3 Analytical Results

Product slurry recovered was filtered to remove the catalyst. The catalyst cake was analyzed using TGA and elemental analysis. The results of the elemental analyses are presented in Table 25. The catalyst cake appeared to contain too few solids. This is probably due to the difficulty in obtaining representative small samples when solids are present. The hydrogen-to-carbon ratio of 1.7 was also considered to be high, presumably due to excess hydrogen adsorbed on the catalyst. For the calculation of conversions, the liquids absorbed by the catalyst were considered to be the same as filtrate.

The filtrate was distilled to provide a cresol-rich solvent fraction and a converted ChemCoal solid fraction. The distillation results are presented in Table 26. With the exception of sulfur, good elemental and water balances were obtained for the total filtrate and the two fractions. The higher sulfur mass balance error is due to the low sulfur concentrations; this problem also occurs with the nitrogen compounds. Special calibrations would be necessary to improve the mass balances of these compounds.

TABLE 23
SUMMARY OF CHEMCOAL SOLID HYDROTREATMENT

Equipment and Materials

1-gal Autoclave system
800 g m,p-Cresol solvent
200 g ChemCoal solids
200 g HDN-60 catalyst
H₂ Reducing gas

Conditions

390°C Temperature
3 hrs Residence time
3000 psig pressure

Product Recovery

Loss on charging = 17 g
Weight charged = 1183 g
Weight recovered = 1187.6 g
Loss on transfer = 60.8 g
Weight filtered = 1126.8 g

^a Normalized.

TABLE 24
ANALYSIS SCHEME FOR HYDROGENATED CHEMCOAL SOLIDS SAMPLES

Sample	CHN	S	KF Water	Ash	TGA	Proton NMR	GC	GPC	Short Column	Solubility			
										Hex	MeCl ₂	THF	
Feedstocks:													
ChemCoal Solids	X	X	-	X	X	X	-	-	-	X	X	X	
Cresol Solvent	-	-	-	-	-	X	X	-	-	-	-	-	
Products:													
Filtrate	X	X	X	-	-	X	-	X	X	-	-	-	
Catalyst Cake	-	-	-	-	X	-	-	-	-	-	-	-	
Filtrate Distillate	X	X	X	-	-	X	-	X	X	X	X	X	
Filtrate Bottoms (>220°C)	X	X	-	-	X	X	X	X	X	X	X	X	

TABLE 25
RESULTS OF ELEMENTAL ANALYSIS OF DISTILLATE AND BOTTOMS
FRACTIONS OF HYDROGENATED CHEMCOAL SOLIDS

<u>Fraction</u>	<u>C</u> <u>(wt%)</u>	<u>H</u> <u>(wt%)</u>	<u>N</u> <u>(wt%)</u>	<u>S</u> <u>(wt%)</u>	<u>H₂O</u> <u>(wt%)</u>	<u>Ash</u> <u>(wt%)</u>	<u>H:C</u> <u>Ratio</u>
ChemCoal Solids	74.26	6.42	1.06	0.30	-- ^a	4.53	1.037
Filter Cake	17.44	2.47	0.28	0.27	--	53.26 ^b	1.700
Filtrate	75.67	8.73	0.23	0.07	4.26	--	1.384
Distillate	76.12	8.90	0.21	0.00	5.28	--	1.403
Bottoms	80.78	8.62	0.14	0.06	--	3.86 ^b	1.281
Dist. Bottoms	77.42	8.82	0.19	0.02	3.81	--	--
Bottoms Aromatics	86.78	9.01	0.37	0.04	--	--	1.246

^a Not determined.

^b Determined by TGA.

TABLE 26
HYDROGENATED CHEMCOAL FILTRATE D86 DISTILLATION DATA

<u>Volume Distilled (ml)</u>	<u>Filtrate (wt%)^a</u>	<u>Temp. (°C)</u>
IBP	0	76
5	4.78	84
10	9.56	86
20	19.12	93
30	28.68	195
40	38.24	198
50	47.80	200
60	57.36	200
70	66.92	202
80	76.48	205
90	86.04	210
95	90.82	--
Max. Volume (ml)		90
Max. Temp. (°C)		222
wt% Distilled		80.88
wt% Resid		18.45
wt% Lost		0.67

^a Assumes a density of 1.

Thermogravimetric analysis was used to obtain information about the volatility of the distillate bottoms; the information is presented in Table 27. At 45°C, light material was removed that had been trapped in the distillate bottoms during the bulk distillation. This material would not be observed during the GC analysis due to co-elution with the GC solvent. Material removed at 205°C would be approximately the same as would be seen by the GC. The material observed at 460°C consisted of the volatile matter contained in the solids, the fixed carbon of the solids as determined by combustion weight loss obtained by introducing air, and the ash (or catalyst) remaining after combustion.

TABLE 27
RESULTS OF TGA OF HYDROGENATED CHEMCOAL
FILTER CAKE AND DISTILLATION BOTTOMS^a

Component	Filter Cake (wt%)	Distillation Bottoms (wt%)
Moisture (Solvent) (45°C)	14.37	1.25
Volatile Matter (250°C)	13.53	36.50
Volatile Matter #2 (460°C)	12.39	44.24
Fixed Carbon	6.15	13.45
Ash	53.26	3.86

^a Unnormalized.

Solubilities in hexane, methylene chloride, and THF were determined for both the total filtrate and the distillate bottoms. The results are presented in Tables 28 and 29. From a fuels production point of view, the most important of these values is the conversion to hexane solubles (oils) of 83 to 86 wt%. Proton NMR analysis uses deuterated MeCl₂, and a high solubility of 90 to 94 wt% indicates that most of the material can be analyzed by NMR spectroscopy. Molecular weight determinations are made by GPC, which uses THF as a solvent. The high solubility of the product in THF indicates that the molecular weight distribution of virtually all of the product can be observed by GPC. In general, the solubility of the product in the various solvents tested indicated that the results of the planned analyses would be representative of virtually the entire product sample.

The quantity of normal aliphatics, branched aliphatics, aromatics, and polar compounds in a number of fractions was determined using short-column chromatography. The results of the short-column fractionation are listed in Table 29. The resulting compound-type samples were analyzed by NMR and GC to identify the specific compounds present and their structures. Polar compounds (primarily cresol solvent) comprised the main compound type present in the distillate fraction, while aromatic compounds (i.e., converted ChemCoal solids) made up the bottoms fraction.

TABLE 28
SOLUBILITY OF CHEMCOAL SOLID IN VARIOUS SOLVENTS^a

<u>Solvent</u>	<u>ChemCoal Solid</u>	<u>Hydrogenated Product</u>
Hexane	0	83-86
MeCl ₂	19	90-94
THF	61	91-95
Cresol	90	100

^a Values in wt%.

TABLE 29
RESULTS OF ANALYSIS OF FRACTIONATED PRODUCT SLURRY^a

<u>Analysis</u>	<u>Filtrate</u>	<u>Bottoms</u>	<u>Distillate</u>
Short-Column Chromatography:			
Normal Aliphatics	6.8	4.9	4.8
Branched Aliphatics	0.6	0.4	0.4
Aromatics	10.6	65.2	64.0
Polars	<u>65.0</u>	<u>29.4</u>	<u>28.8</u>
Total	83.0	99.9	98.0
Water	4.26	-- ^b	5.28
Solubility:			
HexI	2.70	16.96	--
MeCl ₂ I	1.82	6.19	--
THFI	1.83	5.52	--

^a Results in wt%.

^b Not analyzed.

Molecular weight distribution (MWD) determinations were made using GPC analysis on HPLC equipment at conditions that emphasize the presence of aromatics. The MWD values obtained during the analysis were compared to those of a standard mixture of polyglycols. Figure 35 shows the molecular weight profiles of the hexane-, methylene chloride-, and THF-soluble fractions of the distillate bottoms. The profiles of the methylene chloride- and THF-solubles are only slightly different, while the hexane solubles exhibit the presence of less of the higher molecular weight material. This is consistent with lower solubility. The molecular weight profile of the filtrate is compared to that of the distillate bottoms in Figure 36. The large amount of cresol solvent and toluene product are readily apparent in the filtrate profile. Extensive depolymerization of the solids during hydrotreating into distinct molecular weight groups can be seen by the shoulder between the cresol and toluene peaks and the peak at slightly higher molecular weights than cresol. In the initial coal product, only 60 wt% was soluble in THF and the solubles had a molecular weight profile that indicated the presence of material greater than 570 MW units. After hydrotreating, over 90 wt% was soluble in THF and the MW profile shows that most of the material weighed less than 570 MW units.

Proton NMR analyses were performed to provide information on the hydrogen distribution in the samples. As shown in Figure 37, the distillate contained aromatic cresol protons located near 7 ppm, while alkyl groups resonated near 2.3 ppm. The peaks near 0.9 and 1.2 ppm indicate that aliphatic functionalities were present either in longer side chains on aromatics or in discrete aliphatic molecules. The splitting of the 0.9-ppm peak indicates that the aliphatics were branched.

Figure 38 shows the proton NMR spectrum for the distillation bottoms. The strong aromatic peaks due to cresol are missing, but a sizable alkyl proton peak is still present. The multiple overlapping peaks occurring between 2 and 3 ppm indicate the presence of numerous different alkyl groups on aromatics, while the peaks between 0.9 and 2 ppm indicate the presence of numerous aliphatic functionalities. The low terminal methyl peak at 0.9 ppm and the large peak at 1.2 ppm indicating methyl groups located nearer to a more polar group (an aromatic) or methyl groups in an aliphatic functionality suggest that the aliphatic functionalities were in general longer and/or highly branched and/or were attached to an aromatic ring.

Proton NMR spectra of the short-column fractions of the distillation bottoms are shown in Figure 39. Branching of the aliphatic fraction is indicated by the splitting of the peak at 0.9 ppm. The aromatics appear to have been highly alkylated, with diverse aliphatic material present in longer chains. The polar fraction exhibits the presence of residual cresol and diverse aliphatic functionalities attached to polar aromatics. However, the aliphatics attached to the polar aromatics were shorter in length than those attached to the nonpolar material.

The aromatics present after hydrotreating contained less multiple-ring aromatics. This can be seen in Figure 40. Comparison of the aromatic NMR region of the distillate bottoms to that of the THF-soluble fraction of the ChemCoal solids indicates a substantial decrease in multiple-ring material.

Figure 35. Molecular weight profiles of the hexane-, methylene chloride-, and THF-soluble fractions of the distillation bottoms of hydrogenated ChemCoal solids.

Figure 36. Molecular weight profiles of hydrogenated ChemCoal solids distillation bottoms and filtrate.

Figure 37. Proton NMR spectrum of hydrogenated ChemCoal solids distillate.

Figure 38. Proton NMR spectrum of hydrogenated ChemCoal solids distillation bottoms.

Figure 39. Proton NMR spectra of the short-column fractions of hydrogenated ChemCoal solids distillation bottoms.

Figure 40. Proton NMR spectra of (top) THF-soluble fraction of ChemCoal solids and (bottom) hydrotreated ChemCoal solids aromatic material.

The volatile components of the various fractions were analyzed by GC with a flame ionization detector (FID) to obtain relative concentrations and by GC/MS to identify individual compounds. It was found that the distillate fraction was entirely volatile and contained primarily methyl cyclohexane, toluene, phenol, cresol, and more alkylated phenolics. The methyl cyclohexane and toluene are undoubtedly hydrotreated products of the initial cresol solvent. The phenol could have been coal derived or dealkylated cresol. However, the higher alkylated phenols are likely to be coal derived. The majority of coal products are observed in the distillate bottoms fraction. Residual cresol processing solvent was present as was dimethylphenylether, which may have been produced from the solvent. The presence of alkylated tetralins or indanes as well as phenanthrene and tetrahydrophenanthrene were noted. A series of easily identified alkanes (C21-C29) was present in the bottoms. These alkanes must have been present originally as long side chains on aromatics that broke off during processing.

The results of the analyses of the hydrotreated ChemCoal solids show that the ChemCoal solids can be upgraded to a liquid fuel. The fact that the hydrogenation required a catalyst that is used in other catalytic upgrading processes indicates that the transfer of hydrogen to the ChemCoal solid occurs by a reaction mechanism that is at least similar to that of the other upgrading processes. The products of the hydrogenation of ChemCoal solids fall into three distinct distillate regions: a gasoline fraction, a recycle phenolic fraction, and a heavy oil bottoms fraction. This product yield structure is similar to that of other catalytic upgrading processes.

3.9 Results of Task K - Low-Severity Direct Liquefaction

Further investigations of staged liquefaction were performed during the April through June transition quarter. The studies were performed on a batch scale using CO as the first-stage reductant and H₂S as a reaction promoter. It is known that staged liquefaction results in higher conversions of the coal and a higher yield than liquefaction in which the conversion and hydro-treatment take place in a single step. The highest conversions have been obtained when a low-severity first stage is employed prior to subsequent higher-severity treatment. The EMRC data base for staged liquefaction consists primarily of data from runs in which CO served as the first-stage reductant and H₂S was added as a reaction promoter. The ability to make direct comparisons with the existing data base determined that CO and H₂S would be used in the current studies.

Ten autoclave runs were performed. Indian Head lignite and phenolic solvent in a lignite to liquid solvent (as opposed to liquid and vapor-phase solvent) ratio of 1:3 were the feedstocks for each of the seven first-stage runs. Three second-stage runs were attempted using first-stage products as feedstocks. Difficulties were experienced during the quenching of one of the second-stage runs and no product was obtained. The autoclave runs are summarized in Table 30.

TABLE 30

SUMMARY OF THE BATCH STAGED LIQUEFACTION TESTS PERFORMED DURING JUNE
(all runs performed with POH and Indian Head lignite)

	Run No.	Temp. (°C)	Avg. Press. (psi)	Res. Time (min)	Reductant	Additive
1st Stage	N439	356	3379	60	CO	None
1st Stage	N440	370	4153	60	CO	None
1st Stage	N441	375	3405	60	CO	H ₂ S
1st Stage	N442	374	3469	60	CO	None
1st Stage	N443	374	3373	60	CO	H ₂ S
2nd Stage	N444	430	3831	12	H ₂	HA061
1st Stage	N445	374	3457	60	CO	H ₂ S
2nd Stage	N446	Run not completed.				
1st Stage	N447	374	3470	60	CO	H ₂ S
2nd Stage	N448	412	4092	19	H ₂	POH

The analytical results were not available for all of the runs. Table 31 presents the analytical results obtained for Runs N441 and N442. The runs were made with the same feedstocks at nominally the same conditions. The only difference was that H₂S was added to Run N441 as a promoter. Both product slurries were fairly light, but they differed greatly. The product of N441 was quite homogenous and thin, while the N442 product contained some hard solid material, indicating that coking may have occurred. During these runs, the lignite was converted to soluble resid.

The solubility of the product slurries was determined both in THF and in the phenolic solvent (POH). The THF solubility was determined using the standard method used during previous analyses. The phenolic solvent-insoluble (POHI) fraction was determined by dissolving approximately 0.2 g of the product slurry in 25 ml of the phenolic solvent. This solution was heated to boiling and, while hot, filtered through a 0.5-micron Millipore filter. When all of the liquid had passed through the filter, the solid residue was rinsed with room temperature POH until the washings were colorless.

Neither the THFI or POHI values are true conversion numbers; they are, however, indicative of the conversions and can serve as rough estimates. The low POHI value indicates a high conversion in the N441 sample in which H₂S was present. The POHI value for the product of Run N442 (5.19 wt%) was nearly as low as the POHI value of the N441 product (4.18 wt%). This is most likely due to the adsorption of H₂S on the reactor walls during Run N441.

TABLE 31
ANALYTICAL RESULTS OF N441 AND N442

	Indian Head		Solvent	Prod. Slurry	Prod. Slurry
	(as recd.)	(MF)	(POH)	N441 (H ₂ S)	N442 (no H ₂ S)
Elemental:					
C (wt%)	44.34	60.07	77.97	70.63	70.03
H (wt%)	6.09	8.25	7.61	7.57	7.44
N (wt%)	0.50	0.68	0.01	0.01	0.00
S (wt%)	0.71	1.00	0.00	0.53	0.18
Ash (wt%)	8.25	11.18	-- ^a	3.03	2.51
H ₂ O (wt%)	26.18	NA ^b	0.15	7.05	7.96
Solubility:					
THFI (wt%)	--	--	--	4.90	5.48
POHI (wt%)	--	--	--	4.19	5.18
ASTM D86 Distillation					
Sp. Gr.				1.085	1.085
Baro. Press. (mm Hg)				741.0	730.8
Room Temp. (°C)				21	19
Wt% Dist.				79.24	78.56
Wt% Resid.				18.68	20.15
Wt% Lost				2.07	1.29
Vol. % Dist.					
				Temp. (°C)	
IBP				100	100
5%				101	101
10%				195	106
20%				200	200
30%				201	201
40%				201	202
50%				202	202
60%				202	202
70%				203	203
80%				210	210
Max. Vol.				85	83.5
Max. Temp.				215	215

^a Not performed yet.

^b Not applicable.

The results of these preliminary analytical workups indicate that the addition of H_2S results in higher conversions and a more homogeneous product.

3.10 Papers/Presentations Made Based Upon the Results of Year 3 Work

The following presentations were made based upon the results of Year 3 work:

- "Low-Severity Liquefaction Using a Phenolic Solvent" by John R. Rindt, Melanie D. Hetland, and Curtis L. Knudson. Presented at the Direct Liquefaction Contractors' Review Meeting; Pittsburgh, PA; October 1988.
- ChemCoal Program Review Meeting; Washington, DC; February 1989.
- ChemCoal Program Review Meeting; Pittsburgh, PA; May 1989.
- "Preliminary Investigation of the ChemCoal Process Using Wyodak Subbituminous Coal" by John R. Rindt, Melanie D. Hetland, and Randal S. Sauer. Presented at the Fifteenth Biennial Low-Rank Fuels Symposium; St. Paul, MN; May 1989.
- "Low-Rank Coal Oil Agglomeration" by R.C. Timpe, R.W. Kulas, and C.L. Knudson. Presented at the Fifteenth Biennial Low-Rank Fuels Symposium; St. Paul, MN; May 1989.
- ChemCoal Technical Review Meeting; Grand Forks, ND; June 1989.

3.11 Conclusions

Task A - ChemCoal Process Verification:

- The phenolic solvent cuts deep into the coal to extract very heavy materials that appear to be heavier than preasphaltenes.
- Changes made in the CPU in the reactor, downstream processing, and control panel areas improved system operability, reliability, and safety.
- Mass balances of $\pm 2\%$ were easily obtained with the redesigned CPU.
- Due to retrograde polymerization reactions involving the solvent, the ChemCoal Process should not take place at temperatures greater than $360^\circ C$.
- Changes in temperature, pressure, and caustic loading were found to significantly affect the conversion and product slate. Surprisingly, residence time had very little effect on either conversion or the product slate.
- Pittsburgh No. 8 bituminous coal did not perform well in the ChemCoal Process system.
- The original Indian Head recycle run was successfully verified.

- It is easier to recover the ash/sodium if the partitioning solvent has been acidified.

Task B - Utilization Testing:

- Modification of the downstream processing loop to incorporate slightly warm partitioning solvent could eliminate at least one rinse of the ash cake and improve the operability of the primary centrifuge.
- It appears that the ChemCoal Process could produce an acceptable commercial coal-fired gas turbine fuel.

Task C - ChemCoal Economics:

- From an engineering economics point of view, the recommended ChemCoal operating conditions are as follows:

Temperature = 350°C
 Pressure = 1750 psi
 Residence Time = 3 hours
 Gas Flow Rate = 12 scfh
 Caustic Loading = 8 wt% MAF coal loading

OR

Temperature = 350°C
 Pressure = 2000 psi
 Residence Time = 0.6 hours
 Gas Flow Rate = 12 scfh
 Caustic Loading = 8 wt% MAF coal loading

Both sets of conditions result in an approximately 85% conversion. Selection of the appropriate set of conditions would be made based upon the capital costs of the pressure and the residence time.

Task D - LRC Agglomeration:

- Indian Head lignite can be successfully agglomerated in the GPGP crude phenol stream by the addition of Triton X-100 surfactant. An addition of 3 wt% Triton X-100 appears to be the most effective.

Task I - Hydrogen Transfer in the ChemCoal Process:

- The ChemCoal solid product can be upgraded to a liquid fuel. It appears that the mechanism by which this occurs is similar to that of other catalytic hydrogenation reactions.

Task K - Low-Severity Direct Liquefaction:

- The addition of H₂S to low-severity first-stage reactions involving Indian Head lignite and a phenolic solvent appears to result in higher conversions and a more homogeneous product.

4.0 FUTURE OBJECTIVES

- The Year 3 efforts involving CPU co-processing runs (Tasks E, F, G, and H) will be completed when the runs can be scheduled during the Year 4 activities.
- The analytical work on the low-severity staged liquefaction samples will be completed and the data reduced.
- The CPU will be operated at the preferred conditions established by the batch tests to confirm the batch data and to obtain process performance information.
- Analysis of various fractions of the ChemCoal Process and co-processing product slates will be performed to enable their comparison to the products of conventional direct liquefaction processes.
- Further investigations into low-severity liquefaction processes will continue with the investigation of preconversion treatment of LRCs. These tests will be performed on the microreactor system and will be used to screen conditions, solvents, and gases for their effects on the conversion of LRCs.
- Preconversion treatment tests will be performed on a batch scale using hydrogen-donating solvents in an effort to improve product selectivity and overall conversion.

5.0 ACKNOWLEDGMENTS

The authors wish to thank Dr. John Erjavec of the University of North Dakota Department of Chemical Engineering for his help with the statistical analysis of CPU Runs C152 and C153 and his assistance in interpreting the statistical results.

6.0 REFERENCES

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1. Program/Project Identification No. DE-FC21-86MC10637	2. Program/Project Title Direct Liquefaction of Low-Rank Coals	3. Reporting Period 4/01/88 through 6/30/89
4. Name and Address University of North Dakota Energy and Mineral Research Center Box 8213, University Station, Grand Forks, ND 58202		5. Program/Project Start Date 4/01/86
		6. Completion Date 3/31/92

11. Major Milestone Status	Units Planned	
	Units Complete	
a. ChemCoal Process Verification	P	▲ 1,2
	C	
b. Utilization Testing	P	▲ 1,2
	C	
c. ChemCoal Economics	P	▲ 1
	C	
d. LRC Agglomeration	P	▲ 1
	C	
e. CPU Co-Processing Screening Tests	P	▲ 1
	C	
g. Comparison of Co-processing and Coal-Derived Solvents	P	▲ 1
	C	
h. CPU Support	P	
	C	
i. H Transfer in the ChemCoal Process	P	
	C	
j. Final Report	P	
	C	
	P	
	C	
	P	
	C	
	P	
	C	
	P	
	C	
	P	
	C	
	P	
	C	
	P	
	C	

12. Remarks	
13. Signature of Recipient and Date	14. Signature of DOE Reviewing Representative and Date

1. Program/Project Identification No. DE-FC21-86MC10637	2. Program/Project Title Direct Liquefaction of Low-Rank Coals (5.1)	3. Reporting Period 4/1/88 through 6/30/89
4. Name and Address University of North Dakota Energy and Mineral Research Center Box 8213, University Station, Grand Forks, ND 58202		5. Program/Project Start Date 4/01/86
		6. Completion Date 3/31/92

7. FY	8. Months or Quarters	(89)	A	M	J		
88/89	Quarters						
9. Cost Status a. Dollars Expressed in		b. Dollar Scale					
		↓					
Thousands							
10. Cost Chart							
		Quarter				Cum. to Date	Tot. Plan
Fund Source		1st	2nd	3rd	4th		
DOE	P	130				625	625
	A	128				594	
	P						
	A						
	P						
	A						
	P						
	A						
Total P		130				625	625
Total A		128				594	
Variance		2				31	
P = Planned A = Actual							
Total Planned Costs for Program/Project							
\$624.8							
		c	Cumulative Accrued Costs				
		Planned			625		
		Actual			594		
		Variance			31		

[illegible]

12. Remarks

13. Signature of Recipient and Date	14. Signature of DOE Reviewing Representative and Date
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U.S. DEPARTMENT OF ENERGY
FEDERAL ASSISTANCE MANAGEMENT SUMMARY REPORT

1. Program/Project Identification No.	2. Program/Project Title Direct Liquefaction of Low-Rank Coals	3. Reporting Period 4/01/88 through 6/30/89
4. Name and Address University of North Dakota Energy and Mineral Research Center Box 8213, University Station, Grand Forks, ND 58202		5. Program/Project Start Date 4/01/86
		6. Completion Date 3/31/92

Milestone ID No.	Description	Planned Completion Date	Actual Completion Date	Comments
a.1	CPU operation, CC mode.	09/88	12/88	
a.2	CPU mass balancing analysis.	09/88	03/89	
b.1	Sample prep. for heat engine testing.	09/88	10/88	
b.2	Sample prep. for LRC-derived dist's.	09/88	10/88	
c.1	ChemCoal economic support.	10/88	03/89	
d.1	Agglomeration testing using LRC-derived solvents.	10/88	12/88	
e.1	CPU reconfiguration.	10/88	05/89	
e.2	CPU operation on co-processing matrix.	05/89	*	Changed from 01/89
e.3	CPU mass balancing analysis.	05/89	*	" "
e.4	Test evaluation.	06/89	*	Changed from 02/89
g.1	LRC-derived solvent preparation.	10/88	10/88	
g.2	CPU operation utilizing LRC-derived solvent.	05/89	*	Changed from 02/89
g.3	CPU mass balancing analysis support.	06/89	*	" "
h.1	Characterization of co-processing products.	06/89	*	" "
i.1	H transfer in the ChemCoal Process.	03/89	05/89	
j.1	Final Report.	06/89	08/89	Changed from 03/89
k.1	Batch testing.	06/89	06/89	
k.2	Analytical workup.	06/89		
k.3	Data reduction.	06/89		
k.4	Comparison of coal-derived liquids from ChemCoal Process and conventional liquefaction.	06/89	*	
* CPU runs (and associated analysis) that will be performed during Year 4.				

APPENDIX
RESULTS OF STATISTICAL ANALYSES


```

55      infile 'a:wyopooch1.dat';
56      input runid $ x1 x2 x3 y1 x4 x5;
57      label x1='Avg Temperature';
58      label x2='Avg Pressure';
59      label x3='Avg MAF Feed';
60      label x4='Gas Flow In';
61      label x5='Caustic Loading';
62      label y1='Liquid Flow Out';
63      proc print;
NOTE: The infile 'a:wyopooch1.dat' is file A:\WYOPOOH1.DAT.
NOTE: 19 records were read from the infile A:\WYOPOOH1.DAT.
      The minimum record length was 69.
      The maximum record length was 69.
NOTE: The data set WORK.X has 19 observations and 7 variables.
NOTE: The DATA statement used 23.00 seconds.
64      data ya;
NOTE: The PROCEDURE PRINT used 20.00 seconds.
65      infile 'a:wyopooch2.dat';
66      input y2-y8;
67      label y2='Gas Flow Out, scfh';
68      label y3='H2';
69      label y4='CO2';
70      label y5='H2S';
71      label y6='C2';
72      label y7='C1';
73      label y8='CO';
74      proc print;
NOTE: The infile 'a:wyopooch2.dat' is file A:\WYOPOOH2.DAT.
NOTE: 19 records were read from the infile A:\WYOPOOH2.DAT.
      The minimum record length was 63.
      The maximum record length was 63.
NOTE: The data set WORK.YA has 19 observations and 7 variables.
NOTE: The DATA statement used 24.00 seconds.
75      data yb;
NOTE: The PROCEDURE PRINT used 20.00 seconds.
76      infile 'a:wyopooch3.dat';
77      input y9-y11;
78      label y9='POHTHFI';
79      label y10='Conversion';
80      label y11='Water';
81      proc print;
NOTE: The infile 'a:wyopooch3.dat' is file A:\WYOPOOH3.DAT.
NOTE: 19 records were read from the infile A:\WYOPOOH3.DAT.
      The minimum record length was 30.
      The maximum record length was 30.
NOTE: The data set WORK.YB has 19 observations and 3 variables.
NOTE: The DATA statement used 20.00 seconds.
82      data z;
NOTE: The PROCEDURE PRINT used 17.00 seconds.
83      set x;
84      z1=(x1-345)/35;
85      z2=(x2-1750)/750;
86      z3=(x3-300)/200;
87      z4=(x4-15)/3;
88      z5=(x5-.05)/.03;
89      data regtot;
NOTE: The data set WORK.Z has 19 observations and 12 variables.
NOTE: The DATA statement used 21.00 seconds.
90      set z;
91      drop x1-x5;
92      z6=z1*z1;
93      z7=z2*z2;

```

```

98      merge ya;
99      merge yb;
100     proc print;
NOTE: The data set WORK.REGTOT has 19 observations and 23 variables.
NOTE: The DATA statement used 34.00 seconds.
101     proc reg data=regtot;
NOTE: The PROCEDURE PRINT used 37.00 seconds.
102         model y1=z1-z11/selection=stepwise r;
103     proc reg data=regtot;
NOTE: 19 observations read.
      19 observations used in computations.
NOTE: The PROCEDURE REG used 1.35 minutes.
104         model y2=z1-z11/selection=stepwise r;
105     proc reg data=regtot;
NOTE: 19 observations read.
      19 observations used in computations.
NOTE: The PROCEDURE REG used 1.32 minutes.
106         model y3=z1-z11/selection=stepwise r;
107     proc reg data=regtot;
NOTE: 19 observations read.
      19 observations used in computations.
NOTE: The PROCEDURE REG used 1.57 minutes.
108         model y4=z1-z11/selection=stepwise r;
109     proc reg data=regtot;
NOTE: 19 observations read.
      19 observations used in computations.
NOTE: The PROCEDURE REG used 1.33 minutes.
110         model y5=z1-z11/selection=stepwise r;
111     proc reg data=regtot;
NOTE: 19 observations read.
      16 observations have missing values.
      3 observations used in computations.
NOTE: The PROCEDURE REG used 56.00 seconds.
112         model y6=z1-z11/selection=stepwise r;
113     proc reg data=regtot;
NOTE: 19 observations read.
      13 observations have missing values.
      6 observations used in computations.
NOTE: The PROCEDURE REG used 1.20 minutes.
114         model y7=z1-z11/selection=stepwise r;
115     proc reg data=regtot;
NOTE: 19 observations read.
      7 observations have missing values.
      12 observations used in computations.
NOTE: The PROCEDURE REG used 1.48 minutes.
116         model y8=z1-z11/selection=stepwise r;
117     proc reg data=regtot;
NOTE: 19 observations read.
      19 observations used in computations.
NOTE: The PROCEDURE REG used 1.43 minutes.
118         model y9=z1-z11/selection=stepwise r;
119     proc reg data=regtot;
NOTE: 19 observations read.
      19 observations used in computations.
NOTE: The PROCEDURE REG used 1.43 minutes.
120         model y10=z1-z11/selection=stepwise r;
121     proc reg data=regtot;
NOTE: 19 observations read.
      19 observations used in computations.
NOTE: The PROCEDURE REG used 1.43 minutes.
122         model y11=z1-z11/selection=stepwise r;
123     run;

```

OBS	RUNID	X1	X2	X3	Y1	X4	X5
1	152-03-2	309.4	2495	288.192	2.8186	17.5616	0.05
2	152-04-3	345.1	2504	148.608	1.4183	17.5616	0.05
3	153-01-2	343.6	2521	471.043	4.5585	17.5616	0.05
4	153-02-2	375.4	2499	209.497	1.9567	17.5616	0.05
5	152-01-2	351.3	1756	315.019	3.0248	16.4080	0.02
6	152-02-2	350.2	1759	306.147	2.9701	16.4080	0.05
7	153-03-2	307.4	1746	469.669	4.6307	16.4080	0.05
8	153-04-2	307.6	1739	123.436	1.2218	16.4080	0.05
9	153-05-2	346.2	1741	298.787	2.8943	16.4080	0.05
10	153-06-2	347.2	1739	298.787	2.9388	12.6224	0.05
11	153-07-2	346.4	1765	298.787	2.9374	20.4064	0.05
12	153-08-2	343.7	1744	298.787	2.8565	16.4080	0.05
13	153-09-2	378.9	1741	441.292	4.2197	16.4080	0.05
14	153-10-2	383.0	1750	123.436	1.0690	16.4080	0.05
15	153-15-2	344.4	1757	311.044	2.9611	16.4080	0.08
16	153-11-2	376.8	1017	343.605	3.4615	15.9936	0.05
17	153-12-2	344.8	1019	507.486	5.0635	15.9936	0.05
18	153-13-2	344.9	985	101.494	0.9749	15.9936	0.05
19	153-14-2	308.9	986	321.811	3.2911	15.9936	0.05

OBS	Y2	Y3	Y4	Y5	Y6	Y7	Y8
1	18.24	1.6033	8.1880	.	.	.	90.2087
2	18.34	1.4443	5.4551	.	.	0.0416	93.0590
3	19.26	2.4974	13.0216	.	.	0.0411	84.4399
4	18.91	2.9109	11.7788	.	0.0312	0.1351	85.1440
5	17.60	0.6130	6.6371	.	.	.	92.7499
6	17.28	2.1548	11.4058	.	0.0207	0.0622	86.3566
7	17.30	0.9677	8.5032	.	.	.	90.5291
8	16.48	0.5392	3.8588	.	.	.	95.6021
9	17.31	1.4102	10.0463	.	.	0.0515	88.4920
10	13.02	2.3342	13.2095	.	0.0212	0.0637	84.3714
11	20.83	0.6715	6.8734	.	.	.	92.4551
12	17.92	1.3892	8.5231	.	.	0.0522	90.0355
13	18.44	2.2948	14.6185	0.0326	0.0489	0.2108	82.7943
14	18.34	1.7299	6.5695	0.0300	0.0477	0.1979	91.4250
15	18.31	2.5687	10.6610	.	.	0.0522	86.7182
16	15.59	0.7344	8.2040	0.0361	0.0467	0.2059	90.7729
17	16.17	0.6274	9.2849	.	.	0.0597	90.0280
18	16.32	0.7405	4.8994	.	.	.	94.3601
19	15.11	0.4726	5.9694	.	.	.	93.5580

OBS	Y9	Y10	Y11
1	0.1700	0.4023	0.108
2	0.0998	0.7248	0.045
3	0.1035	0.7025	0.054
4	0.1015	0.7268	0.041
5	0.1315	0.5459	0.068
6	0.1134	0.6577	0.057
7	0.1528	0.4732	0.075
8	0.1593	0.4413	0.049
9	0.1240	0.6119	0.069
10	0.1131	0.6522	0.058
11	0.1248	0.6002	0.071
12	0.1191	0.6402	0.065
13	0.1065	0.6948	0.087
14	0.1092	0.7278	0.069
15	0.1005	0.7603	0.054
16	0.1361	0.5347	0.098
17	0.1445	0.5026	0.084
18	0.1257	0.6090	0.055
19	0.1544	0.4403	0.089

OBS	RUNID	Y1	Z1	Z2	Z3	Z4	Z5	Z6
1	152-03-2	2.8186	-1.01714	0.99333	-0.05904	0.85387	0	1.03458
2	152-04-3	1.4183	0.00286	1.00533	-0.75696	0.85387	0	0.00001
3	153-01-2	4.5585	-0.04000	1.02800	0.85522	0.85387	0	0.00160
4	153-02-2	1.9567	0.86857	0.99867	-0.45251	0.85387	0	0.75442
5	152-01-2	3.0248	0.18000	0.00800	0.07510	0.46933	-1	0.03240
6	152-02-2	2.9701	0.14857	0.01200	0.03073	0.46933	0	0.02207
7	153-03-2	4.6307	-1.07429	-0.00533	0.84835	0.46933	0	1.15409
8	153-04-2	1.2218	-1.06857	-0.01467	-0.88282	0.46933	0	1.14184
9	153-05-2	2.8943	0.03429	-0.01200	-0.00606	0.46933	0	0.00118
10	153-06-2	2.9388	0.06286	-0.01467	-0.00606	-0.79253	0	0.00395
11	153-07-2	2.9374	0.04000	0.02000	-0.00606	1.80213	0	0.00160
12	153-08-2	2.8565	-0.03714	-0.00800	-0.00606	0.46933	0	0.00138
13	153-09-2	4.2197	0.96857	-0.01200	0.70646	0.46933	0	0.93813
14	153-10-2	1.0690	1.08571	0.00000	-0.88282	0.46933	0	1.17878
15	153-15-2	2.9611	-0.01714	0.00933	0.05522	0.46933	1	0.00029
16	153-11-2	3.4615	0.90857	-0.97733	0.21803	0.33120	0	0.82550

OBS	Z7	Z8	Z9	Z10	Z11	Y2	Y3	Y4
1	0.98671	0.00349	-1.01036	0.06005	-0.05864	18.24	1.6033	8.1880
2	1.01070	0.57299	0.00287	-0.00216	-0.76100	18.34	1.4443	5.4551
3	1.05678	0.73140	-0.04112	-0.03421	0.87916	19.26	2.4974	13.0216
4	0.99734	0.20477	0.86741	-0.39304	-0.45191	18.91	2.9109	11.7788
5	0.00006	0.00564	0.00144	0.01352	0.00060	17.60	0.6130	6.6371
6	0.00014	0.00094	0.00178	0.00457	0.00037	17.28	2.1548	11.4058
7	0.00003	0.71969	0.00573	-0.91137	-0.00452	17.30	0.9677	8.5032
8	0.00022	0.77938	0.01567	0.94336	0.01295	16.48	0.5392	3.8588
9	0.00014	0.00004	-0.00041	-0.00021	0.00007	17.31	1.4102	10.0463
10	0.00022	0.00004	-0.00092	-0.00038	0.00009	13.02	2.3342	13.2095
11	0.00040	0.00004	0.00080	-0.00024	-0.00012	20.83	0.6715	6.8734
12	0.00006	0.00004	0.00030	0.00023	0.00005	17.92	1.3892	8.5231
13	0.00014	0.49909	-0.01162	0.68426	-0.00848	18.44	2.2948	14.6185
14	0.00000	0.77938	0.00000	-0.95849	0.00000	18.34	1.7299	6.5695
15	0.00009	0.00305	-0.00016	-0.00095	0.00052	18.31	2.5687	10.6610
16	0.95518	0.04754	-0.88798	0.19809	-0.21308	15.59	0.7344	8.2040

OBS	Y5	Y6	Y7	Y8	Y9	Y10	Y11
1	.	.	.	90.2087	0.1700	0.4023	0.108
2	.	.	0.0416	93.0590	0.0998	0.7248	0.045
3	.	.	0.0411	84.4399	0.1035	0.7025	0.054
4	.	0.0312	0.1351	85.1440	0.1015	0.7268	0.041
5	.	.	.	92.7499	0.1315	0.5459	0.068
6	.	0.0207	0.0622	86.3566	0.1134	0.6577	0.057
7	.	.	.	90.5291	0.1528	0.4732	0.075
8	.	.	.	95.6021	0.1593	0.4413	0.049
9	.	.	0.0515	88.4920	0.1240	0.6119	0.069
10	.	0.0212	0.0637	84.3714	0.1131	0.6522	0.058
11	.	.	.	92.4551	0.1248	0.6002	0.071
12	.	.	0.0522	90.0355	0.1191	0.6402	0.065
13	0.0326	0.0489	0.2108	82.7943	0.1065	0.6948	0.087
14	0.0300	0.0477	0.1979	91.4250	0.1092	0.7278	0.069
15	.	.	0.0522	86.7182	0.1005	0.7603	0.054
16	0.0361	0.0467	0.2059	90.7729	0.1361	0.5347	0.098

OBS	RUNID	Y1	Z1	Z2	Z3	Z4	Z5	Z6
17	153-12-2	5.0635	-0.00571	-0.97467	1.03743	0.33120	0	0.00003
18	153-13-2	0.9749	-0.00286	-1.02000	-0.99253	0.33120	0	0.00001
19	153-14-2	3.2911	-1.03143	-1.01867	0.10906	0.33120	0	1.06384
OBS	Z7	Z8	Z9	Z10	Z11	Y2	Y3	Y4
17	0.94998	1.07626	0.00557	-0.00593	-1.01115	16.17	0.6274	9.2849
18	1.04040	0.98511	0.00291	0.00284	1.01238	16.32	0.7405	4.8994
19	1.03768	0.01189	1.05068	-0.11248	-0.11109	15.11	0.4726	5.9694
OBS	Y5	Y6	Y7	Y8	Y9	Y10	Y11	
17	.	.	0.0597	90.0280	0.1445	0.5026	0.084	
18	.	.	.	94.3601	0.1257	0.6090	0.055	
19	.	.	.	93.5580	0.1544	0.4403	0.089	

Stepwise Procedure for Dependent Variable Y1

Step 1 Variable Z3 Entered R-square = 0.99663950 C(p) = 28.83705246

	DF	Sum of Squares	Mean Square	F	Prob>F
Regression	1	25.54477390	25.54477390	5041.77	0.0001
Error	17	0.08613271	0.00506663		
Total	18	25.63090661			

Variable	Parameter Estimate	Standard Error	Type II Sum of Squares	F	Prob>F
INTERCEP	2.92091599	0.01633076	162.08557153	31990.8	0.0001
Z3	1.99471836	0.02809248	25.54477390	5041.77	0.0001

Bounds on condition number: 1, 1

Step 2 Variable Z2 Entered R-square = 0.99774010 C(p) = 16.47989494

	DF	Sum of Squares	Mean Square	F	Prob>F
Regression	2	25.57298339	12.78649169	3531.98	0.0001
Error	16	0.05792322	0.00362020		
Total	18	25.63090661			

Variable	Parameter Estimate	Standard Error	Type II Sum of Squares	F	Prob>F
INTERCEP	2.92093012	0.01380426	162.08711804	44773.0	0.0001
Z2	-0.05954227	0.02133016	0.02820949	7.79	0.0131
Z3	1.98809910	0.02386445	25.12498480	6940.22	0.0001

Bounds on condition number: 1.009972, 4.039886

Step 3 Variable Z1 Entered R-square = 0.99861538 C(p) = 7.06209092

	DF	Sum of Squares	Mean Square	F	Prob>F
Regression	3	25.59541752	8.53180584	3606.10	0.0001
Error	15	0.03548908	0.00236594		
Total	18	25.63090661			

Variable	Parameter Estimate	Standard Error	Type II Sum of Squares	F	Prob>F
INTERCEP	2.92092053	0.01115960	162.08604151	68508.1	0.0001
Z1	-0.05258066	0.01707549	0.02243414	9.48	0.0076
Z2	-0.05990165	0.01724406	0.02854974	12.07	0.0034
Z3	1.98386154	0.01934145	24.89134441	10520.7	0.0001

Bounds on condition number: 1.01511, 9.090649

Step 4 Variable Z7 Entered R-square = 0.99908803 C(p) = 2.89642686

	DF	Sum of Squares	Mean Square	F	Prob>F
Regression	4	25.60753206	6.40188301	3834.36	0.0001
Error	14	0.02337455	0.00166961		
Total	18	25.63090661			

Variable	Parameter Estimate	Standard Error	Type II Sum of Squares	F	Prob>F
INTERCEP	2.89936057	0.01232666	92.36962985	55324.0	0.0001
Z1	-0.05010976	0.01437359	0.02029222	12.15	0.0036
Z2	-0.06045023	0.01448733	0.02906931	17.41	0.0009
Z3	1.98437720	0.01624894	24.90082927	14914.2	0.0001
Z7	0.05098063	0.01892603	0.01211453	7.26	0.0175

Bounds on condition number: 1.015251, 16.15617

Step 5 Variable Z11 Entered R-square = 0.99929790 C(p) = 2.15871213

	DF	Sum of Squares	Mean Square	F	Prob>F
Regression	5	25.61291122	5.12258224	3700.59	0.0001
Error	13	0.01799539	0.00138426		
Total	18	25.63090661			

Variable	Parameter Estimate	Standard Error	Type II Sum of Squares	F	Prob>F
INTERCEP	2.89893494 ✓	0.01122605	92.30835117	66684.2	0.0001
Z1	-0.05269755 ✓	0.01315347	0.02221868	16.05	0.0015
Z2	-0.06123928 ✓	0.01319743	0.02980569	21.53	0.0005
Z3	1.98040202 ✓	0.01493217	24.34884793	17589.8	0.0001
Z7	0.04846444 ✓	0.01728020	0.01088846	7.87	0.0149
Z11	-0.03905440 ✓	0.01981168	0.00537917	3.89	0.0704

Bounds on condition number: 1.034111, 25.53053

All variables in the model are significant at the 0.1500 level.
No other variable met the 0.1500 significance level for entry into the model.

Summary of Stepwise Procedure for Dependent Variable Y1

Step	Variable Entered	Number Removed	In	Partial R**2	Model R**2	C(p)	F	Prob>F
1	Z3		1	0.9966	0.9966	28.8371	5041.7681	0.0001
2	Z2		2	0.0011	0.9977	16.4799	7.7922	0.0171
3	Z1		3	0.0009	0.9986	7.0621	9.4821	0.0076
4	Z7		4	0.0005	0.9991	2.8964	7.2559	0.0175
5	Z11		5	0.0002	0.9993	2.1587	3.8859	0.0704

Obs	Dep Var Y1	Predict Value	Std Err Predict	Residual	Std Err Residual	Student Residual
1	2.8186	2.8249	0.022	-0.00630	0.030	-0.211
2	1.4183	1.4168	0.026	0.00147	0.027	0.054
3	4.5585	4.5486	0.032	0.0099	0.019	0.512
4	1.9567	1.9618	0.023	-0.00513	0.029	-0.177
5	3.0248	3.0377	0.011	-0.0129	0.035	-0.363
6	2.9701	2.9512	0.011	0.0189	0.035	0.533
7	4.6307	4.6361	0.022	-0.00542	0.030	-0.179
8	1.2218	1.2073	0.023	0.0145	0.029	0.499
9	2.8943	2.8859	0.011	0.00844	0.035	0.238
10	2.9388	2.8845	0.011	0.0543	0.035	1.530
11	2.9374	2.8836	0.011	0.0538	0.035	1.516
12	2.8565	2.8894	0.011	-0.0329	0.035	-0.927
13	4.2197	4.2480	0.020	-0.0283	0.031	-0.908
14	1.0690	1.0934	0.021	-0.0244	0.030	-0.801
15	2.9611	3.0086	0.011	-0.0475	0.035	-1.340
16	3.4615	3.3973	0.022	0.0642	0.030	2.149
17	5.0635	5.0990	0.028	-0.0355	0.024	-1.483
18	0.9749	1.0068	0.031	-0.0319	0.020	-1.604
19	3.2911	3.2863	0.023	0.00482	0.029	0.166

Obs	-2	-1	-0	1	2	Cook's D
1						0.004
2						0.000
3				*		0.120
4						0.003
5						0.002
6				*		0.005
7						0.003
8						0.026
9						0.001
10				***		0.039
11				***		0.038
12			*			0.014
13			*			0.058
14			*			0.053
15			**			0.030
16				****		0.424
17			**			0.521
18			***			1.070
19						0.003

Sum of Residuals 7.771561E-16
 Sum of Squared Residuals 0.0180
 Predicted Resid SS (Press) 0.0467

Stepwise Procedure for Dependent Variable Y2

Step 1 Variable Z4 Entered R-square = 0.78924342 C(p) = 21.76871095

	DF	Sum of Squares	Mean Square	F	Prob>F
Regression	1	42.19198947	42.19198947	63.66	0.0001
Error	17	11.26678948	0.66275232		
Total	18	53.45877895			

Variable	Parameter Estimate	Standard Error	Type II Sum of Squares	F	Prob>F
INTERCEP	15.69929042	0.28424474	2021.74518540	3050.53	0.0001
Z4	3.25685946	0.40818745	42.19198947	63.66	0.0001

Bounds on condition number: 1, 1

Step 2 Variable Z2 Entered R-square = 0.85085968 C(p) = 13.01910355

	DF	Sum of Squares	Mean Square	F	Prob>F
Regression	2	45.48591956	22.74295978	45.64	0.0001
Error	16	7.97285938	0.49830371		
Total	18	53.45877895			

Variable	Parameter Estimate	Standard Error	Type II Sum of Squares	F	Prob>F
INTERCEP	15.89435650	0.25788312	1892.92834935	3798.74	0.0001
Z2	0.69186289	0.26909765	3.29393010	6.61	0.0205
Z4	2.88406043	0.38249055	28.33096750	56.85	0.0001

Bounds on condition number: 1.167829, 4.671316

Step 3 Variable Z1 Entered R-square = 0.89330068 C(p) = 7.61482372

	DF	Sum of Squares	Mean Square	F	Prob>F
Regression	3	47.75476337	15.91825446	41.86	0.0001
Error	15	5.70401558	0.38026771		
Total	18	53.45877895			

Variable	Parameter Estimate	Standard Error	Type II Sum of Squares	F	Prob>F
INTERCEP	15.88767498	0.22529554	1891.05841859	1972.97	0.0001
Z1	0.52749939	0.21595556	2.26884380	5.97	0.0274
Z2	0.68837701	0.23507994	3.26070126	8.57	0.0104
Z4	2.89649241	0.33417100	28.56911123	75.13	0.0001

Bounds on condition number: 1.1681, 10.00861

Step 4 Variable Z7 Entered R-square = 0.92313115 C(p) = 4.41058188

	DF	Sum of Squares	Mean Square	F	Prob>F
Regression	4	49.34946429	12.33736607	42.03	0.0001
Error	14	4.10931466	0.29352248		
Total	18	53.45877895			

Variable	Parameter Estimate	Standard Error	Type II Sum of Squares	F	Prob>F
INTERCEP	16.08888691	0.21594278	1629.35603490	5551.04	0.0001
Z1	0.50017872	0.19009360	2.03215475	6.92	0.0197
Z2	0.67065198	0.20667394	3.09075347	10.53	0.0059
Z4	2.98874858	0.29624827	29.87503827	101.78	0.0001
Z7	-0.59016371	0.25319409	1.59470092	5.43	0.0352

Bounds on condition number: 1.18933, 17.54129

Step 5 Variable Z8 Entered R-square = 0.93606338 C(p) = 4.15441803

	DF	Sum of Squares	Mean Square	F	Prob>F
Regression	5	50.04080545	10.00816109	38.07	0.0001
Error	13	3.41797350	0.26292104		
Total	18	53.45877895			

Variable	Parameter Estimate	Standard Error	Type II Sum of Squares	F	Prob>F
INTERCEP	15.95803179	0.21973097	1386.76045615	5274.44	0.0001
Z1	0.50200705	0.17991527	2.04695801	7.79	0.0153
Z2	0.70984840	0.19709187	3.41050848	12.97	0.0032
Z4	2.99131190	0.28038517	29.92650962	113.82	0.0001
Z7	-0.69551955	0.24828417	2.06322205	7.85	0.0150
Z8	0.51490196	0.31753457	0.69134116	2.63	0.1289

Bounds on condition number: 1.189369, 27.85408

All variables in the model are significant at the 0.1500 level.
No other variable met the 0.1500 significance level for entry into the model.

Summary of Stepwise Procedure for Dependent Variable Y2

Step	Variable Entered	Variable Removed	Number In	Partial R**2	Model R**2	C(p)	F	Prob>F
1	Z4		1	0.7892	0.7892	21.7687	63.6618	0.0001
2	Z2		2	0.0616	0.8509	13.0191	6.6103	0.0205
3	Z1		3	0.0424	0.8933	7.6148	5.9664	0.0274
4	Z7		4	0.0298	0.9231	4.4106	5.4330	0.0352
5	Z8		5	0.0129	0.9361	4.1544	2.6295	0.1289

Obs	Dep Var Y2	Predict Value	Std Err Predict	Residual	Std Err Residual	Student Residual
1	18.2400	18.0223	0.329	0.2177	0.394	0.553
2	18.3400	18.8194	0.263	-0.4794	0.440	-1.090
3	19.2600	18.8635	0.286	0.3965	0.425	0.932
4	18.9100	19.0690	0.307	-0.1590	0.411	-0.387
5	17.6000	17.4609	0.175	0.1391	0.482	0.289
6	17.2800	17.4455	0.175	-0.1655	0.482	-0.343
7	17.3000	17.1894	0.292	0.1106	0.421	0.262
8	16.4800	17.2163	0.301	-0.7363	0.415	-1.775
9	17.3100	17.3706	0.174	-0.0606	0.482	-0.126
10	13.0200	13.6083	0.396	-0.5883	0.326	-1.803
11	20.8300	21.3829	0.409	-0.5529	0.310	-1.785
12	17.9200	17.3376	0.175	0.5824	0.482	1.208
13	18.4400	18.0966	0.242	0.3434	0.452	0.759
14	18.3400	18.3083	0.297	0.0317	0.418	0.076
15	18.3100	17.3615	0.174	0.9485	0.482	1.966
16	15.5900	16.0713	0.337	-0.4813	0.386	-1.246
17	16.1700	16.1475	0.304	0.0225	0.413	0.055
18	16.3200	16.0069	0.300	0.3131	0.416	0.753
19	15.1100	14.9923	0.360	0.1177	0.365	0.323

Obs	-2	-1	0	1	2	Cook's D
1				*		0.036
2		**				0.071
3				*		0.066
4						0.014
5						0.002
6						0.003
7						0.006
8		***				0.277
9						0.000
10		***				0.796
11		***				0.924
12				**		0.032
13				*		0.027
14						0.000
15				***		0.084
16		**				0.197
17						0.000
18				*		0.049
19						0.017

Sum of Residuals 7.993606E-14
 Sum of Squared Residuals 3.4180
 Predicted Resid SS (Press) 9.4945

Stepwise Procedure for Dependent Variable Y3

Step 1 Variable Z2 Entered R-square = 0.37261882 C(p) = 70.68969790

	DF	Sum of Squares	Mean Square	F	Prob>F
Regression	1	4.32132421	4.32132421	10.10	0.0055
Error	17	7.27584694	0.42799100		
Total	18	11.59717115			

Variable	Parameter Estimate	Standard Error	Type II Sum of Squares	F	Prob>F
INTERCEP	1.45743629	0.15008626	40.35821071	94.30	0.0001
Z2	0.73329992	0.23077594	4.32132421	10.10	0.0055

Bounds on condition number: 1, 1

Step 2 Variable Z1 Entered R-square = 0.54241815 C(p) = 49.49796980

	DF	Sum of Squares	Mean Square	F	Prob>F
Regression	2	6.29051617	3.14525808	9.48	0.0019
Error	16	5.30665498	0.33166594		
Total	18	11.59717115			

Variable	Parameter Estimate	Standard Error	Type II Sum of Squares	F	Prob>F
INTERCEP	1.45728865	0.13212169	40.35002612	121.66	0.0001
Z1	0.49137529	0.20165998	1.96919196	5.94	0.0269
Z2	0.73314137	0.20315320	4.31945541	13.02	0.0024

Bounds on condition number: 1, 4

Step 3 Variable Z5 Entered R-square = 0.72431983 C(p) = 26.65326622

	DF	Sum of Squares	Mean Square	F	Prob>F
Regression	3	8.40006101	2.80002034	13.14	0.0002
Error	15	3.19711014	0.21314068		
Total	18	11.59717115			

Variable	Parameter Estimate	Standard Error	Type II Sum of Squares	F	Prob>F
INTERCEP	1.45728134	0.10591485	40.34962117	189.31	0.0001
Z1	0.51623053	0.16185289	2.16826702	10.17	0.0061
Z2	0.73296275	0.16285700	4.31735037	20.26	0.0004
Z5	1.02824694	0.32684076	2.10954485	9.90	0.0067

Bounds on condition number: 1.002389, 9.014332

Step 4 Variable Z4 Entered R-square = 0.84967963 C(p) = 11.53122958

	DF	Sum of Squares	Mean Square	F	Prob>F
Regression	4	9.85388009	2.46347002	19.78	0.0001
Error	14	1.74329106	0.12452079		
Total	18	11.59717115			

Variable	Parameter Estimate	Standard Error	Type II Sum of Squares	F	Prob>F
INTERCEP	1.80012052	0.12892256	24.27656320	194.96	0.0001
Z1	0.50978120	0.12372537	2.11393651	16.98	0.0010
Z2	0.90723090	0.13452155	5.66361570	45.48	0.0001
Z4	-0.65340038	0.19122520	1.45381908	11.68	0.0042
Z5	1.02749504	0.24981824	2.10645916	16.92	0.0011

Bounds on condition number: 1.168101, 17.36394

Step 5 Variable Z3 Entered R-square = 0.87564475 C(p) = 9.98483154

	DF	Sum of Squares	Mean Square	F	Prob>F
Regression	5	10.15500205	2.03100041	18.31	0.0001
Error	13	1.44216910	0.11093608		
Total	18	11.59717115			

Variable	Parameter Estimate	Standard Error	Type II Sum of Squares	F	Prob>F
INTERCEP	1.80078292	0.12168772	24.29416761	218.99	0.0001
Z1	0.52358507	0.11708173	2.21854935	20.00	0.0006
Z2	0.92628002	0.12749717	5.85539685	52.78	0.0001
Z3	0.21821260	0.13244789	0.30112195	2.71	0.1234
Z4	-0.65217943	0.18049463	1.44836650	13.06	0.0032
Z5	1.03101144	0.23580739	2.12072797	19.12	0.0008

Bounds on condition number: 1.177557, 26.85571

Step 6 Variable Z9 Entered R-square = 0.90558903 C(p) = 7.89494808

	DF	Sum of Squares	Mean Square	F	Prob>F
Regression	6	10.50227094	1.75037849	19.18	0.0001
Error	12	1.09490021	0.09124168		
Total	18	11.59717115			

Variable	Parameter Estimate	Standard Error	Type II Sum of Squares	F	Prob>F
INTERCEP	1.80131501	0.11035914	24.30837811	266.42	0.0001
Z1	0.53054521	0.10624154	2.27535603	24.94	0.0003
Z2	0.94367986	0.11597087	6.04150084	66.21	0.0001
Z3	0.24307672	0.12079147	0.36949409	4.05	0.0672

Z4	-0.65302054	0.16369146	1.45209475	15.91	0.0018
Z5	1.03218125	0.21385497	2.12552645	23.30	0.0004
Z9	0.31032570	0.15906750	0.34726889	3.81	0.0748

Bounds on condition number: 1.184563, 38.4472

Step 7 Variable Z11 Entered R-square = 0.93823011 C(p) = 5.43672584

	DF	Sum of Squares	Mean Square	F	Prob>F
Regression	7	10.88081519	1.55440217	23.87	0.0001
Error	11	0.71635596	0.06512327		
Total	18	11.59717115			

Variable	Parameter Estimate	Standard Error	Type II Sum of Squares	F	Prob>F
INTERCEP	1.81148376	0.09333052	24.53339740	376.72	0.0001
Z1	0.55213458	0.09020206	2.44001878	37.47	0.0001
Z2	0.95117948	0.09802552	6.13172783	94.16	0.0001
Z3	0.27898451	0.10312985	0.47657097	7.32	0.0205
Z4	-0.64850203	0.13830483	1.43180605	21.99	0.0007
Z5	1.03470177	0.18067501	2.13584840	32.80	0.0001
Z9	0.34354755	0.13509026	0.42117426	6.47	0.0273
Z11	0.32847430	0.13624205	0.37854425	5.81	0.0346

Bounds on condition number: 1.185757, 52.42236

All variables in the model are significant at the 0.1500 level.
No other variable met the 0.1500 significance level for entry into the model.

Summary of Stepwise Procedure for Dependent Variable Y3

Step	Variable Entered	Number Removed	Number In	Partial R**2	Model R**2	C(p)	F	Prob>F
1	Z2		1	0.3726	0.3726	70.6897	10.0968	0.0055
2	Z1		2	0.1698	0.5424	49.4980	5.9373	0.0269
3	Z5		3	0.1819	0.7243	26.6533	9.8974	0.0067
4	Z4		4	0.1254	0.8497	11.5312	11.6753	0.0042
5	Z3		5	0.0260	0.8756	9.9848	2.7144	0.1234
6	Z9		6	0.0299	0.9056	7.8949	3.8060	0.0748
7	Z11		7	0.0326	0.9382	5.4367	5.8127	0.0346

Obs	Dep Var Y3	Predict Value	Std Err Predict	Residual	Std Err Residual	Student Residual
1	1.6033	1.2581	0.194	0.3452	0.165	2.086
2	1.4443	1.7554	0.166	-0.3111	0.194	-1.602
3	2.4974	2.7267	0.203	-0.2293	0.155	-1.484
4	2.9109	2.7105	0.187	0.2004	0.174	1.154
5	0.6130	0.6011	0.190	0.0119	0.170	0.070
6	2.1548	1.6099	0.061	0.5449	0.248	2.199
7	0.9677	1.1461	0.139	-0.1784	0.214	-0.832
8	0.5392	0.6665	0.149	-0.1273	0.207	-0.615
9	1.4102	1.5128	0.059	-0.1026	0.248	-0.413
10	2.3342	2.3442	0.191	-0.0100	0.169	-0.059
11	0.6715	0.6824	0.186	-0.0109	0.175	-0.063
12	1.3892	1.4774	0.059	-0.0882	0.248	-0.355
13	2.2948	2.2208	0.133	0.0740	0.218	0.340
14	1.7299	1.8603	0.140	-0.1304	0.213	-0.612
15	2.5687	2.5568	0.190	0.0119	0.170	0.070
16	0.7344	0.8545	0.184	-0.1201	0.177	-0.679
17	0.6274	0.6257	0.188	0.00173	0.173	0.010
18	0.7405	0.6816	0.200	0.0589	0.159	0.371
19	0.4726	0.4132	0.195	0.0594	0.165	0.360

Obs	-2	-1	-0	1	2	Cook's D
1				****		0.749
2		***				0.233
3		**				0.475
4			**			0.193
5						0.001
6			****			0.037
7		*				0.036
8		*				0.024
9						0.001
10						0.001
11						0.001
12						0.001
13						0.005
14		*				0.020
15						0.001
16		*				0.062
17						0.000
18						0.027
19						0.022

Sum of Residuals	-6.10623E-16
Sum of Squared Residuals	0.7164
Predicted Resid SS (Press)	2.1499

Stepwise Procedure for Dependent Variable Y4

Step 1 Variable Z3 Entered R-square = 0.33908980 C(p) = 42.43152127

	DF	Sum of Squares	Mean Square	F	Prob>F
Regression	1	55.98796948	55.98796948	8.72	0.0089
Error	17	109.12454335	6.41909079		
Total	18	165.11251283			

Variable	Parameter Estimate	Standard Error	Type II Sum of Squares	F	Prob>F
INTERCEP	8.84463469	0.58127768	1486.16156499	231.52	0.0001
Z3	2.95309836	0.99992474	55.98796948	8.72	0.0089

Bounds on condition number: 1, 1

Step 2 Variable Z1 Entered R-square = 0.52927390 C(p) = 27.90497657

	DF	Sum of Squares	Mean Square	F	Prob>F
Regression	2	87.38974335	43.69487167	9.00	0.0024
Error	16	77.72276948	4.85767309		
Total	18	165.11251283			

Variable	Parameter Estimate	Standard Error	Type II Sum of Squares	F	Prob>F
INTERCEP	8.84499652	0.50566285	1486.28304789	305.97	0.0001
Z1	1.96715456	0.77370524	31.40177387	6.46	0.0217
Z3	3.11013981	0.87204085	61.78946773	12.72	0.0026

Bounds on condition number: 1.005042, 4.020168

Step 3 Variable Z2 Entered R-square = 0.64725525 C(p) = 19.65267830

	DF	Sum of Squares	Mean Square	F	Prob>F
Regression	3	106.86994067	35.62331356	9.17	0.0011
Error	15	58.24257216	3.88283814		
Total	18	165.11251283			

Variable	Parameter Estimate	Standard Error	Type II Sum of Squares	F	Prob>F
INTERCEP	8.84462710	0.45208654	1486.15869960	382.75	0.0001
Z1	1.97764101	0.69174493	31.73600382	8.17	0.0119
Z2	1.56471196	0.69857392	19.48019732	5.02	0.0407
Z3	3.28492462	0.78354118	68.24588259	17.58	0.0008

Bounds on condition number: 1.01511, 9.090649

Step 4 Variable Z4 Entered R-square = 0.77554375 C(p) = 10.50471369

	DF	Sum of Squares	Mean Square	F	Prob>F
Regression	4	128.05197660	32.01299415	12.09	0.0002
Error	14	37.06053623	2.64718116		
Total	18	165.11251283			

Variable	Parameter Estimate	Standard Error	Type II Sum of Squares	F	Prob>F
INTERCEP	10.15322955	0.59443187	772.30332146	291.75	0.0001
Z1	1.95262167	0.57123556	30.93067528	11.68	0.0042
Z2	2.22924240	0.62281054	33.91457187	12.81	0.0030
Z3	3.27742548	0.64696779	67.93350089	25.66	0.0002
Z4	-2.49408659	0.88169729	21.18203593	8.00	0.0134

Bounds on condition number: 1.177557, 17.46453

Step 5 Variable Z5 Entered R-square = 0.83622763 C(p) = 7.23142892

	DF	Sum of Squares	Mean Square	F	Prob>F
Regression	5	138.07164489	27.61432898	13.28	0.0001
Error	13	27.04086794	2.08006676		
Total	18	165.11251283			

Variable	Parameter Estimate	Standard Error	Type II Sum of Squares	F	Prob>F
INTERCEP	10.15245543	0.52692522	772.18521385	371.23	0.0001
Z1	2.00752399	0.50698061	32.61490134	15.68	0.0016
Z2	2.22944474	0.55208096	33.92072772	16.31	0.0014
Z3	3.28881857	0.57351827	68.40102282	32.88	0.0001
Z4	-2.49251195	0.78156751	21.15528001	10.17	0.0071
Z5	2.24103002	1.02107970	10.01966829	4.82	0.0469

Bounds on condition number: 1.177557, 26.85571

All variables in the model are significant at the 0.1500 level.
No other variable met the 0.1500 significance level for entry into the model.

Summary of Stepwise Procedure for Dependent Variable Y4

Step	Variable Entered	Number Removed	Number In	Partial R**2	Model R**2	C(p)	F	Prob>F
1	Z3		1	0.3391	0.3391	42.4315	8.7221	0.0089
2	Z1		2	0.1902	0.5293	27.9050	6.4644	0.0217
3	Z2		3	0.1180	0.6473	19.6527	5.0170	0.0407
4	Z4		4	0.1283	0.7755	10.5047	8.0017	0.0134
5	Z5		5	0.0607	0.8362	7.2314	4.8170	0.0469

Obs	Dep Var Y4	Predict Value	Std Err Predict	Residual	Std Err Residual	Student Residual
1	8.1880	8.0027	0.795	0.1853	1.204	0.154
2	5.4551	7.7817	0.719	-2.3266	1.250	-1.861
3	13.0216	13.0484	0.826	-0.0268	1.182	-0.023
4	11.7788	10.5061	0.770	1.2727	1.219	1.044
5	6.6371	7.3678	1.075	-0.7307	0.962	-0.760
6	11.4058	9.4087	0.343	1.9971	1.401	1.426
7	8.5032	9.6042	0.781	-1.1010	1.212	-0.908
8	3.8588	3.9013	0.836	-0.0425	1.175	-0.036
9	10.0463	9.0048	0.334	1.0415	1.403	0.742
10	13.2095	12.2014	1.078	1.0081	0.958	1.053
11	6.8734	5.7656	1.048	1.1078	0.990	1.119
12	8.5231	8.8703	0.334	-0.3472	1.403	-0.247
13	14.6185	13.2237	0.739	1.3948	1.238	1.126
14	6.5695	8.2588	0.792	-1.6893	1.205	-1.401
15	10.6610	11.3917	1.075	-0.7307	0.962	-0.760
16	8.2040	9.6891	0.764	-1.4851	1.223	-1.214
17	9.2849	10.5544	0.812	-1.2695	1.192	-1.065
18	4.8994	3.7829	0.874	1.1165	1.147	0.973
19	5.9694	5.3439	0.809	0.6255	1.194	0.524

Obs	-2	-1	-0	1	2	Cook's D
1						0.002
2		***				0.191
3						0.000
4				**		0.072
5		*				0.120
6				**		0.020
7		*				0.057
8						0.000
9				*		0.005
10				**		0.234
11				**		0.234
12						0.001
13				**		0.075
14		**				0.141
15		*				0.120
16		**				0.096
17		**				0.088
18				*		0.092
19				*		0.021

Sum of Residuals	-2.93099E-14
Sum of Squared Residuals	27.0409
Predicted Resid SS (Press)	58.3266

Stepwise Procedure for Dependent Variable Y5

Step 1 Variable Z8 Entered R-square = 0.99756950 C(p) = .

	DF	Sum of Squares	Mean Square	F	Prob>F
Regression	1	0.00001869	0.00001869	410.44	0.0314
Error	1	0.00000005	0.00000005		
Total	2	0.00001874			

Variable	Parameter Estimate	Standard Error	Type II Sum of Squares	F	Prob>F
INTERCEP	0.03655973	0.00021867	0.00127323	27953.9	0.0038
Z8	-0.00827994	0.00040870	0.00001869	410.44	0.0314

Bounds on condition number: 1, 1

All variables in the model are significant at the 0.1500 level.
No other variable met the 0.1500 significance level for entry into the model.

Summary of Stepwise Procedure for Dependent Variable Y5

Step	Variable Entered	Variable Removed	Number In	Partial R**2	Model R**2	C(p)	F	Prob>F
1	Z8		1	0.9976	0.9976	.	410.4383	0.0314

Obs	Dep Var Y5	Predict Value	Std Err Predict	Residual	Std Err Residual	Student Residual
1	.	0.0365	0.000	.	.	.
2	.	0.0318	0.000	.	.	.
3	.	0.0305	0.000	.	.	.
4	.	0.0349	0.000	.	.	.
5	.	0.0365	0.000	.	.	.
6	.	0.0366	0.000	.	.	.
7	.	0.0306	0.000	.	.	.
8	.	0.0301	0.000	.	.	.
9	.	0.0366	0.000	.	.	.
10	.	0.0366	0.000	.	.	.
11	.	0.0366	0.000	.	.	.
12	.	0.0366	0.000	.	.	.
13	0.0326	0.0324	0.000	0.000173	0.000	1.000
14	0.0300	0.0301	0.000	-0.00011	0.000	-1.000
15	.	0.0365	0.000	.	.	.
16	0.0361	0.0362	0.000	-0.00007	0.000	-1.000
17	.	0.0276	0.000	.	.	.
18	.	0.0284	0.000	.	.	.
19	.	0.0365	0.000	.	.	.

Obs	-2	-1	0	1	2	Cook's D
1						.
2						.
3						.
4						.
5						.
6						.
7						.
8						.
9						.
10						.
11						.
12						.
13			*			0.264
14		*				1.506
15						.
16		*				4.706
17						.
18						.
19						.

Sum of Residuals	2.775558E-17
Sum of Squared Residuals	0.0000
Predicted Resid SS (Press)	0.0000

Stepwise Procedure for Dependent Variable Y6

Step 1 Variable Z6 Entered R-square = 0.85727089 C(p) = .

	DF	Sum of Squares	Mean Square	F	Prob>F
Regression	1	0.00076634	0.00076634	24.03	0.0080
Error	4	0.00012759	0.00003190		
Total	5	0.00089393			

Variable	Parameter Estimate	Standard Error	Type II Sum of Squares	F	Prob>F
INTERCEP	0.02045657	0.00393176	0.00086347	27.07	0.0065
Z6	0.02515830	0.00513273	0.00076634	24.03	0.0080

Bounds on condition number: 1, 1

Step 2 Variable Z2 Entered R-square = 0.96417150 C(p) = .

	DF	Sum of Squares	Mean Square	F	Prob>F
Regression	2	0.00086191	0.00043095	40.37	0.0068
Error	3	0.00003203	0.00001068		
Total	5	0.00089393			

Variable	Parameter Estimate	Standard Error	Type II Sum of Squares	F	Prob>F
INTERCEP	0.02071039	0.00227623	0.00088380	82.78	0.0028
Z2	-0.00700201	0.00234038	0.00009556	8.95	0.0580
Z6	0.02476177	0.00297241	0.00074090	69.40	0.0036

Bounds on condition number: 1.001992, 4.007969

Step 3 Variable Z3 Entered R-square = 0.99398605 C(p) = .

	DF	Sum of Squares	Mean Square	F	Prob>F
Regression	3	0.00088856	0.00029619	110.19	0.0090
Error	2	0.00000538	0.00000269		
Total	5	0.00089393			

Variable	Parameter Estimate	Standard Error	Type II Sum of Squares	F	Prob>F
INTERCEP	0.02022891	0.00115235	0.00082834	308.16	0.0032
Z2	-0.00532721	0.00128918	0.00004590	17.08	0.0539
Z3	0.00473429	0.00150351	0.00002665	9.92	0.0878
Z6	0.02602587	0.00154457	0.00076319	283.92	0.0035

Bounds on condition number: 1.267238, 10.64806

Step 4 Variable Z1 Entered R-square = 0.99995930 C(p) = .

	DF	Sum of Squares	Mean Square	F	Prob>F
Regression	4	0.00089390	0.00022347	6142.65	0.0096
Error	1	0.00000004	0.00000004		
Total	5	0.00089393			

Variable	Parameter Estimate	Standard Error	Type II Sum of Squares	F	Prob>F
INTERCEP	0.02230268.	0.00021742	0.00038280	10522.0	0.0062
Z1	-0.01900836.	0.00156900	0.00000534	146.77	0.0524
Z2	-0.00466092	0.00015975	0.00003097	851.30	0.0218
Z3	0.00590536	0.00019985	0.00003177	873.17	0.0215
Z6	0.04344619.	0.00144910	0.00003270	898.89	0.0212

Bounds on condition number: 69.88552, 561.9617

All variables in the model are significant at the 0.1500 level.
No other variable met the 0.1500 significance level for entry into the model.

Summary of Stepwise Procedure for Dependent Variable Y6

Step	Variable Entered	Number Removed	Number In	Partial R**2	Model R**2	C(p)	F	Prob>F
1	Z6		1	0.8573	0.8573	.	24.0251	0.0080
2	Z2		2	0.1069	0.9642	.	8.9510	0.0580
3	Z3		3	0.0298	0.9940	.	9.9151	0.0878
4	Z1		4	0.0060	1.0000	.	146.7724	0.0524

Obs	Dep Var Y6	Predict Value	Std Err Predict	Residual	Std Err Residual	Student Residual
1	.	0.0816	0.003	.	.	.
2	.	0.0131	0.000	.	.	.
3	.	0.0234	0.000	.	.	.
4	0.0312	0.0312	0.000	-0.00004	0.000	-1.000
5	.	0.0207	0.000	.	.	.
6	0.0207	0.0206	0.000	0.000137	0.000	1.000
7	.	0.0979	0.004	.	.	.
8	.	0.0871	0.003	.	.	.
9	.	0.0217	0.000	.	.	.
10	0.0212	0.0213	0.000	-0.00011	0.000	-1.000
11	.	0.0215	0.000	.	.	.
12	.	0.0231	0.000	.	.	.
13	0.0489	0.0489	0.000	0.000022	0.000	1.000
14	0.0477	0.0477	0.000	0.000035	0.000	1.000
15	.	0.0229	0.000	.	.	.
16	0.0467	0.0467	0.000	-0.00004	0.000	-1.000
17	.	0.0331	0.000	.	.	.
18	.	0.0213	0.000	.	.	.
19	.	0.0935	0.003	.	.	.

Obs	-2	-1	0	1	2	Cook's D
1						.
2						.
3						.
4		*				3.903
5						.
6			*			0.188
7						.
8						.
9						.
10		*				0.379
11						.
12						.
13			*			14.524
14			*			5.725
15						.
16		*				4.361
17						.
18						.
19						.

Sum of Residuals	3.816392E-17
Sum of Squared Residuals	0.0000
Predicted Resid SS (Press)	0.0000

Stepwise Procedure for Dependent Variable Y7

Step 1 Variable Z1 Entered R-square = 0.94000478 C(p) = .

	DF	Sum of Squares	Mean Square	F	Prob>F
Regression	1	0.04927827	0.04927827	156.68	0.0001
Error	10	0.00314515	0.00031452		
Total	11	0.05242342			

Variable	Parameter Estimate	Standard Error	Type II Sum of Squares	F	Prob>F
INTERCEP	0.05037197	0.00637036	0.01966489	62.52	0.0001
Z1	0.14307446	0.01143024	0.04927827	156.68	0.0001

Bounds on condition number: 1, 1

Step 2 Variable Z9 Entered R-square = 0.98030220 C(p) = .

	DF	Sum of Squares	Mean Square	F	Prob>F
Regression	2	0.05139080	0.02569540	223.95	0.0001
Error	9	0.00103263	0.00011474		
Total	11	0.05242342			

Variable	Parameter Estimate	Standard Error	Type II Sum of Squares	F	Prob>F
INTERCEP	0.05038541	0.00384763	0.01967537	171.48	0.0001
Z1	0.14243612	0.00690535	0.04881686	425.47	0.0001
Z9	-0.03701679	0.00862676	0.00211253	18.41	0.0020

Bounds on condition number: 1.000464, 4.001857

Step 3 Variable Z10 Entered R-square = 0.98818870 C(p) = .

	DF	Sum of Squares	Mean Square	F	Prob>F
Regression	3	0.05180423	0.01726808	223.11	0.0001
Error	8	0.00061919	0.00007740		
Total	11	0.05242342			

Variable	Parameter Estimate	Standard Error	Type II Sum of Squares	F	Prob>F
INTERCEP	0.05023376	0.00316085	0.01954868	252.57	0.0001
Z1	0.14525203	0.00580094	0.04852669	626.97	0.0001
Z9	-0.03090416	0.00756291	0.00129238	16.70	0.0035
Z10	0.01769795	0.00765746	0.00041344	5.34	0.0496

Bounds on condition number: 1.18211, 10.10582

Step 4 Variable Z6 Entered R-square = 0.99356946 C(p) = .

	DF	Sum of Squares	Mean Square	F	Prob>F
Regression	4	0.05208631	0.01302158	270.39	0.0001
Error	7	0.00033711	0.00004816		
Total	11	0.05242342			

Variable	Parameter Estimate	Standard Error	Type II Sum of Squares	F	Prob>F
INTERCEP	0.05144296	0.00254287	0.01970967	409.27	0.0001
Z1	0.06137518	0.03495807	0.00014844	3.08	0.1226
Z6	0.08673932	0.03584006	0.00028208	5.86	0.0461
Z9	-0.02675039	0.00620766	0.00089429	18.57	0.0035
Z10	0.02501832	0.00675527	0.00066055	13.72	0.0076

Bounds on condition number: 63.02571, 507.3034

Step 5 Variable Z2 Entered R-square = 0.99860254 C(p) = .

	DF	Sum of Squares	Mean Square	F	Prob>F
Regression	5	0.05235016	0.01047003	857.50	0.0001
Error	6	0.00007326	0.00001221		
Total	11	0.05242342			

Variable	Parameter Estimate	Standard Error	Type II Sum of Squares	F	Prob>F
INTERCEP	0.05297259	0.00132200	0.01960443	1605.62	0.0001
Z1	0.04950020	0.01778658	0.00009457	7.75	0.0319
Z2	-0.00952447	0.00204889	0.00026385	21.61	0.0035
Z6	0.09743820	0.01819245	0.00035026	28.69	0.0017
Z9	-0.01596349	0.00389288	0.00020532	16.82	0.0064
Z10	0.02547687	0.00340286	0.00068441	56.05	0.0003

Bounds on condition number: 64.05083, 657.4807

Step 6 Variable Z4 Entered R-square = 0.99979202 C(p) = .

	DF	Sum of Squares	Mean Square	F	Prob>F
Regression	6	0.05241252	0.00873542	4006.00	0.0001
Error	5	0.00001090	0.00000218		
Total	11	0.05242342			

Variable	Parameter Estimate	Standard Error	Type II Sum of Squares	F	Prob>F
INTERCEP	0.05538153	0.00071767	0.01298540	5955.01	0.0001
Z1	0.04294503	0.00761592	0.00006934	31.80	0.0024
Z2	-0.00735184	0.00095644	0.00012884	59.08	0.0006
Z4	-0.00647525	0.00121088	0.00006236	28.60	0.0031

Z6	0.10527399	0.00782654	0.00039453	180.93	0.0001
Z9	-0.01609562	0.00164532	0.00020868	95.70	0.0002
Z10	0.02615682	0.00144366	0.00071583	328.28	0.0001

Bounds on condition number: 66.37752, 823.4959

All variables in the model are significant at the 0.1500 level.
 No other variable met the 0.1500 significance level for entry into the model.

Summary of Stepwise Procedure for Dependent Variable Y7

Step	Variable Entered Removed	Number In	Partial R**2	Model R**2	C(p)	F	Prob>F
1	Z1	1	0.9400	0.9400	.	156.6800	0.0001
2	Z9	2	0.0403	0.9803	.	18.4120	0.0020
3	Z10	3	0.0079	0.9882	.	5.3417	0.0496
4	Z6	4	0.0054	0.9936	.	5.8573	0.0461
5	Z2	5	0.0050	0.9986	.	21.6096	0.0035
6	Z4	6	0.0012	0.9998	.	28.5963	0.0031

Obs	Dep Var Y7	Predict Value	Std Err Predict	Residual	Std Err Residual	Student Residual
1	.	0.1256	0.016	.	.	.
2	0.0416	0.0425	0.001	-0.00088	0.001	-0.766
3	0.0411	0.0405	0.001	0.000587	0.001	0.548
4	0.1351	0.1350	0.001	0.000111	0.001	0.187
5	.	0.0638	0.001	.	.	.
6	0.0622	0.0610	0.001	0.00115	0.001	1.037
7	.	0.1038	0.017	.	.	.
8	.	0.1512	0.018	.	.	.
9	0.0515	0.0540	0.001	-0.00253	0.001	-1.853
10	0.0637	0.0637	0.001	-0.00004	0.000	-0.202
11	.	0.0454	0.002	.	.	.
12	0.0522	0.0510	0.001	0.00125	0.001	0.962
13	0.2108	0.2109	0.001	-0.00007	0.000	-0.173
14	0.1979	0.1980	0.001	-0.00009	0.000	-0.212
15	0.0522	0.0515	0.001	0.000654	0.001	0.487
16	0.2059	0.2058	0.001	0.000081	0.001	0.142
17	0.0597	0.0599	0.001	-0.00022	0.001	-0.246
18	.	0.0606	0.001	.	.	.
19	.	0.1086	0.017	.	.	.

Obs	-2	-1	-0	1	2	Cook's D
1						.
2		*				0.054
3			*			0.038
4						0.026
5						.
6			**			0.119
7						.
8						.
9		***				0.084
10						0.299
11						.
12			*			0.039
13						0.049
14						0.068
15						0.007
16						0.016
17						0.016
18						.
19						.

Sum of Residuals	-2.77556E-17
Sum of Squared Residuals	0.0000
Predicted Resid SS (Press)	0.0000

Stepwise Procedure for Dependent Variable Y8

Step 1 Variable Z3 Entered R-square = 0.23787422 C(p) = 59.05581977

	DF	Sum of Squares	Mean Square	F	Prob>F
Regression	1	59.67437724	59.67437724	5.31	0.0341
Error	17	191.19087888	11.24652229		
Total	18	250.86525612			

Variable	Parameter Estimate	Standard Error	Type II Sum of Squares	F	Prob>F
INTERCEP	89.61832130	0.76940678	152580.78144434	13566.9	0.0001
Z3	-3.04876887	1.32354794	59.67437724	5.31	0.0341

Bounds on condition number: 1, 1

Step 2 Variable Z1 Entered R-square = 0.45502218 C(p) = 39.95553646

	DF	Sum of Squares	Mean Square	F	Prob>F
Regression	2	114.14925475	57.07462738	6.68	0.0078
Error	16	136.71600137	8.54475009		
Total	18	250.86525612			

Variable	Parameter Estimate	Standard Error	Type II Sum of Squares	F	Prob>F
INTERCEP	89.61784472	0.67065102	152579.14656340	17856.5	0.0001
Z1	-2.59095294	1.02615054	54.47487751	6.38	0.0225
Z3	-3.25560926	1.15657119	67.70475625	7.92	0.0125

Bounds on condition number: 1.005042, 4.020168

Step 3 Variable Z2 Entered R-square = 0.62370126 C(p) = 25.56497678

	DF	Sum of Squares	Mean Square	F	Prob>F
Regression	3	156.46497713	52.15499238	8.29	0.0017
Error	15	94.40027899	6.29335193		
Total	18	250.86525612			

Variable	Parameter Estimate	Standard Error	Type II Sum of Squares	F	Prob>F
INTERCEP	89.61838920	0.57555647	152580.98025634	24244.8	0.0001
Z1	-2.60640843	0.88066827	55.12419520	8.76	0.0097
Z2	-2.30615560	0.88936234	42.31572238	6.72	0.0204
Z3	-3.51321639	0.99753511	78.06123887	12.40	0.0031

Bounds on condition number: 1.01511, 9.090649

Step 4 Variable Z4 Entered R-square = 0.76081866 C(p) = 14.24126902

	DF	Sum of Squares	Mean Square	F	Prob>F
Regression	4	190.86296778	47.71574195	11.13	0.0003
Error	14	60.00228834	4.28587774		
Total	18	250.86525612			

Variable	Parameter Estimate	Standard Error	Type II Sum of Squares	F	Prob>F
INTERCEP	87.95079485	0.75636277	57950.74590858	13521.3	0.0001
Z1	-2.57452548	0.72684749	53.77093367	12.55	0.0033
Z2	-3.15298819	0.79247216	67.84478002	15.83	0.0014
Z3	-3.50365999	0.82321015	77.63583950	18.11	0.0008
Z4	3.17829507	1.12188300	34.39799065	8.03	0.0133

Bounds on condition number: 1.177557, 17.46453

Step 5 Variable Z5 Entered R-square = 0.84797619 C(p) = 7.77216562

	DF	Sum of Squares	Mean Square	F	Prob>F
Regression	5	212.72776286	42.54555257	14.50	0.0001
Error	13	38.13749326	2.93365333		
Total	18	250.86525612			

Variable	Parameter Estimate	Standard Error	Type II Sum of Squares	F	Prob>F
INTERCEP	87.95193840	0.62577001	57952.22691283	19754.3	0.0001
Z1	-2.65562844	0.60208403	57.07280292	19.45	0.0007
Z2	-3.15328709	0.65564466	67.85764186	23.13	0.0003
Z3	-3.52049013	0.68110335	78.37707034	26.72	0.0002
Z4	3.17596897	0.92818011	34.34763049	11.71	0.0045
Z5	-3.31050089	1.21262188	21.86479508	7.45	0.0172

Bounds on condition number: 1.177557, 26.85571

Step 6 Variable Z11 Entered R-square = 0.87364579 C(p) = 7.27784839

	DF	Sum of Squares	Mean Square	F	Prob>F
Regression	6	219.16737429	36.52789571	13.83	0.0001
Error	12	31.69788183	2.64149015		
Total	18	250.86525612			

Variable	Parameter Estimate	Standard Error	Type II Sum of Squares	F	Prob>F
INTERCEP	87.91044987	0.59438693	57781.85657197	21874.7	0.0001
Z1	-2.74115222	0.57393684	60.25416861	22.81	0.0005
Z2	-3.17641517	0.62231704	68.81769764	26.05	0.0003
Z3	-3.65689799	0.65217652	83.05090513	31.44	0.0001

	3.15706010	0.88083266	33.93343918	12.85	0.0038
	-3.32032872	1.15067320	21.99414893	8.33	0.0137
1	-1.34772650	0.86317020	6.43961143	2.44	0.1444

unds on condition number: 1.178224, 38.55648

1 variables in the model are significant at the 0.1500 level.

other variable met the 0.1500 significance level for entry into the model.

Summary of Stepwise Procedure for Dependent Variable Y8

ep	Variable Entered Removed	Number In	Partial R**2	Model R**2	C(p)	F	Prob>F
1	Z3	1	0.2379	0.2379	59.0558	5.3060	0.0341
2	Z1	2	0.2171	0.4550	39.9555	6.3752	0.0225
3	Z2	3	0.1687	0.6237	25.5650	6.7239	0.0204
4	Z4	4	0.1371	0.7608	14.2413	8.0259	0.0133
5	Z5	5	0.0872	0.8480	7.7722	7.4531	0.0172
6	Z11	6	0.0257	0.8736	7.2778	2.4379	0.1444

Obs	Dep Var Y8	Predict Value	Std Err Predict	Residual	Std Err Residual	Student Residual
1	90.2087	90.5340	0.897	-0.3253	1.355	-0.240
2	93.0590	91.1987	1.052	1.8603	1.239	1.501
3	84.4399	83.1381	1.283	1.3018	0.998	1.305
4	85.1440	87.3169	0.929	-2.1729	1.334	-1.629
5	92.7499	91.9182	1.212	0.8317	1.083	0.768
6	86.3566	88.8339	0.389	-2.4773	1.578	-1.570
7	90.5291	89.2577	0.881	1.2714	1.366	0.931
8	95.6	95.6	0.946	0.0233	1.321	0.018
9	88.4920	89.3584	0.378	-0.8664	1.581	-0.548
10	84.3714	85.3047	1.216	-0.9333	1.079	-0.865
11	92.4551	93.4491	1.182	-0.9940	1.115	-0.891
12	90.0355	89.5415	0.378	0.4940	1.581	0.313
13	82.7943	84.2032	0.845	-1.4089	1.389	-1.015
14	91.4250	89.6444	0.892	1.7806	1.358	1.311
15	86.7182	85.8865	1.212	0.8317	1.083	0.768
16	90.7729	89.0598	0.867	1.7131	1.375	1.246
17	90.0280	89.6367	1.194	0.3913	1.103	0.355
18	94.3601	94.5	1.271	-0.1089	1.013	-0.107
19	93.5580	94.8	0.920	-1.2120	1.340	-0.905

Obs	-2	-1	-0	1	2	Cook's D
1						0.004
2				***		0.232
3				**		0.403
4		***				0.184
5				*		0.106
6		***				0.021
7				*		0.052
8						0.000
9			*			0.002
10			*			0.136
11			*			0.128
12						0.001
13			**			0.054
14				**		0.106
15				*		0.106
16				**		0.088
17						0.021
18						0.003
19			*			0.055

Sum of Residuals	-1.98952E-13
Sum of Squared Residuals	31.6979
Predicted Resid SS (Press)	79.9799

Stepwise Procedure for Dependent Variable Y9

Step 1 Variable Z1 Entered R-square = 0.50846380 C(p) = 45.00646002

	DF	Sum of Squares	Mean Square	F	Prob>F
Regression	1	0.00433578	0.00433578	17.59	0.0006
Error	17	0.00419144	0.00024656		
Total	18	0.00852722			

Variable	Parameter Estimate	Standard Error	Type II Sum of Squares	F	Prob>F
INTERCEP	0.12578062	0.00360230	0.30059445	1219.18	0.0001
Z1	-0.02305701	0.00549827	0.00433578	17.59	0.0006

Bounds on condition number: 1, 1

Step 2 Variable Z6 Entered R-square = 0.64714159 C(p) = 30.07675467

	DF	Sum of Squares	Mean Square	F	Prob>F
Regression	2	0.00551832	0.00275916	14.67	0.0002
Error	16	0.00300890	0.00018806		
Total	18	0.00852722			

Variable	Parameter Estimate	Standard Error	Type II Sum of Squares	F	Prob>F
INTERCEP	0.11899578	0.00414951	0.15465301	822.38	0.0001
Z1	-0.02110182	0.00486479	0.00353834	18.82	0.0005
Z6	0.01580497	0.00630276	0.00118254	6.29	0.0233

Bounds on condition number: 1.026365, 4.105459

Step 3 Variable Z2 Entered R-square = 0.75224625 C(p) = 19.24563712

	DF	Sum of Squares	Mean Square	F	Prob>F
Regression	3	0.00641457	0.00213819	15.18	0.0001
Error	15	0.00211265	0.00014084		
Total	18	0.00852722			

Variable	Parameter Estimate	Standard Error	Type II Sum of Squares	F	Prob>F
INTERCEP	0.11914776	0.00359155	0.15500466	1100.55	0.0001
Z1	-0.02113948	0.00421009	0.00355094	25.21	0.0002
Z2	-0.01056365	0.00418762	0.00089625	6.36	0.0234
Z6	0.01547339	0.00545608	0.00113278	8.04	0.0125

Bounds on condition number: 1.026961, 9.161757

Step 4 Variable Z9 Entered R-square = 0.83318020 C(p) = 11.36526661

	DF	Sum of Squares	Mean Square	F	Prob>F
Regression	4	0.00710471	0.00177618	17.48	0.0001
Error	14	0.00142251	0.00010161		
Total	18	0.00852722			

Variable	Parameter Estimate	Standard Error	Type II Sum of Squares	F	Prob>F
INTERCEP	0.11917321	0.00305056	0.15506929	1526.16	0.0001
Z1	-0.02138450	0.00357714	0.00363122	35.74	0.0001
Z2	-0.01122818	0.00356595	0.00100738	9.91	0.0071
Z6	0.01542008	0.00463426	0.00112497	11.07	0.0050
Z9	-0.01375702	0.00527860	0.00069014	6.79	0.0207

Bounds on condition number: 1.027087, 16.26244

Step 5 Variable Z5 Entered R-square = 0.90408910 C(p) = 4.70874883

	DF	Sum of Squares	Mean Square	F	Prob>F
Regression	5	0.00770936	0.00154187	24.51	0.0001
Error	13	0.00081785	0.00006291		
Total	18	0.00852722			

Variable	Parameter Estimate	Standard Error	Type II Sum of Squares	F	Prob>F
INTERCEP	0.11926259	0.00240056	0.15527958	2468.21	0.0001
Z1	-0.02183152	0.00281843	0.00377471	60.00	0.0001
Z2	-0.01123019	0.00280594	0.00100774	16.02	0.0015
Z5	-0.01741130	0.00561621	0.00060466	9.61	0.0084
Z6	0.01521218	0.00364717	0.00109447	17.40	0.0011
Z9	-0.01378171	0.00415358	0.00069262	11.01	0.0056

Bounds on condition number: 1.029782, 25.35694

Step 6 Variable Z11 Entered R-square = 0.92450782 C(p) = 4.21604222

	DF	Sum of Squares	Mean Square	F	Prob>F
Regression	6	0.00788348	0.00131391	24.49	0.0001
Error	12	0.00064374	0.00005364		
Total	18	0.00852722			

Variable	Parameter Estimate	Standard Error	Type II Sum of Squares	F	Prob>F
INTERCEP	0.11928412	0.00221675	0.15533114	2895.55	0.0001
Z1	-0.02232367	0.00261689	0.00390381	72.77	0.0001
Z2	-0.01135524	0.00259198	0.00102957	19.19	0.0009
Z5	-0.01747116	0.00518621	0.00060880	11.35	0.0056

Z6	0.01454912	0.00338791	0.00098932	18.44	0.0010
Z9	-0.01438801	0.00385022	0.00074913	13.96	0.0028
Z11	-0.00701175	0.00389200	0.00017411	3.25	0.0968

Bounds on condition number: 1.041127, 36.78499

All variables in the model are significant at the 0.1500 level.
 No other variable met the 0.1500 significance level for entry into the model.

Summary of Stepwise Procedure for Dependent Variable Y9

Step	Variable Entered Removed	Number In	Partial R**2	Model R**2	C(p)	F	Prob>F
1	Z1	1	0.5085	0.5085	45.0065	17.5854	0.0006
2	Z6	2	0.1387	0.6471	30.0768	6.2882	0.0233
3	Z2	3	0.1051	0.7522	19.2456	6.3635	0.0234
4	Z9	4	0.0809	0.8332	11.3653	6.7922	0.0207
5	Z5	5	0.0709	0.9041	4.7087	9.6112	0.0084
6	Z11	6	0.0204	0.9245	4.2160	3.2457	0.0968

Obs	Dep Var Y9	Predict Value	Std Err Predict	Residual	Std Err Residual	Student Residual
1	0.1700	0.1607	0.006	0.00929	0.005	2.058
2	0.0998	0.1131	0.004	-0.0133	0.006	-2.290
3	0.1035	0.1030	0.005	0.000546	0.005	0.100
4	0.1015	0.0902	0.006	0.0113	0.005	2.337
5	0.1315	0.1331	0.006	-0.00159	0.005	-0.339
6	0.1134	0.1161	0.002	-0.00272	0.007	-0.389
7	0.1528	0.1601	0.004	-0.00727	0.006	-1.160
8	0.1593	0.1596	0.004	-0.0003	0.006	-0.048
9	0.1240	0.1187	0.002	0.00532	0.007	0.762
10	0.1131	0.1181	0.002	-0.00502	0.007	-0.718
11	0.1248	0.1182	0.002	0.00662	0.007	0.948
12	0.1191	0.1202	0.002	-0.00112	0.007	-0.160
13	0.1065	0.1117	0.004	-0.00517	0.006	-0.820
14	0.1092	0.1122	0.004	-0.00300	0.006	-0.517
15	0.1005	0.1021	0.006	-0.00159	0.005	-0.339
16	0.1361	0.1364	0.005	-0.00028	0.005	-0.058
17	0.1445	0.1375	0.005	0.00701	0.005	1.374
18	0.1257	0.1238	0.005	0.00191	0.005	0.370
19	0.1544	0.1550	0.006	-0.00062	0.004	-0.138

Obs	-2	-1	0	1	2	Cook's D
1				****		0.989
2		****				0.443
3						0.001
4				****		1.015
5						0.023
6						0.002
7		**				0.071
8						0.000
9				*		0.008
10			*			0.007
11				*		0.013
12						0.000
13		*				0.033
14		*				0.023
15						0.023
16						0.001
17				**		0.286
18						0.020
19						0.005

Sum of Residuals 2.775558E-16
 Sum of Squared Residuals 0.0006
 Predicted Resid SS (Press) 0.0023

Stepwise Procedure for Dependent Variable Y10

Step 1 Variable Z1 Entered R-square = 0.49314456 C(p) = 72.19486958

	DF	Sum of Squares	Mean Square	F	Prob>F
Regression	1	0.11020572	0.11020572	16.54	0.0008
Error	17	0.11326977	0.00666293		
Total	18	0.22347549			

Variable	Parameter Estimate	Standard Error	Type II Sum of Squares	F	Prob>F
INTERCEP	0.60251767	0.01872646	6.89752188	1035.21	0.0001
Z1	0.11624421	0.02858260	0.11020572	16.54	0.0008

Bounds on condition number: 1, 1

Step 2 Variable Z5 Entered R-square = 0.61945312 C(p) = 52.46587571

	DF	Sum of Squares	Mean Square	F	Prob>F
Regression	2	0.13843259	0.06921629	13.02	0.0004
Error	16	0.08504290	0.00531518		
Total	18	0.22347549			

Variable	Parameter Estimate	Standard Error	Type II Sum of Squares	F	Prob>F
INTERCEP	0.60251681	0.01672562	6.89750208	1297.70	0.0001
Z1	0.11911932	0.02555914	0.11544891	21.72	0.0003
Z5	0.11894176	0.05161335	0.02822687	5.31	0.0349

Bounds on condition number: 1.002388, 4.009554

Step 3 Variable Z2 Entered R-square = 0.74520377 C(p) = 32.83285983

	DF	Sum of Squares	Mean Square	F	Prob>F
Regression	3	0.16653478	0.05551159	14.62	0.0001
Error	15	0.05694071	0.00379605		
Total	18	0.22347549			

Variable	Parameter Estimate	Standard Error	Type II Sum of Squares	F	Prob>F
INTERCEP	0.60246286	0.01413479	6.89625354	1816.69	0.0001
Z1	0.11909952	0.02159997	0.11541052	30.40	0.0001
Z2	0.05913483	0.02173397	0.02810219	7.40	0.0158
Z5	0.11890039	0.04361831	0.02820723	7.43	0.0156

Bounds on condition number: 1.002389, 9.014332

Step 4 Variable Z6 Entered R-square = 0.83534802 C(p) = 19.32525095

	DF	Sum of Squares	Mean Square	F	Prob>F
Regression	4	0.18667981	0.04666995	17.76	0.0001
Error	14	0.03679568	0.00262826		
Total	18	0.22347549			

Variable	Parameter Estimate	Standard Error	Type II Sum of Squares	F	Prob>F
INTERCEP	0.63048059	0.01551598	4.33964143	1651.14	0.0001
Z1	0.11098171	0.01821066	0.09761586	37.14	0.0001
Z2	0.05792841	0.01808980	0.02695161	10.25	0.0064
Z5	0.11705333	0.03630035	0.02732843	10.40	0.0061
Z6	-0.06526344	0.02357330	0.02014503	7.66	0.0151

Bounds on condition number: 1.029068, 16.23873

Step 5 Variable Z9 Entered R-square = 0.90023331 C(p) = 10.16296831

	DF	Sum of Squares	Mean Square	F	Prob>F
Regression	5	0.20118008	0.04023602	23.46	0.0001
Error	13	0.02229541	0.00171503		
Total	18	0.22347549			

Variable	Parameter Estimate	Standard Error	Type II Sum of Squares	F	Prob>F
INTERCEP	0.63036311	0.01253381	4.33797935	2529.39	0.0001
Z1	0.11210901	0.01471560	0.09953987	58.04	0.0001
Z2	0.06097445	0.01465037	0.02970784	17.32	0.0011
Z5	0.11721682	0.02932333	0.02740473	15.98	0.0015
Z6	-0.06501711	0.01904260	0.01999286	11.66	0.0046
Z9	0.06305857	0.02168663	0.01450027	8.45	0.0122

Bounds on condition number: 1.029782, 25.35694

Step 6 Variable Z11 Entered R-square = 0.92497910 C(p) = 7.90592418

	DF	Sum of Squares	Mean Square	F	Prob>F
Regression	6	0.20671015	0.03445169	24.66	0.0001
Error	12	0.01676533	0.00139711		
Total	18	0.22347549			

Variable	Parameter Estimate	Standard Error	Type II Sum of Squares	F	Prob>F
INTERCEP	0.63024175	0.01131277	4.33618312	3103.68	0.0001
Z1	0.11488258	0.01335478	0.10338700	74.00	0.0001
Z2	0.06167922	0.01322768	0.03037675	21.74	0.0005
Z5	0.11755415	0.02646681	0.02756155	19.73	0.0008

Z6	-0.06128033	0.01728955	0.01755116	12.56	0.0040
Z9	0.06647548	0.01964884	0.01599116	11.45	0.0054
Z11	0.03951609	0.01986204	0.00553008	3.96	0.0699

Bounds on condition number: 1.041127, 36.78499

All variables in the model are significant at the 0.1500 level.
 No other variable met the 0.1500 significance level for entry into the model.

Summary of Stepwise Procedure for Dependent Variable Y10

Step	Variable Entered	Removed	Number In	Partial R**2	Model R**2	C(p)	F	Prob>F
1	Z1		1	0.4931	0.4931	72.1949	16.5401	0.0008
2	Z5		2	0.1263	0.6195	52.4659	5.3106	0.0349
3	Z2		3	0.1258	0.7452	32.8329	7.4030	0.0158
4	Z6		4	0.0901	0.8353	19.3253	7.6648	0.0151
5	Z9		5	0.0649	0.9002	10.1630	8.4548	0.0122
6	Z11		6	0.0247	0.9250	7.9059	3.9582	0.0699

Obs	Dep Var Y10	Predict Value	Std Err Predict	Residual	Std Err Residual	Student Residual
1	0.4023	0.4418	0.029	-0.0395	0.023	-1.714
2	0.7248	0.6627	0.023	0.0621	0.030	2.096
3	0.7025	0.7210	0.025	-0.0185	0.028	-0.662
4	0.7268	0.7852	0.028	-0.0584	0.025	-2.370
5	0.5459	0.5320	0.029	0.0139	0.024	0.579
6	0.6577	0.6468	0.011	0.0109	0.036	0.304
7	0.4732	0.4360	0.019	0.0372	0.032	1.165
8	0.4413	0.4382	0.019	0.00314	0.032	0.098
9	0.6119	0.6333	0.011	-0.0214	0.036	-0.602
10	0.6522	0.6363	0.011	0.0159	0.036	0.447
11	0.6002	0.6360	0.011	-0.0358	0.036	-1.005
12	0.6402	0.6254	0.011	0.0148	0.036	0.415
13	0.6948	0.6822	0.019	0.0126	0.032	0.392
14	0.7278	0.6827	0.023	0.0451	0.030	1.522
15	0.7603	0.7464	0.029	0.0139	0.024	0.579
16	0.5347	0.5563	0.028	-0.0216	0.025	-0.874
17	0.5026	0.5299	0.027	-0.0273	0.026	-1.047
18	0.6090	0.6072	0.027	0.00180	0.026	0.068
19	0.4403	0.4492	0.030	-0.00888	0.023	-0.390

Obs	-2	-1	-0	1	2	Cook's D
1	***					0.686
2				*****		0.371
3		*				0.050
4	****					1.044
5			*			0.068
6						0.001
7			**			0.071
8						0.000
9		*				0.005
10						0.003
11		**				0.014
12						0.003
13						0.008
14				***		0.197
15			*			0.068
16		*				0.141
17		**				0.166
18						0.001
19						0.037

Sum of Residuals	2.775558E-15
Sum of Squared Residuals	0.0168
Predicted Resid SS (Press)	0.0591

Stepwise Procedure for Dependent Variable Y11

Step 1 Variable Z9 Entered R-square = 0.21123363 C(p) = 21.44867729

	DF	Sum of Squares	Mean Square	F	Prob>F
Regression	1	0.00127314	0.00127314	4.55	0.0477
Error	17	0.00475402	0.00027965		
Total	18	0.00602716			

Variable	Parameter Estimate	Standard Error	Type II Sum of Squares	F	Prob>F
INTERCEP	0.06821307	0.00383645	0.08840744	316.14	0.0001
Z9	-0.01863087	0.00873175	0.00127314	4.55	0.0477

Bounds on condition number: 1, 1

Step 2 Variable Z6 Entered R-square = 0.38629720 C(p) = 15.35903795

	DF	Sum of Squares	Mean Square	F	Prob>F
Regression	2	0.00232827	0.00116414	5.04	0.0201
Error	16	0.00369888	0.00023118		
Total	18	0.00602716			

Variable	Parameter Estimate	Standard Error	Type II Sum of Squares	F	Prob>F
INTERCEP	0.06188753	0.00457538	0.04229627	182.96	0.0001
Z6	0.01473636	0.00689781	0.00105514	4.56	0.0484
Z9	-0.01865632	0.00793910	0.00127662	5.52	0.0319

Bounds on condition number: 1.000002, 4.000009

Step 3 Variable Z3 Entered R-square = 0.58038170 C(p) = 8.39044667

	DF	Sum of Squares	Mean Square	F	Prob>F
Regression	3	0.00349805	0.00116602	6.92	0.0038
Error	15	0.00252911	0.00016861		
Total	18	0.00602716			

Variable	Parameter Estimate	Standard Error	Type II Sum of Squares	F	Prob>F
INTERCEP	0.06141868	0.00391147	0.04157158	246.56	0.0001
Z3	0.01360672	0.00516582	0.00116978	6.94	0.0188
Z6	0.01602052	0.00591094	0.00123856	7.35	0.0161
Z9	-0.01693959	0.00681132	0.00104284	6.19	0.0251

Bounds on condition number: 1.016114, 9.096627

Step 4 Variable Z2 Entered R-square = 0.69021906 C(p) = 5.31489200

	DF	Sum of Squares	Mean Square	F	Prob>F
Regression	4	0.00416006	0.00104001	7.80	0.0016
Error	14	0.00186710	0.00013336		
Total	18	0.00602716			

Variable	Parameter Estimate	Standard Error	Type II Sum of Squares	F	Prob>F
INTERCEP	0.06158588	0.00347955	0.04177878	313.27	0.0001
Z2	-0.00915688	0.00410994	0.00066201	4.96	0.0428
Z3	0.01248110	0.00462202	0.00097248	7.29	0.0172
Z6	0.01563491	0.00525985	0.00117837	8.84	0.0101
Z9	-0.01804893	0.00607820	0.00117596	8.82	0.0101

Bounds on condition number: 1.028401, 16.28104

Step 5 Variable Z8 Entered R-square = 0.76025468 C(p) = 4.07856544

	DF	Sum of Squares	Mean Square	F	Prob>F
Regression	5	0.00458217	0.00091643	8.24	0.0011
Error	13	0.00144498	0.00011115		
Total	18	0.00602716			

Variable	Parameter Estimate	Standard Error	Type II Sum of Squares	F	Prob>F
INTERCEP	0.06518660	0.00367489	0.03497411	314.65	0.0001
Z2	-0.01006751	0.00378110	0.00078800	7.09	0.0195
Z3	0.01226314	0.00422108	0.00093816	8.44	0.0123
Z6	0.01702467	0.00485457	0.00136702	12.30	0.0039
Z8	-0.01242196	0.00637432	0.00042212	3.80	0.0732
Z9	-0.01771963	0.00555157	0.00113239	10.19	0.0071

Bounds on condition number: 1.041287, 25.75616

Step 6 Variable Z7 Entered R-square = 0.80935046 C(p) = 3.80986294

	DF	Sum of Squares	Mean Square	F	Prob>F
Regression	6	0.00487808	0.00081301	8.49	0.0009
Error	12	0.00114907	0.00009576		
Total	18	0.00602716			

Variable	Parameter Estimate	Standard Error	Type II Sum of Squares	F	Prob>F
INTERCEP	0.06267109	0.00369891	0.02748875	287.07	0.0001
Z2	-0.01038364	0.00351408	0.00083607	8.73	0.0120
Z3	0.01222319	0.00391792	0.00093202	9.73	0.0089
Z6	0.01696519	0.00450596	0.00135741	14.18	0.0027

Z7	0.00824460	0.00469002	0.00029591	3.09	0.1042
Z8	-0.01522144	0.00612699	0.00059100	6.17	0.0287
Z9	-0.01782828	0.00515313	0.00114616	11.97	0.0047

Bounds on condition number: 1.11673, 37.83024

All variables in the model are significant at the 0.1500 level.
 No other variable met the 0.1500 significance level for entry into the model.

Summary of Stepwise Procedure for Dependent Variable Y11

Step	Variable Entered	Removed	Number In	Partial R**2	Model R**2	C(p)	F	Prob>F
1	Z9		1	0.2112	0.2112	21.4487	4.5526	0.0477
2	Z6		2	0.1751	0.3863	15.3590	4.5641	0.0484
3	Z3		3	0.1941	0.5804	8.3904	6.9379	0.0188
4	Z2		4	0.1098	0.6902	5.3149	4.9639	0.0428
5	Z8		5	0.0700	0.7603	4.0786	3.7976	0.0732
6	Z7		6	0.0491	0.8094	3.8099	3.0902	0.1042

Obs	Dep Var Y11	Predict Value	Std Err Predict	Residual	Std Err Residual	Student Residual
1	0.1080	0.0953	0.008	0.0127	0.006	2.165
2	0.0450	0.0425	0.006	0.00246	0.008	0.321
3	0.0540	0.0608	0.007	-0.00679	0.007	-0.986
4	0.0410	0.0492	0.007	-0.00821	0.007	-1.208
5	0.0680	0.0639	0.004	0.00406	0.009	0.446
6	0.0570	0.0633	0.004	-0.00625	0.009	-0.689
7	0.0750	0.0816	0.006	-0.00662	0.008	-0.878
8	0.0490	0.0593	0.006	-0.0103	0.008	-1.332
9	0.0690	0.0627	0.004	0.00625	0.009	0.690
10	0.0580	0.0628	0.004	-0.00483	0.009	-0.533
11	0.0710	0.0624	0.004	0.00860	0.009	0.948
12	0.0650	0.0627	0.004	0.00230	0.009	0.254
13	0.0870	0.0800	0.005	0.00704	0.008	0.835
14	0.0690	0.0600	0.006	0.00898	0.008	1.176
15	0.0540	0.0632	0.004	-0.00921	0.009	-1.016
16	0.0980	0.1125	0.008	-0.0145	0.006	-2.335
17	0.0840	0.0768	0.007	0.00718	0.006	1.110
18	0.0550	0.0547	0.008	0.000338	0.006	0.055
19	0.0890	0.0823	0.009	0.00673	0.005	1.406

Obs	-2 -1 0 1 2	Cook's D
1	****	1.189
2		0.009
3	*	0.141
4	**	0.223
5		0.005
6	*	0.011
7	*	0.075
8	**	0.156
9	*	0.011
10	*	0.007
11	*	0.021
12		0.002
13	*	0.034
14	**	0.126
15	**	0.024
16	****	1.162
17	**	0.227
18		0.001
19	**	0.899

Sum of Residuals	2.63678E-16
Sum of Squared Residuals	0.0011
Predicted Resid SS (Press)	0.0052

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NOTE: SAS (r) Proprietary Software Release 6.03

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NOTE: AUTOEXEC processing completed.

```
1  option ps=58;
2  data x;
3      infile 'a:shortx.dat';
4      input run $ x1-x5 y5;
5      label x1='Average Temperature';
6      label x2='Pressure';
7      label x3='MAF in, gm';
8      label x4='Gas Flow in, scfh';
9      label x5='Caustic Loading, fr MAF';
10     label y5='H2S Produced, %';
11     proc print;
```

NOTE: The infile 'a:shortx.dat' is file A:\SHORTX.DAT.

NOTE: 19 records were read from the infile A:\SHORTX.DAT.

The minimum record length was 70.

The maximum record length was 70.

NOTE: The data set WORK.X has 19 observations and 7 variables.

NOTE: The DATA statement used 26.00 seconds.

```
12     data y;
NOTE: The PROCEDURE PRINT used 22.00 seconds.
13     infile 'a:shorty.dat';
14     input y6-y10;
15     label y6='C2 Produced, %';
16     label y7='C1 Produced, %';
17     label y8='MeOH Insolubles, mass fr';
18     label y9='KF Water';
19     label y10='HPLC';
20     proc print;
```

NOTE: The infile 'a:shorty.dat' is file A:\SHORTY.DAT.

NOTE: 19 records were read from the infile A:\SHORTY.DAT.

The minimum record length was 48.

The maximum record length was 48.

NOTE: The data set WORK.Y has 19 observations and 5 variables.

NOTE: The DATA statement used 21.00 seconds.

```
21     data z;
NOTE: The PROCEDURE PRINT used 20.00 seconds.
```

```
22     set x;
23     z1=(x1-345)/35;
24     z2=(x2-1750)/750;
25     z3=(x3-300)/200;
26     z4=(x4-15)/3;
27     z5=(x5-.05)/.03;
28     z6=z1*z1;
29     z7=z2*z2;
30     z8=z3*z3;
31     z9=z1*z2;
32     z10=z1*z3;
33     z11=z2*z3;
```

```
34     data regtot;
```

NOTE: The data set WORK.Z has 19 observations and 18 variables.

NOTE: The DATA statement used 25.00 seconds.

```
35     set z;
36     drop x1-x5;
37     merge y;
```

```
38    proc print;
NOTE: The data set WORK.REGTOT has 19 observations and 18 variables.
NOTE: The DATA statement used 28.00 seconds.
39    proc reg data=regtot;
NOTE: The PROCEDURE PRINT used 31.00 seconds.
40        model y5=z1-z11/r;
41        model y5=z1-z11/selection=stepwise r;
42        model y6=z1-z11/r;
43        model y6=z1-z11/selection=stepwise r;
44        model y7=z1-z11/r;
45        model y7=z1-z11/selection=stepwise r;
46        model y8=z1-z11/r;
47        model y8=z1-z11/selection=stepwise r;
48        model y9=z1-z11/r;
49        model y9=z1-z11/selection=stepwise r;
50        model y10=z1-z11/r;
51        model y10=z1-z11/selection=stepwise r;
52    run;
NOTE: 19 observations read.
      19 observations used in computations.
53    quit;
NOTE: The PROCEDURE REG used 10.70 minutes.
```

OBS	RUN	X1	X2	X3	X4	X5	Y5
1	152-03-2	309.4	2495	288.193	17.5616	0.05	0.0000
2	152-04-3	345.1	2504	148.608	17.5616	0.05	0.0000
3	153-01-2	343.6	2521	471.043	17.5616	0.05	0.0000
4	153-02-2	375.4	2499	209.497	17.5616	0.05	0.0000
5	152-01-2	351.3	1756	315.019	16.4080	0.02	0.0000
6	152-02-2	350.2	1759	306.147	16.4080	0.05	0.0000
7	153-03-2	307.4	1746	469.669	16.4080	0.05	0.0000
8	153-04-2	307.6	1739	123.436	16.4080	0.05	0.0000
9	153-05-2	346.2	1741	298.787	16.4080	0.05	0.0000
10	153-06-2	347.2	1739	298.787	12.6224	0.05	0.0000
11	153-07-2	346.4	1765	298.787	20.4064	0.05	0.0000
12	153-08-2	343.7	1744	298.787	16.4080	0.05	0.0000
13	153-09-2	378.9	1741	441.292	16.4080	0.05	0.0326
14	153-10-2	383.0	1750	123.436	16.4080	0.05	0.0300
15	153-15-2	344.4	1757	311.044	16.4080	0.08	0.0000
16	153-11-2	376.8	1017	343.605	15.9936	0.05	0.0361
17	153-12-2	344.8	1019	507.486	15.9936	0.05	0.0000
18	153-13-2	344.9	985	101.494	15.9936	0.05	0.0000
19	153-14-2	308.9	986	321.811	15.9936	0.05	0.0000

OBS	Y6	Y7	Y8	Y9	Y10
1	0.0000	0.0000	0.1824	0.1554	0.87
2	0.0000	0.0416	0.2028	0.0909	0.94
3	0.0000	0.0411	0.1882	0.1168	0.88
4	0.0312	0.1351	0.1775	0.1104	1.00
5	0.0000	0.0000	0.1993	0.1157	0.90
6	0.0207	0.0622	0.2090	0.1134	0.97
7	0.0000	0.0000	0.2182	0.1289	0.79
8	0.0000	0.0000	0.2383	0.1209	0.82
9	0.0000	0.0515	0.1839	0.1263	0.95
10	0.0212	0.0637	0.1968	0.1223	0.91
11	0.0000	0.0000	0.1903	0.1297	0.89
12	0.0000	0.0522	0.2051	0.1197	0.92
13	0.0489	0.2108	0.1737	0.1397	1.05
14	0.0477	0.1979	0.2136	0.1199	1.50
15	0.0000	0.0522	0.1990	0.1423	0.90
16	0.0467	0.2059	0.1955	0.1365	1.09
17	0.0000	0.0597	0.2081	0.1110	0.91
18	0.0000	0.0000	0.1964	0.1395	1.21
19	0.0000	0.0000	0.1673	0.1206	0.89

OBS	RUN	Y5	Z1	Z2	Z3	Z4	Z5	Z6	Z7
1	152-03-2	0.0000	-1.01714	0.99333	-0.05904	0.85387	0	1.03458	0.98671
2	152-04-3	0.0000	0.00286	1.00533	-0.75696	0.85387	0	0.00001	1.01070
3	153-01-2	0.0000	-0.04000	1.02800	0.85522	0.85387	0	0.00160	1.05678
4	153-02-2	0.0000	0.86857	0.99867	-0.45251	0.85387	0	0.75442	0.99734
5	152-01-2	0.0000	0.18000	0.00800	0.07510	0.46933	-1	0.03240	0.00006
6	152-02-2	0.0000	0.14857	0.01200	0.03073	0.46933	0	0.02207	0.00014
7	153-03-2	0.0000	-1.07429	-0.00533	0.84834	0.46933	0	1.15409	0.00003
8	153-04-2	0.0000	-1.06857	-0.01467	-0.88282	0.46933	0	1.14184	0.00022
9	153-05-2	0.0000	0.03429	-0.01200	-0.00607	0.46933	0	0.00118	0.00014
10	153-06-2	0.0000	0.06286	-0.01467	-0.00607	-0.79253	0	0.00395	0.00022
11	153-07-2	0.0000	0.04000	0.02000	-0.00607	1.80213	0	0.00160	0.00040
12	153-08-2	0.0000	-0.03714	-0.00800	-0.00607	0.46933	0	0.00138	0.00006
13	153-09-2	0.0326	0.96857	-0.01200	0.70646	0.46933	0	0.93813	0.00014
14	153-10-2	0.0300	1.08571	0.00000	-0.88282	0.46933	0	1.17878	0.00000
15	153-15-2	0.0000	-0.01714	0.00933	0.05522	0.46933	1	0.00029	0.00009
16	153-11-2	0.0361	0.90857	-0.97733	0.21803	0.33120	0	0.82550	0.95518
17	153-12-2	0.0000	-0.00571	-0.97467	1.03743	0.33120	0	0.00003	0.94998
18	153-13-2	0.0000	-0.00286	-1.02000	-0.99253	0.33120	0	0.00001	1.04040
19	153-14-2	0.0000	-1.03143	-1.01867	0.10905	0.33120	0	1.06384	1.03768

OBS	Z8	Z9	Z10	Z11	Y6	Y7	Y8	Y9	Y10
1	0.00349	-1.01036	0.06005	-0.05864	0.0000	0.0000	0.1824	0.1554	0.87
2	0.57299	0.00287	-0.00216	-0.76100	0.0000	0.0416	0.2028	0.0909	0.94
3	0.73139	-0.04112	-0.03421	0.87916	0.0000	0.0411	0.1882	0.1168	0.88
4	0.20477	0.86741	-0.39304	-0.45191	0.0312	0.1351	0.1775	0.1104	1.00
5	0.00564	0.00144	0.01352	0.00060	0.0000	0.0000	0.1993	0.1157	0.90
6	0.00094	0.00178	0.00457	0.00037	0.0207	0.0622	0.2090	0.1134	0.97
7	0.71969	0.00573	-0.91136	-0.00452	0.0000	0.0000	0.2182	0.1289	0.79
8	0.77937	0.01567	0.94336	0.01295	0.0000	0.0000	0.2383	0.1209	0.82
9	0.00004	-0.00041	-0.00021	0.00007	0.0000	0.0515	0.1839	0.1263	0.95
10	0.00004	-0.00092	-0.00038	0.00009	0.0212	0.0637	0.1968	0.1223	0.91
11	0.00004	0.00080	-0.00024	-0.00012	0.0000	0.0000	0.1903	0.1297	0.89
12	0.00004	0.00030	0.00023	0.00005	0.0000	0.0522	0.2051	0.1197	0.92
13	0.49909	-0.01162	0.68426	-0.00848	0.0489	0.2108	0.1737	0.1397	1.05
14	0.77937	0.00000	-0.95849	0.00000	0.0477	0.1979	0.2136	0.1199	1.50
15	0.00305	-0.00016	-0.00095	0.00052	0.0000	0.0522	0.1990	0.1423	0.90
16	0.04753	-0.88798	0.19809	-0.21308	0.0467	0.2059	0.1955	0.1365	1.09
17	1.07626	0.00557	-0.00593	-1.01115	0.0000	0.0597	0.2081	0.1110	0.91
18	0.98512	0.00291	0.00284	1.01238	0.0000	0.0000	0.1964	0.1395	1.21
19	0.01189	1.05068	-0.11248	-0.11109	0.0000	0.0000	0.1673	0.1206	0.89

Model: MODEL1

Dependent Variable: Y5

H2S Produced, %

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Value	Prob>F
Model	11	0.00254	0.00023	7.601	0.0064
Error	7	0.00021	0.00003		
C Total	18	0.00275			
Root MSE		0.00551	R-square	0.9227	
Dep Mean		0.00519	Adj R-sq	0.8014	
C.V.		106.11218			

Parameter Estimates

Variable	DF	Parameter Estimate	Standard Error	T for H0: Parameter=0	Prob > T
INTERCEP	1	-0.000721	0.00255026	-0.283	0.7855
Z1	1	0.013926	0.00200413	6.949	0.0002
Z2	1	-0.004202	0.00215043	-1.954	0.0916
Z3	1	0.002090	0.00225096	0.929	0.3840
Z4	1	0.000177	0.00301426	0.059	0.9549
Z5	1	0.001641	0.00390389	0.420	0.6868
Z6	1	0.014325	0.00262120	5.465	0.0009
Z7	1	-0.000801	0.00268152	-0.299	0.7737
Z8	1	0.000476	0.00348475	0.137	0.8952
Z9	1	-0.007846	0.00299389	-2.621	0.0344
Z10	1	0.002850	0.00317716	0.897	0.3995
Z11	1	0.001528	0.00299344	0.510	0.6255

Variable	DF	Variable Label
INTERCEP	1	Intercept
Z1	1	
Z2	1	
Z3	1	
Z4	1	
Z5	1	
Z6	1	
Z7	1	
Z8	1	
Z9	1	
Z10	1	
Z11	1	

Obs	Dep Var Y5	Predict Value	Std Err Predict	Residual	Std Err Residual	Student Residual
1	0	0.00301	0.005	-0.00301	0.003	-1.073
2	0	-0.00807	0.004	0.00807	0.004	2.281
3	0	-0.00257	0.005	0.00257	0.003	1.019
4	0	0.00787	0.004	-0.00787	0.003	-2.431
5	0	0.000845	0.004	-0.00085	0.003	-0.256
6	0	0.00176	0.002	-0.00176	0.005	-0.344
7	0	0.000423	0.005	-0.00042	0.003	-0.147
8	0	0.00201	0.005	-0.00201	0.002	-0.864
9	0	-0.0001	0.002	0.000104	0.005	0.020
10	0	0.000126	0.004	-0.00013	0.003	-0.037
11	0	0.000073	0.004	-0.00007	0.003	-0.023
12	0	-0.00112	0.002	0.00112	0.005	0.219
13	0.0326	0.0301	0.005	0.00252	0.003	0.827
14	0.0300	0.0272	0.005	0.00284	0.003	1.027
15	0	0.000845	0.004	-0.00085	0.003	-0.256
16	0.0361	0.0348	0.005	0.00126	0.003	0.440
17	0	0.00367	0.005	-0.00367	0.002	-1.685
18	0	0.00268	0.005	-0.00268	0.002	-1.132
19	0	-0.00484	0.005	0.00484	0.002	2.219

Obs	-2-1-0 1 2	Cook's D
1	**	0.275
2	*****	0.621
3	**	0.328
4	*****	0.934
5		0.010
6		0.002
7		0.005
8	*	0.287
9		0.000
10		0.000
11		0.000
12		0.001
13	*	0.130
14	**	0.262
15		0.010
16		0.044
17	***	1.281
18	**	0.474
19	*****	2.211

Sum of Residuals 1.214306E-17
Sum of Squared Residuals 0.0002
Predicted Resid SS (Press) 0.0033

Stepwise Procedure for Dependent Variable Y5

Step 1 Variable Z1 Entered R-square = 0.41830139 C(p) = 37.70914696

	DF	Sum of Squares	Mean Square	F	Prob>F
Regression	1	0.00115169	0.00115169	12.22	0.0028
Error	17	0.00160156	0.00009421		
Total	18	0.00275325			

Variable	Parameter Estimate	Standard Error	Type II Sum of Squares	F	Prob>F
INTERCEP	0.00519116	0.00222675	0.00051202	5.43	0.0323
Z1	0.01188329	0.00339873	0.00115169	12.22	0.0028

Bounds on condition number: 1, 1

Step 2 Variable Z6 Entered R-square = 0.74615300 C(p) = 10.00170318

	DF	Sum of Squares	Mean Square	F	Prob>F
Regression	2	0.00205435	0.00102717	23.52	0.0001
Error	16	0.00069890	0.00004368		
Total	18	0.00275325			

Variable	Parameter Estimate	Standard Error	Type II Sum of Squares	F	Prob>F
INTERCEP	-0.00073664	0.00199987	0.00000593	0.14	0.7174
Z1	0.01359150	0.00234460	0.00146789	33.60	0.0001
Z6	0.01380855	0.00303763	0.00090266	20.66	0.0003

Bounds on condition number: 1.026365, 4.105459

Step 3 Variable Z9 Entered R-square = 0.83901769 C(p) = 3.58700503

	DF	Sum of Squares	Mean Square	F	Prob>F
Regression	3	0.00231002	0.00077001	26.06	0.0001
Error	15	0.00044322	0.00002955		
Total	18	0.00275325			

Variable	Parameter Estimate	Standard Error	Type II Sum of Squares	F	Prob>F
INTERCEP	-0.00072699	0.00164482	0.00000577	0.20	0.6648
Z1	0.01344419	0.00192900	0.00143528	48.57	0.0001
Z6	0.01378884	0.00249836	0.00090008	30.46	0.0001
Z9	-0.00835200	0.00283928	0.00025568	8.65	0.0101

Bounds on condition number: 1.027057, 9.162317

Step 4 Variable Z2 Entered R-square = 0.90118546 C(p) = -0.04617058

	DF	Sum of Squares	Mean Square	F	Prob>F
Regression	4	0.00248119	0.00062030	31.92	0.0001
Error	14	0.00027206	0.00001943		
Total	18	0.00275325			

Variable	Parameter Estimate	Standard Error	Type II Sum of Squares	F	Prob>F
INTERCEP	-0.00065984	0.00133409	0.00000475	0.24	0.6286
Z1	0.01341905	0.00156438	0.00142987	73.58	0.0001
Z2	-0.00462826	0.00155949	0.00017116	8.81	0.0102
Z6	0.01364242	0.00202668	0.00088054	45.31	0.0001
Z9	-0.00884188	0.00230847	0.00028509	14.67	0.0018

Bounds on condition number: 1.027087, 16.26244

All variables in the model are significant at the 0.1500 level.

No other variable met the 0.1500 significance level for entry into the model.

Summary of Stepwise Procedure for Dependent Variable Y5

Step	Variable Entered	Variable Removed	Number In	Partial R**2	Model R**2	C(p)	F	Prob>F
1	Z1		1	0.4183	0.4183	37.7091	12.2248	0.0028
2	Z6		2	0.3279	0.7462	10.0017	20.6645	0.0003
3	Z9		3	0.0929	0.8390	3.5870	8.6529	0.0101
4	Z2		4	0.0622	0.9012	-0.0462	8.8079	0.0102

Obs	Dep Var Y5	Predict Value	Std Err Predict	Residual	Std Err Residual	Student Residual
1	0	0.00414	0.003	-0.00414	0.003	-1.518
2	0	-0.00530	0.002	0.00530	0.004	1.356
3	0	-0.00557	0.002	0.00557	0.004	1.431
4	0	0.00900	0.003	-0.00900	0.003	-3.043
5	0	0.00215	0.001	-0.00215	0.004	-0.510
6	0	0.00156	0.001	-0.00156	0.004	-0.371
7	0	0.000643	0.002	-0.00064	0.004	-0.170
8	0	0.000508	0.002	-0.00051	0.004	-0.134
9	0	-0.00012	0.001	0.000125	0.004	0.030
10	0	0.000314	0.001	-0.00031	0.004	-0.075
11	0	-0.0002	0.001	0.000201	0.004	0.048
12	0	-0.00111	0.001	0.00111	0.004	0.263
13	0.0326	0.0253	0.002	0.00731	0.004	1.915
14	0.0300	0.0300	0.003	9.246E-6	0.004	0.003
15	0	-0.00093	0.001	0.000928	0.004	0.221
16	0.0361	0.0352	0.003	0.000931	0.003	0.317
17	0	0.00373	0.002	-0.00373	0.004	-0.953
18	0	0.00400	0.002	-0.00400	0.004	-1.030
19	0	-0.00456	0.003	0.00456	0.003	1.699

Obs	-2-1-0 1 2	Cook's D
1	***	0.743
2	**	0.100
3	**	0.116
4	*****	2.265
5	*	0.005
6		0.003
7		0.002
8		0.001
9		0.000
10		0.000
11		0.000
12		0.001
13	***	0.246
14		0.000
15		0.001
16		0.025
17	*	0.049
18	**	0.062
19	***	0.979

Sum of Residuals 4.336809E-18
Sum of Squared Residuals 0.0003
Predicted Resid SS (Press) 0.0009

Model: MODEL3

Dependent Variable: Y6

C2 Produced, %

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Value	Prob>F
Model	11	0.00588	0.00053	10.681	0.0023
Error	7	0.00035	0.00005		
C Total	18	0.00623			

Root MSE	0.00708	R-square	0.9438
Dep Mean	0.01139	Adj R-sq	0.8554
C.V.	62.13307		

Parameter Estimates

Variable	DF	Parameter Estimate	Standard Error	T for H0: Parameter=0	Prob > T
INTERCEP	1	0.008236	0.00327403	2.516	0.0401
Z1	1	0.023945	0.00257290	9.307	0.0001
Z2	1	0.000460	0.00276072	0.167	0.8724
Z3	1	0.001558	0.00288978	0.539	0.6065
Z4	1	-0.007853	0.00386971	-2.029	0.0820
Z5	1	0.002719	0.00501182	0.542	0.6044
Z6	1	0.020646	0.00336510	6.135	0.0005
Z7	1	-0.000492	0.00344254	-0.143	0.8903
Z8	1	-0.003778	0.00447373	-0.844	0.4264
Z9	1	-0.002450	0.00384356	-0.637	0.5442
Z10	1	0.002545	0.00407884	0.624	0.5524
Z11	1	0.000823	0.00384298	0.214	0.8365

Variable	DF	Variable Label
INTERCEP	1	Intercept
Z1	1	
Z2	1	
Z3	1	
Z4	1	
Z5	1	
Z6	1	
Z7	1	
Z8	1	
Z9	1	
Z10	1	
Z11	1	

Obs	Dep Var Y6	Predict Value	Std Err Predict	Residual	Std Err Residual	Student Residual
1	0	0.00098	0.006	-0.00098	0.004	-0.272
2	0	-0.00242	0.005	0.00242	0.005	0.533
3	0	-0.00013	0.006	0.000134	0.003	0.042
4	0.0312	0.0329	0.006	-0.00170	0.004	-0.408
5	0	0.00694	0.006	-0.00694	0.004	-1.634
6	0.0207	0.00862	0.003	0.0121	0.007	1.840
7	0	-0.00108	0.006	0.00108	0.004	0.293
8	0	0.000585	0.006	-0.00058	0.003	-0.196
9	0	0.00538	0.003	-0.00538	0.007	-0.822
10	0.0212	0.0160	0.006	0.00517	0.004	1.191
11	0	-0.00493	0.006	0.00493	0.004	1.200
12	0	0.00368	0.003	-0.00368	0.007	-0.562
13	0.0489	0.0481	0.006	0.000816	0.004	0.209
14	0.0477	0.0481	0.006	-0.00043	0.004	-0.120
15	0	0.00694	0.006	-0.00694	0.004	-1.634
16	0.0467	0.0462	0.006	0.000521	0.004	0.142
17	0	0.00127	0.007	-0.00127	0.003	-0.455
18	0	0.000152	0.006	-0.00015	0.003	-0.050
19	0	-0.0009	0.006	0.000904	0.003	0.323

Obs	-2	-1	0	1	2	Cook's D
1						0.018
2				*		0.034
3						0.001
4						0.026
5		***				0.395
6			***			0.046
7						0.019
8						0.015
9		*				0.010
10			**			0.196
11			**			0.236
12		*				0.005
13						0.008
14						0.004
15		***				0.395
16						0.005
17						0.094
18						0.001
19						0.047

Sum of Residuals 1.582935E-17
Sum of Squared Residuals 0.0004
Predicted Resid SS (Press) 0.0016

Stepwise Procedure for Dependent Variable Y6

Step 1 Variable Z1 Entered R-square = 0.58881753 C(p) = 36.18632383

	DF	Sum of Squares	Mean Square	F	Prob>F
Regression	1	0.00367073	0.00367073	24.34	0.0001
Error	17	0.00256334	0.00015078		
Total	18	0.00623408			

Variable	Parameter Estimate	Standard Error	Type II Sum of Squares	F	Prob>F
INTERCEP	0.01138309	0.00281710	0.00246192	16.33	0.0008
Z1	0.02121513	0.00429980	0.00367073	24.34	0.0001

Bounds on condition number: 1, 1

Step 2 Variable Z6 Entered R-square = 0.88344141 C(p) = 1.50987382

	DF	Sum of Squares	Mean Square	F	Prob>F
Regression	2	0.00550744	0.00275372	60.64	0.0001
Error	16	0.00072664	0.00004541		
Total	18	0.00623408			

Variable	Parameter Estimate	Standard Error	Type II Sum of Squares	F	Prob>F
INTERCEP	0.00292734	0.00203916	0.00009359	2.06	0.1704
Z1	0.02365183	0.00239066	0.00444518	97.88	0.0001
Z6	0.01969730	0.00309731	0.00183671	40.44	0.0001

Bounds on condition number: 1.026365, 4.105459

Step 3 Variable Z4 Entered R-square = 0.92167945 C(p) = -1.25021358

	DF	Sum of Squares	Mean Square	F	Prob>F
Regression	3	0.00574582	0.00191527	58.84	0.0001
Error	15	0.00048826	0.00003255		
Total	18	0.00623408			

Variable	Parameter Estimate	Standard Error	Type II Sum of Squares	F	Prob>F
INTERCEP	0.00701882	0.00229481	0.00030450	9.35	0.0080
Z1	0.02356846	0.00202418	0.00441287	135.57	0.0001
Z4	-0.00774243	0.00286103	0.00023838	7.32	0.0163
Z6	0.01963408	0.00262230	0.00182479	56.06	0.0001

Bounds on condition number: 1.026603, 9.15997

All variables in the model are significant at the 0.1500 level.

No other variable met the 0.1500 significance level for entry into the model.

Summary of Stepwise Procedure for Dependent Variable Y6

Step	Variable Entered Removed	Number In	Partial R**2	Model R**2	G(p)	F	Prob>F
1	Z1	1	0.5888	0.5888	36.1863	24.3442	0.0001
2	Z6	2	0.2946	0.8834	1.5099	40.4430	0.0001
3	Z4	3	0.0382	0.9217	-1.2502	7.3234	0.0163

Obs	Dep Var Y6	Predict Value	Std Err Predict	Residual	Std Err Residual	Student Residual
1	0	-0.00325	0.003	0.00325	0.005	0.660
2	0	0.000475	0.002	-0.00048	0.005	-0.089
3	0	-0.0005	0.002	0.000504	0.005	0.094
4	0.0312	0.0357	0.003	-0.00449	0.005	-0.888
5	0	0.00826	0.002	-0.00826	0.005	-1.516
6	0.0207	0.00732	0.002	0.0134	0.005	2.456
7	0	0.000725	0.003	-0.00073	0.005	-0.149
8	0	0.00062	0.003	-0.00062	0.005	-0.127
9	0	0.00422	0.002	-0.00422	0.005	-0.775
10	0.0212	0.0147	0.004	0.00649	0.004	1.655
11	0	-0.00596	0.004	0.00596	0.004	1.476
12	0	0.00254	0.002	-0.00254	0.005	-0.467
13	0.0489	0.0446	0.003	0.00427	0.005	0.865
14	0.0477	0.0521	0.003	-0.00442	0.005	-0.970
15	0	0.00299	0.002	-0.00299	0.005	-0.550
16	0.0467	0.0421	0.003	0.00462	0.005	0.916
17	0	0.00432	0.002	-0.00432	0.005	-0.799
18	0	0.00439	0.002	-0.00439	0.005	-0.811
19	0	0.00103	0.003	-0.00103	0.005	-0.209

Obs	-2	-1	0	1	2	Cook's D
1				*		0.037
2						0.000
3						0.000
4		*				0.054
5		***				0.055
6			****			0.146
7						0.002
8						0.001
9		*				0.015
10			***			0.767
11			**			0.542
12						0.006
13			*			0.063
14		*				0.134
15		*				0.008
16			*			0.058
17		*				0.018
18		*				0.019
19						0.004

Sum of Residuals 9.107298E-18
Sum of Squared Residuals 0.0005
Predicted Resid SS (Press) 0.0009

Model: MODEL5

Dependent Variable: Y7

C1 Produced, %

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Value	Prob>F
Model	11	0.09236	0.00840	24.821	0.0001
Error	7	0.00237	0.00034		
C Total	18	0.09473			
Root MSE		0.01839	R-square	0.9750	
Dep Mean		0.06178	Adj R-sq	0.9357	
C.V.		29.76937			

Parameter Estimates

Variable	DF	Parameter Estimate	Standard Error	T for H0: Parameter=0	Prob > T
INTERCEP	1	0.045441	0.00850949	5.340	0.0011
Z1	1	0.099595	0.00668720	14.893	0.0001
Z2	1	0.003400	0.00717535	0.474	0.6501
Z3	1	0.015896	0.00751080	2.116	0.0721
Z4	1	-0.023819	0.01005770	-2.368	0.0497
Z5	1	0.037186	0.01302616	2.855	0.0245
Z6	1	0.063818	0.00874618	7.297	0.0002
Z7	1	0.003045	0.00894745	0.340	0.7436
Z8	1	0.000428	0.01162761	0.037	0.9717
Z9	1	-0.011914	0.00998974	-1.193	0.2719
Z10	1	0.013598	0.01060126	1.283	0.2404
Z11	1	-0.012038	0.00998825	-1.205	0.2673

Variable	DF	Variable Label
INTERCEP	1	Intercept
Z1	1	
Z2	1	
Z3	1	
Z4	1	
Z5	1	
Z6	1	
Z7	1	
Z8	1	
Z9	1	
Z10	1	
Z11	1	

Obs	Dep Var Y7	Predict Value	Std Err Predict	Residual	Std Err Residual	Student Residual
1	0	0.00883	0.016	-0.00883	0.009	-0.944
2	0.0416	0.0292	0.014	0.0124	0.012	1.052
3	0.0411	0.0313	0.016	0.0098	0.008	1.168
4	0.1351	0.1488	0.015	-0.0137	0.011	-1.272
5	0	0.0185	0.015	-0.0185	0.011	-1.672
6	0.0622	0.0510	0.007	0.0112	0.017	0.654
7	0	0.00229	0.016	-0.00229	0.010	-0.238
8	0	-0.00056	0.017	0.000556	0.008	0.072
9	0.0515	0.0376	0.007	0.0139	0.017	0.816
10	0.0637	0.0707	0.015	-0.00699	0.011	-0.620
11	0	0.00656	0.015	-0.00656	0.011	-0.615
12	0.0522	0.0305	0.007	0.0217	0.017	1.276
13	0.2108	0.2115	0.015	-0.00074	0.010	-0.073
14	0.1979	0.1909	0.016	0.00701	0.009	0.761
15	0.0522	0.0707	0.015	-0.0185	0.011	-1.672
16	0.2059	0.1996	0.016	0.00627	0.010	0.657
17	0.0597	0.0655	0.017	-0.00584	0.007	-0.804
18	0	0.00943	0.017	-0.00943	0.008	-1.195
19	0	-0.00856	0.017	0.00856	0.007	1.176

Obs	-2 -1 0 1 2	Cook's D
1	*	0.213
2	**	0.132
3	**	0.430
4	**	0.256
5	***	0.414
6	*	0.006
7		0.013
8		0.002
9	*	0.009
10	*	0.053
11	*	0.062
12	**	0.023
13		0.001
14	*	0.144
15	***	0.414
16	*	0.098
17	*	0.292
18	**	0.528
19	**	0.621

Sum of Residuals -3.1225E-16
Sum of Squared Residuals 0.0024
Predicted Resid SS (Press) 0.0213

Stepwise Procedure for Dependent Variable Y7

Step 1 Variable Z1 Entered R-square = 0.69621280 C(p) = 70.06885319

	DF	Sum of Squares	Mean Square	F	Prob>F
Regression	1	0.06595343	0.06595343	38.96	0.0001
Error	17	0.02877828	0.00169284		
Total	18	0.09473171			

Variable	Parameter Estimate	Standard Error	Type II Sum of Squares	F	Prob>F
INTERCEP	0.06175716	0.00943911	0.07246499	42.81	0.0001
Z1	0.08992655	0.01440712	0.06595343	38.96	0.0001

Bounds on condition number: 1, 1

Step 2 Variable Z6 Entered R-square = 0.88582603 C(p) = 18.97188183

	DF	Sum of Squares	Mean Square	F	Prob>F
Regression	2	0.08391581	0.04195791	62.07	0.0001
Error	16	0.01081589	0.00067599		
Total	18	0.09473171			

Variable	Parameter Estimate	Standard Error	Type II Sum of Squares	F	Prob>F
INTERCEP	0.03531396	0.00786726	0.01362034	20.15	0.0004
Z1	0.09754669	0.00922341	0.07561097	111.85	0.0001
Z6	0.06159827	0.01194972	0.01796238	26.57	0.0001

Bounds on condition number: 1.026365, 4.105459

Step 3 Variable Z5 Entered R-square = 0.91434593 C(p) = 12.98551843

	DF	Sum of Squares	Mean Square	F	Prob>F
Regression	3	0.08661755	0.02887252	53.37	0.0001
Error	15	0.00811416	0.00054094		
Total	18	0.09473171			

Variable	Parameter Estimate	Standard Error	Type II Sum of Squares	F	Prob>F
INTERCEP	0.03512514	0.00703817	0.01347314	24.91	0.0002
Z1	0.09849067	0.00826161	0.07687997	142.12	0.0001
Z5	0.03680426	0.01646844	0.00270174	4.99	0.0411
Z6	0.06203749	0.01069143	0.01821329	33.67	0.0001

Bounds on condition number: 1.029055, 9.175481

Step 4 Variable Z3 Entered R-square = 0.93608787 C(p) = 8.89717048

	DF	Sum of Squares	Mean Square	F	Prob>F
Regression	4	0.08867720	0.02216930	51.26	0.0001
Error	14	0.00605450	0.00043246		
Total	18	0.09473171			

Variable	Parameter Estimate	Standard Error	Type II Sum of Squares	F	Prob>F
INTERCEP	0.03437741	0.00630234	0.01286748	29.75	0.0001
Z1	0.09987965	0.00741430	0.07848107	181.47	0.0001
Z3	0.01803919	0.00826600	0.00205965	4.76	0.0466
Z5	0.03715248	0.01472574	0.00275278	6.37	0.0244
Z6	0.06403363	0.00960316	0.01922819	44.46	0.0001

Bounds on condition number: 1.036694, 16.35991

Step 5 Variable Z4 Entered R-square = 0.95535425 C(p) = 5.50205068

	DF	Sum of Squares	Mean Square	F	Prob>F
Regression	5	0.09050234	0.01810047	55.64	0.0001
Error	13	0.00422937	0.00032534		
Total	18	0.09473171			

Variable	Parameter Estimate	Standard Error	Type II Sum of Squares	F	Prob>F
INTERCEP	0.04573906	0.00727258	0.01286854	39.55	0.0001
Z1	0.09959237	0.00643188	0.07800250	239.76	0.0001
Z3	0.01731541	0.00717596	0.00189425	5.82	0.0313
Z4	-0.02144300	0.00905324	0.00182514	5.61	0.0340
Z5	0.03711287	0.01277228	0.00274691	8.44	0.0123
Z6	0.06377815	0.00832993	0.01907187	58.62	0.0001

Bounds on condition number: 1.037063, 25.47228

Step 6 Variable Z10 Entered R-square = 0.96367125 C(p) = 5.17305829

	DF	Sum of Squares	Mean Square	F	Prob>F
Regression	6	0.09129022	0.01521504	53.05	0.0001
Error	12	0.00344148	0.00028679		
Total	18	0.09473171			

Variable	Parameter Estimate	Standard Error	Type II Sum of Squares	F	Prob>F
INTERCEP	0.04514211	0.00683767	0.01250005	43.59	0.0001
Z1	0.10082407	0.00608440	0.07875130	274.60	0.0001
Z3	0.01782192	0.00674439	0.00200257	6.98	0.0215
Z4	-0.02088855	0.00850660	0.00172929	6.03	0.0303

Z5	0.03737996	0.01199289	0.00278609	9.71	0.0089
Z6	0.06548175	0.00788816	0.01976301	68.91	0.0001
Z10	0.01566734	0.00945250	0.00078788	2.75	0.1233

Bounds on condition number: 1.054183, 36.96932

All variables in the model are significant at the 0.1500 level.

No other variable met the 0.1500 significance level for entry into the model.

Summary of Stepwise Procedure for Dependent Variable Y7

Step	Variable Entered Removed	Number In	Partial R**2	Model R**2	C(p)	F	Prob>F
1	Z1	1	0.6962	0.6962	70.0689	38.9602	0.0001
2	Z6	2	0.1896	0.8858	18.9719	26.5718	0.0001
3	Z5	3	0.0285	0.9143	12.9855	4.9945	0.0411
4	Z3	4	0.0217	0.9361	8.8972	4.7626	0.0466
5	Z4	5	0.0193	0.9554	5.5021	5.6100	0.0340
6	Z10	6	0.0083	0.9637	5.1731	2.7472	0.1233

Obs	Dep Var Y7	Predict Value	Std Err Predict	Residual	Std Err Residual	Student Residual
1	0	-0.00761	0.009	0.00761	0.015	0.521
2	0.0416	0.0141	0.008	0.0275	0.015	1.835
3	0.0411	0.0381	0.008	0.00302	0.015	0.203
4	0.1351	0.1501	0.009	-0.0150	0.015	-1.022
5	0	0.0198	0.013	-0.0198	0.011	-1.821
6	0.0622	0.0524	0.005	0.0098	0.016	0.607
7	0	0.00344	0.013	-0.00344	0.010	-0.328
8	0	0.00142	0.014	-0.00142	0.010	-0.144
9	0.0515	0.0388	0.005	0.0127	0.016	0.789
10	0.0637	0.0682	0.012	-0.00448	0.012	-0.386
11	0	0.0115	0.012	-0.0115	0.012	-0.962
12	0.0522	0.0316	0.005	0.0206	0.016	1.279
13	0.2108	0.2177	0.013	-0.00694	0.011	-0.645
14	0.1979	0.1912	0.014	0.00666	0.010	0.656
15	0.0522	0.0720	0.013	-0.0198	0.011	-1.821
16	0.2059	0.1909	0.009	0.0150	0.014	1.039
17	0.0597	0.0560	0.009	0.00365	0.015	0.250
18	0	0.0203	0.009	-0.0203	0.014	-1.407
19	0	0.00407	0.009	-0.00407	0.015	-0.278

Obs	-2-1-0 1 2	Cook's D
1		0.013
2		0.132
3		0.002
4	**	0.050
5	***	0.678
6	*	0.005
7		0.025
8		0.006
9	*	0.009
10		0.024
11	*	0.132
12	**	0.024
13	*	0.088
14	*	0.109
15	***	0.678
16	**	0.057
17		0.003
18	**	0.107
19		0.004

Sum of Residuals -8.67362E-17
Sum of Squared Residuals 0.0034
Predicted Resid SS (Press) 0.0098

Model: MODEL7

Dependent Variable: Y8

MeOH Insolubles, mass fr

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Value	Prob>F
Model	11	0.00371	0.00034	1.676	0.2528
Error	7	0.00141	0.00020		
C Total	18	0.00512			

Root MSE	0.01419	R-square	0.7248
Dep Mean	0.19713	Adj R-sq	0.2923
C.V.	7.19840		

Parameter Estimates

Variable	DF	Parameter Estimate	Standard Error	T for H0: Parameter=0	Prob > T
INTERCEP	1	0.199321	0.00656503	30.361	0.0001
Z1	1	-0.008015	0.00515914	-1.554	0.1642
Z2	1	-0.000950	0.00553575	-0.172	0.8686
Z3	1	-0.009297	0.00579454	-1.605	0.1526
Z4	1	-0.002714	0.00775947	-0.350	0.7368
Z5	1	-0.001109	0.01004962	-0.110	0.9153
Z6	1	-0.004577	0.00674763	-0.678	0.5194
Z7	1	-0.018770	0.00690291	-2.719	0.0298
Z8	1	0.025479	0.00897064	2.840	0.0250
Z9	1	-0.012017	0.00770703	-1.559	0.1629
Z10	1	-0.003671	0.00817882	-0.449	0.6671
Z11	1	-0.009932	0.00770589	-1.289	0.2384

Variable	DF	Variable Label
INTERCEP	1	Intercept
Z1	1	
Z2	1	
Z3	1	
Z4	1	
Z5	1	
Z6	1	
Z7	1	
Z8	1	
Z9	1	
Z10	1	
Z11	1	

Obs	Dep Var Y8	Predict Value	Std Err Predict	Residual	Std Err Residual	Student Residual
1	0.1824	0.1941	0.012	-0.0117	0.007	-1.621
2	0.2028	0.2062	0.011	-0.00342	0.009	-0.376
3	0.1882	0.1791	0.013	0.00912	0.006	1.407
4	0.1775	0.1719	0.011	0.00565	0.008	0.677
5	0.1993	0.1969	0.011	0.00237	0.009	0.278
6	0.2090	0.1964	0.005	0.0126	0.013	0.954
7	0.2182	0.2152	0.012	0.00305	0.007	0.411
8	0.2383	0.2257	0.013	0.0126	0.006	2.107
9	0.1839	0.1978	0.005	-0.0139	0.013	-1.062
10	0.1968	0.2010	0.011	-0.00423	0.009	-0.486
11	0.1903	0.1941	0.012	-0.00382	0.008	-0.464
12	0.2051	0.1984	0.005	0.00670	0.013	0.511
13	0.1737	0.1899	0.012	-0.0162	0.008	-2.061
14	0.2136	0.2155	0.012	-0.00193	0.007	-0.272
15	0.1990	0.1966	0.011	0.00237	0.009	0.278
16	0.1955	0.1816	0.012	0.0139	0.007	1.888
17	0.2081	0.2093	0.013	-0.00124	0.006	-0.221
18	0.1964	0.2041	0.013	-0.00771	0.006	-1.267
19	0.1673	0.1715	0.013	-0.00419	0.006	-0.746

Obs	-2 -1 0 1 2	Cook's D
1	***	0.627
2		0.017
3	**	0.625
4	*	0.073
5		0.011
6	*	0.012
7		0.037
8	*****	1.706 ?
9	**	0.016
10		0.033
11		0.035
12	*	0.004
13	*****	0.806
14		0.018
15		0.011
16	***	0.808
17		0.022
18	**	0.594
19	*	0.250

Sum of Residuals 4.996004E-16
Sum of Squared Residuals 0.0014
Predicted Resid SS (Press) 0.0184

Stepwise Procedure for Dependent Variable Y8

Step 1 Variable Z8 Entered R-square = 0.18356561 C(p) = 5.76467601

	DF	Sum of Squares	Mean Square	F	Prob>F
Regression	1	0.00094006	0.00094006	3.82	0.0672
Error	17	0.00418106	0.00024594		
Total	18	0.00512112			

Variable	Parameter Estimate	Standard Error	Type II Sum of Squares	F	Prob>F
INTERCEP	0.19098729	0.00477541	0.39339159	1599.51	0.0001
Z8	0.01816637	0.00929199	0.00094006	3.82	0.0672

Bounds on condition number: 1, 1

Step 2 Variable Z7 Entered R-square = 0.45488523 C(p) = 0.86410448

	DF	Sum of Squares	Mean Square	F	Prob>F
Regression	2	0.00232952	0.00116476	6.68	0.0078
Error	16	0.00279160	0.00017447		
Total	18	0.00512112			

Variable	Parameter Estimate	Standard Error	Type II Sum of Squares	F	Prob>F
INTERCEP	0.19652407	0.00447517	0.33646871	1928.47	0.0001
Z7	-0.01784107	0.00632214	0.00138946	7.96	0.0123
Z8	0.02411222	0.00810495	0.00154421	8.85	0.0089

Bounds on condition number: 1.072477, 4.289909

All variables in the model are significant at the 0.1500 level.
 No other variable met the 0.1500 significance level for entry into the model.

Summary of Stepwise Procedure for Dependent Variable Y8

Step	Variable Entered	Variable Removed	Number In	Partial R**2	Model R**2	C(p)	F	Prob>F
1	Z8		1	0.1836	0.1836	5.7647	3.8222	0.0672
2	Z7		2	0.2713	0.4549	0.8641	7.9637	0.0123

Obs	Dep Var Y8	Predict Value	Std Err Predict	Residual	Std Err Residual	Student Residual
1	0.1824	0.1790	0.006	0.00340	0.012	0.287
2	0.2028	0.1923	0.005	0.0105	0.012	0.852
3	0.1882	0.1953	0.005	-0.00711	0.012	-0.589
4	0.1775	0.1837	0.005	-0.00617	0.012	-0.505
5	0.1993	0.1967	0.004	0.00264	0.012	0.212
6	0.2090	0.1965	0.004	0.0125	0.012	1.002
7	0.2182	0.2139	0.005	0.00432	0.012	0.360
8	0.2383	0.2153	0.006	0.0230	0.012	1.940
9	0.1839	0.1965	0.004	-0.0126	0.012	-1.016
10	0.1968	0.1965	0.004	0.000279	0.012	0.022
11	0.1903	0.1965	0.004	-0.00622	0.012	-0.500
12	0.2051	0.1965	0.004	0.00858	0.012	0.690
13	0.1737	0.2086	0.004	-0.0349	0.012	-2.803
14	0.2136	0.2153	0.006	-0.00172	0.012	-0.145
15	0.1990	0.1966	0.004	0.00240	0.012	0.193
16	0.1955	0.1806	0.005	0.0149	0.012	1.238
17	0.2081	0.2055	0.007	0.00257	0.011	0.227
18	0.1964	0.2017	0.006	-0.00532	0.012	-0.461
19	0.1673	0.1783	0.006	-0.0110	0.012	-0.937

Obs	-2 -1 0 1 2	Cook's D
1		0.007
2		0.037
3	*	0.023
4	*	0.015
5		0.002
6	**	0.043
7		0.009
8	***	0.305
9	**	0.045
10		0.000
11	*	0.011
12	*	0.021
13	*****	0.336
14		0.002
15		0.002
16	**	0.107
17		0.006
18		0.022
19	*	0.078

Sum of Residuals 1.387779E-16
 Sum of Squared Residuals 0.0028
 Predicted Resid S (Press) 0.0038

Model: MODEL9

Dependent Variable: Y9

KF Water

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Value	Prob>F
Model	11	0.00286	0.00026	1.999	0.1837
Error	7	0.00091	0.00013		
C Total	18	0.00377			

Root MSE	0.01140	R-square	0.7586
Dep Mean	0.12421	Adj R-sq	0.3791
C.V.	9.17718		

Parameter Estimates

Variable	DF	Parameter Estimate	Standard Error	T for H0: Parameter=0	Prob > T
INTERCEP	1	0.122366	0.00527358	23.204	0.0001
Z1	1	-0.000360	0.00414425	-0.087	0.9331
Z2	1	-0.005891	0.00444677	-1.325	0.2269
Z3	1	0.003269	0.00465466	0.702	0.5052
Z4	1	0.003059	0.00623305	0.491	0.6386
Z5	1	0.013462	0.00807270	1.668	0.1393
Z6	1	0.010754	0.00542026	1.984	0.0877
Z7	1	-0.000230	0.00554500	-0.042	0.9680
Z8	1	-0.010817	0.00720597	-1.501	0.1770
Z9	1	-0.014082	0.00619094	-2.275	0.0571
Z10	1	0.001868	0.00656992	0.284	0.7843
Z11	1	0.014708	0.00619001	2.376	0.0492

Variable	DF	Variable Label
INTERCEP	1	Intercept
Z1	1	
Z2	1	
Z3	1	
Z4	1	
Z5	1	
Z6	1	
Z7	1	
Z8	1	
Z9	1	
Z10	1	
Z11	1	

Obs	Dep Var Y9	Predict Value	Std Err Predict	Residual	Std Err Residual	Student Residual
1	0.1554	0.1436	0.010	0.0118	0.006	2.029
2	0.0909	0.0989	0.009	-0.00801	0.007	-1.096
3	0.1168	0.1270	0.010	-0.0102	0.005	-1.966
4	0.1104	0.1034	0.009	0.00702	0.007	1.049
5	0.1157	0.1108	0.009	0.00493	0.007	0.720
6	0.1134	0.1240	0.004	-0.0106	0.011	-1.002
7	0.1289	0.1298	0.010	-0.00087	0.006	-0.146
8	0.1209	0.1270	0.010	-0.00607	0.005	-1.261
9	0.1263	0.1239	0.004	0.00244	0.011	0.232
10	0.1223	0.1200	0.009	0.00226	0.007	0.323
11	0.1297	0.1277	0.009	0.00197	0.007	0.298
12	0.1197	0.1239	0.004	-0.00415	0.011	-0.395
13	0.1397	0.1318	0.010	0.00786	0.006	1.248
14	0.1199	0.1230	0.010	-0.00308	0.006	-0.539
15	0.1423	0.1374	0.009	0.00493	0.007	0.720
16	0.1365	0.1474	0.010	-0.0109	0.006	-1.845
17	0.1110	0.1057	0.010	0.00531	0.005	1.179
18	0.1395	0.1301	0.010	0.00940	0.005	1.922
19	0.1206	0.1245	0.010	-0.00394	0.005	-0.874

Obs	-2 -1 0 1 2	Cook's D
1	*****	0.983
2	**	0.143
3	***	1.219
4	**	0.174
5	*	0.077
6	**	0.014
7		0.005
8	**	0.612
9		0.001
10		0.014
11		0.015
12		0.002
13	**	0.296
14	*	0.072
15	*	0.077
16	***	0.771
17	**	0.627
18	***	1.366
19	*	0.343

Sum of Residuals -2.498E-16
Sum of Squared Residuals 0.0009
Predicted Resid SS (Press) 0.0139

Stepwise Procedure for Dependent Variable Y9

Step 1 Variable Z9 Entered R-square = 0.24561887 C(p) = 6.87108371

	DF	Sum of Squares	Mean Square	F	Prob>F
Regression	1	0.00092521	0.00092521	5.54	0.0309
Error	17	0.00284164	0.00016716		
Total	18	0.00376685			

Variable	Parameter Estimate	Standard Error	Type II Sum of Squares	F	Prob>F
INTERCEP	0.12420743	0.00296608	0.29312222	1753.59	0.0001
Z9	-0.01588237	0.00675080	0.00092521	5.54	0.0309

Bounds on condition number: 1, 1

Step 2 Variable Z11 Entered R-square = 0.39363875 C(p) = 4.57967831

	DF	Sum of Squares	Mean Square	F	Prob>F
Regression	2	0.00148278	0.00074139	5.19	0.0183
Error	16	0.00228407	0.00014275		
Total	18	0.00376685			

Variable	Parameter Estimate	Standard Error	Type II Sum of Squares	F	Prob>F
INTERCEP	0.12467397	0.00275120	0.29315406	2053.55	0.0001
Z9	-0.01486333	0.00625992	0.00080479	5.64	0.0304
Z11	0.01242174	0.00628533	0.00055757	3.91	0.0656

Bounds on condition number: 1.006831, 4.027325

Step 3 Variable Z6 Entered R-square = 0.49861304 C(p) = 3.53625463

	DF	Sum of Squares	Mean Square	F	Prob>F
Regression	3	0.00187820	0.00062607	4.97	0.0136
Error	15	0.00188865	0.00012591		
Total	18	0.00376685			

Variable	Parameter Estimate	Standard Error	Type II Sum of Squares	F	Prob>F
INTERCEP	0.12082143	0.00337668	0.16120092	1280.29	0.0001
Z6	0.00905972	0.00511228	0.00039542	3.14	0.0967
Z9	-0.01479963	0.00587911	0.00079788	6.34	0.0237
Z11	0.01338887	0.00592805	0.00064228	5.10	0.0392

Bounds on condition number: 1.015437, 9.092567

Step 4 Variable Z5 Entered R-square = 0.59444712 C(p) = 2.75782469

	DF	Sum of Squares	Mean Square	F	Prob>F
Regression	4	0.00223919	0.00055980	5.13	0.0093
Error	14	0.00152766	0.00010912		
Total	18	0.00376685			

Variable	Parameter Estimate	Standard Error	Type II Sum of Squares	F	Prob>F
INTERCEP	0.12078336	0.00314354	0.16109220	1476.31	0.0001
Z5	0.01343561	0.00738681	0.00036099	3.31	0.0904
Z6	0.00914932	0.00475945	0.00040324	3.70	0.0751
Z9	-0.01479308	0.00547307	0.00079717	7.31	0.0172
Z11	0.01339924	0.00551862	0.00064328	5.90	0.0293

Bounds on condition number: 1.015438, 16.12429

Step 5 Variable Z8 Entered R-square = 0.66579972 C(p) = 2.68916378

	DF	Sum of Squares	Mean Square	F	Prob>F
Regression	5	0.00250797	0.00050159	5.18	0.0078
Error	13	0.00125888	0.00009684		
Total	18	0.00376685			

Variable	Parameter Estimate	Standard Error	Type II Sum of Squares	F	Prob>F
INTERCEP	0.12363513	0.00342049	0.12651718	1306.50	0.0001
Z5	0.01344266	0.00695872	0.00036137	3.73	0.0755
Z6	0.01036178	0.00454230	0.00050392	5.20	0.0400
Z8	-0.00988362	0.00593257	0.00026877	2.78	0.1196
Z9	-0.01436230	0.00516236	0.00074954	7.74	0.0156
Z11	0.01425812	0.00522429	0.00072129	7.45	0.0172

Bounds on condition number: 1.035294, 25.5273

Step 6 Variable Z2 Entered R-square = 0.73006495 C(p) = 2.82598043

	DF	Sum of Squares	Mean Square	F	Prob>F
Regression	6	0.00275004	0.00045834	5.41	0.0064
Error	12	0.00101680	0.00008473		
Total	18	0.00376685			

Variable	Parameter Estimate	Standard Error	Type II Sum of Squares	F	Prob>F
INTERCEP	0.12403784	0.00320846	0.12664050	1494.57	0.0001
Z2	-0.00554566	0.00328098	0.00024208	2.86	0.1168
Z5	0.01344368	0.00650933	0.00036143	4.27	0.0612
Z6	0.01031392	0.00424906	0.00049925	5.89	0.0319

Z8	-0.01101243	0.00558949	0.00032891	3.88	0.0723
Z9	-0.01491662	0.00484010	0.00080480	9.50	0.0095
Z11	0.01414031	0.00488741	0.00070928	8.37	0.0135

Bounds on condition number: 1.050288, 36.8779

All variables in the model are significant at the 0.1500 level.
 No other variable met the 0.1500 significance level for entry into the model.

Summary of Stepwise Procedure for Dependent Variable Y9

Step	Variable Entered Removed	Number In	Partial R**2	Model R**2	C(p)	F	Prob>F
1	Z9	1	0.2456	0.2456	6.8711	5.5350	0.0309
2	Z11	2	0.1480	0.3936	4.5797	3.9058	0.0656
3	Z6	3	0.1050	0.4986	3.5363	3.1405	0.0967
4	Z5	4	0.0958	0.5944	2.7578	3.3083	0.0904
5	Z8	5	0.0714	0.6658	2.6892	2.7755	0.1196
6	Z2	6	0.0643	0.7301	2.8260	2.8569	0.1168

Obs	Dep Var Y9	Predict Value	Std Err Predict	Residual	Std Err Residual	Student Residual
1	0.1554	0.1434	0.007	0.0120	0.006	1.927
2	0.0909	0.1013	0.006	-0.0104	0.007	-1.505
3	0.1168	0.1233	0.007	-0.00654	0.006	-1.021
4	0.1104	0.1047	0.006	0.00570	0.007	0.842
5	0.1157	0.1108	0.007	0.00489	0.006	0.860
6	0.1134	0.1242	0.003	-0.0108	0.009	-1.245
7	0.1289	0.1279	0.004	0.00100	0.008	0.122
8	0.1209	0.1273	0.004	-0.00636	0.008	-0.776
9	0.1263	0.1241	0.003	0.00218	0.009	0.252
10	0.1223	0.1242	0.003	-0.00187	0.009	-0.217
11	0.1297	0.1239	0.003	0.00577	0.009	0.669
12	0.1197	0.1241	0.003	-0.00439	0.009	-0.509
13	0.1397	0.1283	0.003	0.0114	0.009	1.309
14	0.1199	0.1276	0.004	-0.00771	0.008	-0.946
15	0.1423	0.1374	0.007	0.00489	0.006	0.860
16	0.1365	0.1477	0.007	-0.0112	0.006	-1.725
17	0.1110	0.1032	0.008	0.00779	0.005	1.672
18	0.1395	0.1331	0.007	0.00638	0.006	1.110
19	0.1206	0.1233	0.007	-0.00268	0.006	-0.479

Obs	-2	-1	0	1	2	Cook's D
1				***		0.630
2		***				0.245
3		**				0.158
4				*		0.086
5				*		0.171
6		**				0.030
7						0.001
8		*				0.022
9						0.001
10						0.001
11				*		0.009
12		*				0.005
13				**		0.030
14		*				0.035
15				*		0.171
16		***				0.432
17				***		1.159
18				**		0.274
19						0.056

Sum of Residuals -5.55112E-17
Sum of Squared Residuals 0.0010
Predicted Resid SS (Press) 0.0040

Model: MODEL11

Dependent Variable: Y10

HPLC

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Value	Prob>F
Model	11	0.42451	0.03859	6.401	0.0106
Error	7	0.04220	0.00603		
C Total	18	0.46672			
Root MSE		0.07765	R-square	0.9096	
Dep Mean		0.96789	Adj R-sq	0.7675	
C.V.		8.02212			

Parameter Estimates

Variable	DF	Parameter Estimate	Standard Error	T for H0: Parameter=0	Prob > T
INTERCEP	1	0.914854	0.03592311	25.467	0.0001
Z1	1	0.159005	0.02823024	5.632	0.0008
Z2	1	-0.061463	0.03029097	-2.029	0.0820
Z3	1	-0.110344	0.03170709	-3.480	0.0103
Z4	1	-0.005830	0.04245892	-0.137	0.8946
Z5	1	0.014863	0.05499039	0.270	0.7947
Z6	1	0.062319	0.03692229	1.688	0.1353
Z7	1	0.009130	0.03777197	0.242	0.8159
Z8	1	0.071470	0.04908635	1.456	0.1887
Z9	1	-0.050848	0.04217202	-1.206	0.2671
Z10	1	-0.112004	0.04475360	-2.503	0.0408
Z11	1	0.062259	0.04216574	1.477	0.1833

Variable	DF	Variable Label
INTERCEP	1	Intercept
Z1	1	
Z2	1	
Z3	1	
Z4	1	
Z5	1	
Z6	1	
Z7	1	
Z8	1	
Z9	1	
Z10	1	
Z11	1	

Obs	Dep Var Y10	Predict Value	Std Err Predict	Residual	Std Err Residual	Student Residual
1	0.8700	0.8083	0.067	0.0617	0.039	1.562
2	0.9400	0.9350	0.060	0.00504	0.050	0.101
3	0.8800	0.8686	0.069	0.0114	0.035	0.320
4	1.0000	1.0791	0.063	-0.0791	0.046	-1.733
5	0.9000	0.9180	0.062	-0.0180	0.047	-0.386
6	0.9700	0.9325	0.029	0.0375	0.072	0.521
7	0.7900	0.8729	0.066	-0.0829	0.041	-2.042
8	0.8200	0.8617	0.070	-0.0417	0.033	-1.273
9	0.9500	0.9191	0.030	0.0309	0.072	0.430
10	0.9100	0.9314	0.061	-0.0214	0.048	-0.449
11	0.8900	0.9102	0.063	-0.0202	0.045	-0.449
12	0.9200	0.9074	0.030	0.0126	0.072	0.175
13	1.0500	1.0065	0.065	0.0435	0.043	1.015
14	1.5000	1.4187	0.067	0.0813	0.039	2.089
15	0.9000	0.9180	0.062	-0.0180	0.047	-0.386
16	1.0900	1.1667	0.066	-0.0767	0.040	-1.904
17	0.9100	0.8805	0.071	0.0295	0.031	0.963
18	1.2100	1.2271	0.070	-0.0171	0.033	-0.515
19	0.8900	0.8284	0.071	0.0616	0.031	2.006

Obs	-2	-1	0	1	2	Cook's D
1				***		0.582
2						0.001
3						0.032
4		***				0.475
5						0.022
6				*		0.004
7		****				0.923
8		**				0.623
9						0.003
10						0.028
11						0.033
12						0.000
13				**		0.195
14				****		1.084
15						0.022
16		***				0.822
17				*		0.418
18		*				0.098
19				****		1.807

Sum of Residuals -1.66533E-15
Sum of Squared Residuals 0.0422
Predicted Resid SS (Press) 0.6804

Stepwise Procedure for Dependent Variable Y10

Step 1 Variable Z1 Entered R-square = 0.45213391 C(p) = 27.41230287

	DF	Sum of Squares	Mean Square	F	Prob>F
Regression	1	0.21101804	0.21101804	14.03	0.0016
Error	17	0.25569775	0.01504104		
Total	18	0.46671579			

Variable	Parameter Estimate	Standard Error	Type II Sum of Squares	F	Prob>F
INTERCEPT	0.96784636	0.02813599	17.79780120	1183.28	0.0001
Z1	0.16085296	0.04294457	0.21101804	14.03	0.0016

Bounds on condition number: 1, 1

Step 2 Variable Z3 Entered R-square = 0.61755171 C(p) = 16.60671062

	DF	Sum of Squares	Mean Square	F	Prob>F
Regression	2	0.28822113	0.14411057	12.92	0.0005
Error	16	0.17849466	0.01115592		
Total	18	0.46671579			

Variable	Parameter Estimate	Standard Error	Type II Sum of Squares	F	Prob>F
INTERCEPT	0.96718095	0.02423257	17.77140062	1593.00	0.0001
Z1	0.15394427	0.03707781	0.19231106	17.24	0.0008
Z3	-0.10993620	0.04179035	0.07720310	6.92	0.0182

Bounds on condition number: 1.005042, 4.020169

Step 3 Variable Z10 Entered R-square = 0.69655405 C(p) = 12.49085269

	DF	Sum of Squares	Mean Square	F	Prob>F
Regression	3	0.32509277	0.10836426	11.48	0.0004
Error	15	0.14162302	0.00944153		
Total	18	0.46671579			

Variable	Parameter Estimate	Standard Error	Type II Sum of Squares	F	Prob>F
INTERCEPT	0.96430413	0.02234046	17.59082714	1863.13	0.0001
Z1	0.14717289	0.03428175	0.17400921	18.43	0.0006
Z3	-0.11229192	0.03846390	0.08046981	8.52	0.0106
Z10	-0.10618532	0.05373281	0.03687164	3.91	0.0668

Bounds on condition number: 1.015184, 9.095572

Step 4 Variable Z2 Entered R-square = 0.77662886 C(p) = 8.29197117

	DF	Sum of Squares	Mean Square	F	Prob>F
Regression	4	0.36246495	0.09061624	12.17	0.0002
Error	14	0.10425084	0.00744649		
Total	18	0.46671579			

Variable	Parameter Estimate	Standard Error	Type II Sum of Squares	F	Prob>F
INTERCEP	0.96404745	0.01984056	17.58087699	2360.96	0.0001
Z1	0.14606910	0.03044909	0.17136401	23.01	0.0003
Z2	-0.06883857	0.03072794	0.03737218	5.02	0.0418
Z3	-0.12020493	0.03434134	0.09123502	12.25	0.0035
Z10	-0.11625974	0.04793072	0.04381091	5.88	0.0294

Bounds on condition number: 1.01964, 16.28337

Step 5 Variable Z8 Entered R-square = 0.82446125 C(p) = 6.58909174

	DF	Sum of Squares	Mean Square	F	Prob>F
Regression	5	0.38478908	0.07695782	12.21	0.0002
Error	13	0.08192671	0.00630205		
Total	18	0.46671579			

Variable	Parameter Estimate	Standard Error	Type II Sum of Squares	F	Prob>F
INTERCEP	0.93393611	0.02427151	9.33088622	1480.61	0.0001
Z1	0.14796339	0.02802978	0.17561076	27.87	0.0001
Z2	-0.06135923	0.02854619	0.02911693	4.62	0.0510
Z3	-0.11734477	0.03162892	0.08674426	13.76	0.0026
Z8	0.08980127	0.04771295	0.02232413	3.54	0.0824
Z10	-0.10789844	0.04431720	0.03735663	5.93	0.0301

Bounds on condition number: 1.039125, 25.66991

Step 6 Variable Z6 Entered R-square = 0.85581724 C(p) = 6.16171063

	DF	Sum of Squares	Mean Square	F	Prob>F
Regression	6	0.39942342	0.06657057	11.87	0.0002
Error	12	0.06729237	0.00560770		
Total	18	0.46671579			

Variable	Parameter Estimate	Standard Error	Type II Sum of Squares	F	Prob>F
INTERCEP	0.91305525	0.02629206	6.76284338	1205.99	0.0001
Z1	0.15568354	0.02686899	0.18826401	33.57	0.0001
Z2	-0.06014226	0.02693824	0.02795153	4.98	0.0454
Z3	-0.11257037	0.02998168	0.07905345	14.10	0.0027

Z6	0.05689230	0.03521756	0.01463434	2.61	0.1322
Z8	0.08005696	0.04541017	0.01742916	3.11	0.1033
Z10	-0.09968621	0.04211250	0.03142191	5.60	0.0356

Bounds on condition number: 1.074639, 37.71817

Step 7 Variable Z11 Entered R-square = 0.88889034 C(p) = 5.60140202

	DF	Sum of Squares	Mean Square	F	Prob>F
Regression	7	0.41485916	0.05926559	12.57	0.0002
Error	11	0.05185663	0.00471424		
Total	18	0.46671579			

Variable	Parameter Estimate	Standard Error	Type II Sum of Squares	F	Prob>F
INTERCEP	0.91455724	0.02412101	6.77707666	1437.58	0.0001
Z1	0.16075724	0.02479475	0.19816789	42.04	0.0001
Z2	-0.05911962	0.02470566	0.02699491	5.73	0.0357
Z3	-0.10537805	0.02777554	0.06785578	14.39	0.0030
Z6	0.06469839	0.03257725	0.01859387	3.94	0.0725
Z8	0.07318495	0.04180862	0.01444520	3.06	0.1078
Z10	-0.10037674	0.03861409	0.03185563	6.76	0.0247
Z11	0.06675359	0.03689069	0.01543574	3.27	0.0978

Bounds on condition number: 1.09382, 51.80222

All variables in the model are significant at the 0.1500 level.
No other variable met the 0.1500 significance level for entry into the model.

Summary of Stepwise Procedure for Dependent Variable Y10

Step	Variable Entered	Number Removed	Number In	Partial R**2	Model R**2	C(p)	F	Prob>F
1	Z1		1	0.4521	0.4521	27.4123	14.0295	0.0016
2	Z3		2	0.1654	0.6176	16.6067	6.9204	0.0182
3	Z10		3	0.0790	0.6966	12.4909	3.9053	0.0668
4	Z2		4	0.0801	0.7766	8.2920	5.0188	0.0418
5	Z8		5	0.0478	0.8245	6.5891	3.5424	0.0824
6	Z6		6	0.0314	0.8558	6.1617	2.6097	0.1322
7	Z11		7	0.0331	0.8889	5.6014	3.2743	0.0978

Obs	Dep Var Y10	Predict Value	Std Err Predict	Residual	Std Err Residual	Student Residual
1	0.8700	0.7558	0.043	0.1142	0.053	2.144
2	0.9400	0.9267	0.051	0.0133	0.046	0.290
3	0.8800	0.8730	0.058	0.00702	0.037	0.189
4	1.0000	1.1159	0.042	-0.1159	0.054	-2.131
5	0.9000	0.9363	0.024	-0.0363	0.065	-0.563
6	0.9700	0.9356	0.024	0.0344	0.064	0.534
7	0.7900	0.8713	0.055	-0.0813	0.041	-1.975
8	0.8200	0.8738	0.058	-0.0538	0.036	-1.494
9	0.9500	0.9215	0.024	0.0285	0.064	0.443
10	0.9100	0.9265	0.024	-0.0165	0.064	-0.256
11	0.8900	0.9206	0.024	-0.0306	0.064	-0.475
12	0.9200	0.9098	0.024	0.0102	0.064	0.159
13	1.0500	1.0245	0.054	0.0255	0.042	0.609
14	1.5000 ?	1.4116	0.056	0.0884	0.039	2.248
15	0.9000	0.9058	0.024	-0.00580	0.064	-0.090
16	1.0900	1.1182	0.044	-0.0282	0.053	-0.536
17	0.9100	0.8738	0.063	0.0362	0.028	1.285
18	1.2100	1.2184	0.059	-0.00838	0.034	-0.244
19	0.8900	0.8711	0.046	0.0189	0.051	0.374

Obs	-2 -1 0 1 2	Cook's D
1	****	0.380
2		0.013
3		0.011
4	****	0.337
5	*	0.005
6	*	0.005
7	***	0.869
8	**	0.737
9		0.003
10		0.001
11		0.004
12		0.000
13	*	0.078
14	****	1.297
15		0.000
16	*	0.025
17	**	1.019
18		0.022
19		0.015

Sum of Residuals -8.88178E-16
Sum of Squared Residuals 0.0519
Predicted Resid SS (Press) 0.2954

6.0 GASIFICATION RESEARCH

6.1 Hydrogen Production from Low-Rank Coals

PRODUCTION OF HYDROGEN FROM LOW-RANK COALS

Annual Technical Report for the Period
April 1, 1988 through June 30, 1989

By

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Morgantown, WV 26505

TABLE OF CONTENTS

	<u>Page</u>
1.0 INTRODUCTION.....	1
2.0 GOALS AND OBJECTIVES.....	3
3.0 ACCOMPLISHMENTS.....	4
3.1 Hydrogen-from-Coal Continuous Process Unit (CPU).....	4
3.1.1 Trona Catalyst Testing.....	4
3.1.1.1 Gabbro Bed Material Runs.....	4
3.1.1.2 Taconite Bed Material Runs.....	4
3.1.2 Limestone Testing.....	7
3.1.2.1 Test Matrix.....	7
3.1.2.2 Stream Analyses.....	8
3.1.2.3 Statistical Analysis.....	17
3.1.3 Extended Test Runs.....	32
3.1.3.1 Product Gas.....	32
3.1.3.2 Cyclone Fines.....	32
3.1.3.3 Wastewater Analysis.....	32
3.1.3.4 Bed Material.....	34
3.1.4 Reactor Testing.....	35
3.1.4.1 Bed Probe Testing.....	35
3.1.4.2 Kinetic Effects of Bed Temperature and Steam:Carbon Ratio.....	37
3.1.4.3 Bed Height Testing.....	38
3.1.5 CPU Bench-Scale Support Studies.....	43
3.1.5.1 Bed Material Testing.....	43
3.1.5.2 Wastewater Treatment.....	45
3.2 Coal Properties and Reactivity Analysis.....	48
3.2.1 Thermogravimetric Analysis.....	48
3.2.2 Active Site Measurement.....	48
3.2.3 Surface Analysis.....	51
3.2.3.1 Surface Area.....	51
3.2.3.2 ESCA Analysis of Char Surface.....	52
3.2.4 Topical Report.....	52
3.3 Hydrogen Market Assessment.....	52
3.4 Economic Assessment.....	54
4.0 CONCLUSIONS.....	58
5.0 PRESENTATIONS AND PUBLICATIONS.....	59
6.0 REFERENCES.....	59
APPENDIX A - Unadjusted Material Balances for CPU Limestone Test Matrix.....	A-1
APPENDIX B - Adjusted Material Balances for CPU Limestone Test Matrix..	B-1
APPENDIX C - Definition of Terms Used in Regression Summary Tables.....	C-1

LIST OF TABLES

<u>Table</u>	<u>Page</u>
3-1 Product Gas Compositions and Production Rates for CPU Bed Material Test Runs at 750°C and a 2:1 Steam:Carbon Molar Ratio..	7
3-2 Proximate and Ultimate Analyses of Cyclone Fines for CPU Bed Material Test Runs at 750°C and a 2:1 Steam:Carbon Molar Ratio..	8
3-3 Experimental Design for CPU Limestone Test Matrix.....	9
3-4 Proximate and Ultimate Analyses of Feed Coals.....	10
3-5 Product Gas Compositions for CPU Limestone Test Matrix.....	11
3-6 Proximate and Ultimate Analyses of Cyclone Fines for CPU Limestone Test Matrix.....	13
3-7 Wastewater Analysis for CPU Limestone Test Matrix.....	15
3-8 Proximate and Ultimate Analyses of Bed Material Blowdown for CPU Limestone Test Matrix.....	18
3-9 CPU Results of Limestone Test Matrix.....	20
3-10 Regression Summary -- Limestone Test Matrix..... (Case B: Using [Total Water]/Carbon, Mole Ratio)	23
3-11 Regression Summary -- Limestone Test Matrix..... (Case C: Using X_2 = Oxygen/Steam, Mole Ratio)	25
3-12 Key to Variables Used to Describe Responses.....	27
3-13 Product Gas Compositions for Extended CPU Runs.....	33
3-14 Proximate and Ultimate Analyses of Cyclone Fines for Extended CPU Runs	34
3-15 Wastewater Analysis for Extended CPU Runs.....	35
3-16 Bed Material Analyses for Extended CPU Runs.....	36
3-17 CPU Bed Probe Test Runs, Carbon Content of Bed (wt%).....	37
3-18 Carbon Consumption Rate Constants for CPU Limestone Test Matrix	39
3-19 Laboratory Reactivity Parameters (TGA).....	40
3-20 Product Gas Compositions for CPU Bed Height Test Runs with Martin Lake Coal.....	40

LIST OF TABLES (Cont.)

<u>Table</u>	<u>Page</u>
3-21 Product Gas Compositions for CPU Bed Height Test Runs with Wyodak Coal.....	41
3-22 Heat Capacities of Bed Materials at Various Temperatures.....	45
3-23 Steam Stripper Feed and Final Product Compositions.....	46
3-24 Product Gas Analyses for Laboratory-Scale TGA Experiments (mol%).....	49
3-25 Reactivity Parameter (k) at 25% Carbon Conversion.....	50
3-26 C/Active Site and Reactivity Parameter for Catalyzed and Uncatalyzed Velva Lignite.....	51
3-27 Potassium Active Sites on Velva Char Prepared at 750°C as Determined by Enriched ¹³ C NMR Spectroscopy.....	53
3-28 BET Surface Areas of Velva Lignite and Char With and Without Catalyst.....	53
3-29 Common Plant Design Criteria and Assumptions.....	56
3-30 Economic Evaluation Approach.....	56
A-1 Unadjusted Material Balances for Wyodak Parametric Tests.....	A1-1
A-2 Unadjusted Material Balances for Martin Lake and Velva Parametric Tests.....	A1-3
B-1 Adjusted Material Balances for Wyodak Parametric Tests.....	B1-2
B-2 Adjusted Material Balances for Martin Lake and Velva Parametric Tests.....	B1-4

LIST OF FIGURES

<u>Figure</u>	<u>Page</u>
3-1 Agglomerates From Trona Test Matrix Using Wyodak Subbituminous Coal with 5 wt% Trona Catalyst at Various Steam:Carbon Molar Ratios.....	5
3-2 Hydrogen Production per maf Coal Versus Total Water:Carbon Ratio.....	27
3-3 Carbon Monoxide Production per maf Coal Versus Total Water:Carbon Ratio.....	28
3-4 Carbon Dioxide Production per maf Coal Versus Total Water:Carbon Ratio.....	28
3-5 Hydrogen Production per maf Coal Versus Oxygen:Steam Ratio.....	29
3-6 Carbon Monoxide Production per maf Coal Versus Oxygen:Steam Ratio.....	29
3-7 Carbon Dioxide Production per maf Coal Versus Oxygen:Steam Ratio.....	30
3-8 Hydrogen in Product Gas per Hydrogen in Reactants Versus Total Water:Carbon Ratio.....	31
3-9 Carbon in Product Gas per Carbon Fed Versus Average Bed Temperature.....	31
3-10 Gas Production Rates for Extended CPU Test Runs.....	33
3-11 Schematic of Bed Probe.....	37
3-12 Rates of Reaction for Carbon Consumption and Gas Production Versus Steam:Carbon Ratio.....	38
3-13 Gas Production Versus Bed Height for Martin Lake CPU Test Runs..	41
3-14 Gas Production Versus Bed Height for Wyodak CPU Test Runs.....	42
3-15 Rate of Reaction for Carbon Consumption Versus Bed Height.....	42
3-16 Heat Capacity Versus Temperature for Various Bed Materials.....	44
3-17 Schematic of Bench-Scale Wastewater Treatment Unit.....	47
3-18 Atom % Aliphatic ^{13}C Versus wt% K_2CO_3 for Velsa/ K_2CO_3 Char Reacted with $^{13}\text{CH}_3\text{I}$ as Determined by Solid ^{13}C NMR Spectroscopy.....	52

LIST OF FIGURES (Cont.)

<u>Figure</u>	<u>Page</u>
3-19 Simplified Flow Diagram for Hydrogen Plant.....	57
3-20 Simplified Flow Diagram for Methanol Plant.....	57
3-21 Simplified Flow Diagram for Fuel Cell Plant.....	58

PRODUCTION OF HYDROGEN FROM LOW-RANK COALS

ANNUAL TECHNICAL PROGRESS REPORT APRIL 1, 1988 THROUGH MARCH 31, 1989

1.0 INTRODUCTION

Hydrogen is a key component in ammonia and methanol synthesis, petroleum refining, petrochemical processing, and the production of coal-derived synfuels. Hydrogen can also be used directly as a fuel. The demand for hydrogen has been projected to increase by a factor of 19 to 27 over the next 45 years (1). Most of the hydrogen currently used in chemical applications is produced either through steam reforming of natural gas or, in refining applications, through partial oxidation of petroleum. Advanced coal gasification technologies appear to be the most probable alternative for meeting the future demand for large quantities of hydrogen. Low-rank coals (lignites and subbituminous coals) are the preferred feedstock for such applications because of their low mining cost and higher reactivities relative to higher-rank coals.

The two most important considerations in the design of a process for producing hydrogen from coal are to maintain operating conditions that thermodynamically favor the production of hydrogen and carbon dioxide over carbon monoxide and methane, and to obtain reaction rates that result in sufficient gasifier throughput. Optimization of the conditions for maximum hydrogen content of the product gas requires steam gasification at relatively mild temperature and pressure. Temperatures in the range of 700° to 800°C at atmospheric pressure maximize hydrogen production. In tests at the University of North Dakota Energy & Mineral Research Center (UNDEMRC), a dry synthesis gas containing 63% hydrogen was produced by steam gasification of low-rank coal (2). These mild conditions do not, however, promote high reaction rates. As a result, increasing coal reactivity is perhaps the most critical factor in the selection of a gasification process for producing hydrogen from coal. The rate-limiting step in the production of hydrogen from low-rank coals is the steam gasification of the char.

The primary advantage of lignites and subbituminous coals is their greater reactivity relative to coals of higher rank. This increase in reactivity is caused by higher concentrations of active sites, higher porosity, and a more uniform dispersion of alkali impurities that act as inherent catalysts. In steam gasification tests conducted using bench-scale fixed-bed thermogravimetric analysis (TGA), low-rank coal char reactivities were found to be nearly ten times higher than that of a bituminous coal char gasified at the same conditions (3). In addition to the high reactivity determined for low-rank coal chars relative to bituminous coal chars, increases in reactivity were also observed with increasing temperature, within the range of moderate temperatures that maximize hydrogen production, and with the addition of alkali catalysts. An increase in steam gasification temperature from 700° to 800°C resulted in an increase in reactivity from approximately 1.0 (g/hr)/g to 3.5 (g/hr)/g. Reactivities computed for lignite chars catalyzed with a 10 wt% loading of pure sodium carbonate or potassium carbonate ranged from 4.8 to 5.5 (g/hr)/g at 750°C, compared to 1.6 to 2.0

(g/hr)/g for uncatalyzed lignite chars. Catalysis of a bituminous coal char with similar loadings of the alkali carbonates also increased reactivity; however, catalyzed bituminous coal char was found to be five to six times less reactive than similarly catalyzed lignites.

It is important to provide process operating conditions that maximize the rate of the char-steam reaction. Fixed-bed gasification is not preferred because of heat and mass transfer limitations on the endothermic steam gasification reaction. Entrained-bed systems are also not preferred because they present difficulties in maintaining long enough residence times for reaction without the use of extensive solids recycle.

A fluid-bed system operated with catalyzed low-rank coal offers both excellent heat and mass transfer and processing flexibility; it is, therefore, attractive for process development. Fluid-bed reactors can achieve more uniform temperature and solids distributions than fixed- or entrained-bed gasifiers, and have high heat transfer characteristics. Further, the use of smaller particles in a fluid-bed system results in less diffusional resistance than a fixed-bed system, more efficient waste heat recovery, and smaller pressure drops. Also, because fluid-bed systems allow coal devolatilization, gasification, and ash removal within a single vessel they are likely to be used for eventual scale-up of the hydrogen production process.

The physical and chemical natures of low-rank coals offer several advantages for use in this fluid-bed hydrogen production process. The high volatile matter content of lignites supports their use in steam gasification to produce hydrogen, as devolatilization products can be cracked in the hot zone of a fluid-bed to form additional hydrogen. Under suitable reaction conditions raw product gas from such a system would contain essentially only hydrogen, carbon dioxide, carbon monoxide, and only small quantities of methane and sulfur gases. This was proven in the operation of the CO₂ Acceptor process, a fluid-bed system utilizing low-rank coals (4). In addition to producing hydrogen and simplifying downstream gas clean-up, cracking of tars and oils in the gasifier reduces the contaminant concentrations in the process condensate.

Because of the implications of catalyst cost and associated catalyst recovery costs, several potentially disposable catalysts were also evaluated in bench-scale steam gasification tests (3). Addition of either trona or nahcolite (naturally occurring alkali carbonate minerals) at 10 wt% loadings, resulted in reactivities higher than with equivalent mass loadings of reagent-grade alkali carbonates. The improvement in reactivity obtained using minerals such as trona and nahcolite indicates the need to further evaluate impure sources of alkali as disposable catalysts for steam gasification and subsequent hydrogen production from low-rank coals.

The economics of this process are affected by several market factors. The first is the cost and availability of competing feedstocks. If the projected shortages in gaseous and liquid fossil fuels are realized, hydrogen from coal will become the most probable alternative for large-scale production of replacement fuel. The capital costs of hydrogen production via coal gasification have been shown to make up over 50% of the final product cost. The lower feedstock cost and higher reactivity of lignites or

subbituminous coal used in a catalytic steam gasification process should more than offset any additional capital cost resulting from additional coal handling requirements. The use of disposable catalysts may also have a major impact on the economics of low-rank coal use.

The properties of low-rank coals and selection of gasifier configuration not only influence gasification economics, but also affect the overall design and economics of the hydrogen-from-coal system. Cracking of devolatilization products in a fluid-bed system offers an environmental advantage, as does the low sulfur content of low-rank coals. The degree to which these benefits are realized in the gasification process will significantly impact the extent of gas and wastewater treatment required. The extent of product gas treatment will also be affected by the selection of end-use applications. End uses for hydrogen range from fuel cells and transportation fuel, to chemical feedstock (such as for methanol and ammonia synthesis), to use in synfuels production, each of which requires different hydrogen purity ranging from 65-99%. The end uses for, and economics of producing hydrogen will thus be influenced by the quality of the raw product gas and the extent of gas clean-up required.

A more complete evaluation of the use of low-rank coals in catalytic steam gasification to produce hydrogen is required. To date, much of this work has been performed at the laboratory scale, and has focused only on fundamental reactivity studies. These data must be verified on a larger scale, and a more complete evaluation of the concept must be performed before the technical realities, and also the economic feasibility of the process can be clearly stated. This report describes the third year's activities and results on the production of hydrogen from low-rank coal research project at UNDEMRC. The project involves pilot-scale process development in addition to evaluating reactivity and fundamental properties of low-rank coals under hydrogen-producing conditions.

2.0 GOALS AND OBJECTIVES

The objective of this research is to evaluate the technical feasibility of producing low-cost hydrogen by catalytic steam gasification of low-rank coals. This approach takes advantage of the high reactivity and high volatile matter, moisture, and inherent alkali content of low-rank coals. This effort will provide a proof-of-concept and the early stages of engineering development. The research program will include the design, construction, and testing of a 6-inch diameter fluid-bed system and determination of the optimum operating conditions for producing low-cost hydrogen. Data collected from this process development work will be used to generate an economic assessment of the process. In addition, gas and wastewater treatment, and end use applications will be evaluated as part of a systems approach study to be performed in conjunction with the process economics study.

In parallel with this process development and systems analysis work, an evaluation of the relationship between the fundamental properties of low-rank coals and their reactivity under hydrogen-producing conditions will be conducted. Bench-scale TGA will be used to compute coal char reactivities on both a weight basis and an active-site basis, and to correlate reactivities

with identified coal properties. Instrumental analyses to be performed on each coal, char, and ash derived from reactivity studies include solid ^{13}C Nuclear Magnetic Resonance (NMR), x-ray diffraction (XRD), x-ray fluorescence analysis (XRFA), Electron Spectroscopy for Chemical Analysis (ESCA), and Scanning Electron Microscopy/Energy Dispersive Spectroscopy (SEM/EDS) surface analysis.

3.0 ACCOMPLISHMENTS

3.1 Hydrogen-from-Coal Continuous Process Unit (CPU)

3.1.1 Trona Catalyst Testing

3.1.1.1 Gabbro Bed Material Runs

The trona test matrix was a Box-Behnken design for four factors including steam:carbon molar ratio, bed temperature, catalyst concentration, and coal. The matrix was broken down into three blocks of nine tests for a total of 27 tests. The range of each factor was determined by the operability testing conducted in the second year of the project (5). Steam:carbon molar ratio ranged from 1:1 to 3:1; bed temperature ranged from 700° to 800°C; and trona catalyst concentration ranged from 0 to 10 wt%. The coals used in the test matrix were Wyodak (Wyoming) subbituminous coal, Martin Lake (Texas) lignite, and Velva (North Dakota) lignite. Gabbro was selected as the bed material based on laboratory studies on agglomeration with the trona catalyst at operating temperatures.

Test runs for the first block of the trona test matrix were conducted in April and were plagued by numerous operating problems. The most frequent problem encountered was agglomeration of the gabbro bed material with the trona catalyst causing poor fluidization, and in some cases, seizure of the coal screw feeder. The remainder of the trona test matrix was cancelled due to the difficulties in running the first block of the trona test matrix.

The severity of bed agglomeration increased with decreasing steam:carbon ratio, as shown in Figure 3-1. This may indicate that the agglomeration is due to the surface combustion reactions as follows. As the steam:carbon ratio decreases, less sensible heat from the superheated steam is available to maintain temperature in the gasifier and must be supplemented by increased combustion. With the increased quantity of oxygen in the gasifier, more surface combustion reactions are occurring that have a higher localized surface temperature than the bulk bed temperature. The higher temperatures may cause the sodium carbonate in the trona to melt and adhere to the bed material. This melt then bridges between two or more bed particles and solidifies, resulting in the growth of agglomerates.

3.1.1.2 Taconite Bed Material Runs

Trona, although an excellent catalyst for the gasification reaction, caused agglomeration problems with silica sand, limestone, or gabbro as the bed material. Rather than discontinue the use of trona as a catalyst, it was

Run 1

5-W5T17C

1:1 Steam:Carbon Ratio

RUN 2-W5T275

2:1 Steam:Carbon Ratio

RUN 3-W5T380

3:1 Steam:Carbon Ratio

Figure 3-1. Agglomerates From Trona Test Matrix Using Wyodak Subbituminous Coal with 5 wt% Trona Catalyst at Various Steam:Carbon Molar Ratios.

decided to test taconite as the bed material both with and without trona. The expected reduction of hematite in the taconite to magnetite would allow magnetic separation of the upgraded ore as a byproduct, possibly improving the economics of the hydrogen production process.

A meeting was held at the Coleraine Research Laboratory in Coleraine, Minnesota, between EMRC personnel and scientists at the Coleraine lab to determine the best taconite ore to use in the CPU testing. The recommendation of the Coleraine scientists was to try lean ores that contain 35-45% hematite. Four barrels of lean taconite ore were obtained from the Coleraine lab for CPU testing. The runs were performed using Wyodak subbituminous coal at a 2:1 steam:carbon ratio and a bed temperature of 750°C. Runs 1 and 2 were uncatalyzed to determine how the CPU operated using taconite as the bed material. Runs 3 and 4 were catalyzed with 5 wt% trona. Contrary to expectations, only minor agglomeration occurred during the trona-catalyzed runs. The hot bed material from the first run was exposed to air after blowdown, allowing some of the magnetite to oxidize to hematite. After the first run, a nitrogen purge was set up to prevent oxidation of the blowdown during future taconite runs.

Three additional runs were performed using the lean taconite ore as the bed material with Wyodak subbituminous coal at a 2:1 steam:carbon ratio and a bed temperature of 750°C. One run was a repeat of the first uncatalyzed run. Two runs were catalyzed with 10 wt% trona. Unlike the runs made with taconite and 5 wt% trona, which showed only minor agglomeration, severe agglomeration of the bed material occurred and both runs were terminated prematurely. Large agglomerates were found during the post-run inspection of the gasifier.

Gas compositions and production rates for the uncatalyzed and trona-catalyzed taconite and limestone bed material CPU runs are given in Table 3-1. All the bed material tests listed in Table 3-1 were conducted at 750°C and a 2:1 steam:carbon molar ratio. The hydrogen concentration in the product gas was nominally 45 mol% for all of the bed material test runs. Hydrogen gas production rates were highest for the 5 wt% trona-catalyzed taconite runs and lowest for the uncatalyzed taconite runs, ranging from 13.2 to 15.3 scf/lb moisture- and ash-free (maf) coal. The carbon monoxide concentration and production rates were lower for the taconite runs, which may indicate that the carbon monoxide was utilized for reduction of hematite to magnetite. Percent carbon converted to gas was lowest for the uncatalyzed taconite runs at 78%. Nearly 85% carbon conversion was achieved for the limestone and trona-catalyzed taconite runs.

The proximate and ultimate analyses and fines production rates for the bed material tests are given in Table 3-2. Both the uncatalyzed and trona-catalyzed taconite test runs produced fines lower in carbon content than the limestone run, with the trona-catalyzed runs having the lowest fines carbon content. The ash contents of the fines from the taconite test runs were higher than those from the limestone test. This increase in inorganic content may be from attrition of the bed material and may be the reason for the higher fines production rate with the taconite test runs. The mass mean diameter (MMD) of the fines ranged from 108 to 128 microns. The particle size distributions of the fines for the various bed materials were very similar.

TABLE 3-1

PRODUCT GAS COMPOSITIONS AND PRODUCTION RATES FOR CPU BED MATERIAL
TEST RUNS AT 750°C AND A 2:1 STEAM:CARBON MOLAR RATIO

Bed Material	<u>Limestone</u>	<u>Taconite</u>	<u>Taconite</u>	<u>Taconite</u>	<u>Taconite</u>
Catalyst	None	None	None	Trona	Trona
Concentration	---	---	---	5 wt%	5 wt%
Product Gas Composition (mol%):					
H ₂	44.23	44.49	44.51	45.62	46.26
CO ₂	39.21	41.16	40.53	39.88	38.95
CO	12.72	9.82	10.58	11.60	11.62
CH ₄	3.00	3.74	3.46	2.07	2.41
C ₂ H ₄	0.62	0.54	0.67	0.63	0.50
C ₂ H ₆	0.17	0.19	0.19	0.19	0.18
C ₃ H ₆	0.01	0.00	0.00	0.00	0.00
C ₃ H ₈	0.00	0.00	0.00	0.00	0.00
C ₄ H ₈	0.00	0.00	0.00	0.00	0.00
C ₄ H ₁₀	0.00	0.00	0.00	0.00	0.00
H ₂ S	0.04	0.06	0.06	0.06	0.08
Gas Production Rates:					
scf H ₂ /lb maf coal	14.18	13.24	13.61	14.47	15.29
scf CO/lb maf coal	4.08	2.92	3.24	3.68	3.84
scf CO ₂ /lb maf coal	12.57	12.25	12.39	12.65	12.84
% carbon conv. to gas	85.37	76.48	79.73	83.19	85.45

3.1.2 Limestone Testing

3.1.2.1 Test Matrix

The unsuccessful CPU operation with the trona catalyst led to the development of a test matrix using only limestone as a bed material with no additional catalyst to determine the effects of steam:carbon ratio and bed temperature on gas production. A Box-Behnken experimental design for three factors was chosen for the limestone test matrix, as illustrated in Table 3-3. The three factors included steam:carbon molar ratio, bed temperature, and coal type. The range for each factor and the three test coals used in the limestone matrix were the same as in the trona test matrix. This series of 15 tests was relatively trouble free. The only major operational problem that

TABLE 3-2

PROXIMATE AND ULTIMATE ANALYSES OF CYCLONE FINES FOR CPU BED MATERIAL
TEST RUNS AT 750°C AND A 2:1 STEAM:CARBON MOLAR RATIO

Bed Material	<u>Limestone</u>	<u>Taconite</u>	<u>Taconite</u>	<u>Taconite</u>	<u>Taconite</u>
Catalyst	None	None	None	Trona	Trona
Concentration	---	---	---	5 wt%	5 wt%
Proximate Analysis (wt%):					
Moisture ^a	4.40	2.30	2.10	1.50	4.00
Volatile Matter ^b	14.71	19.28	20.90	24.16	25.60
Fixed Carbon ^b (by diff.)	54.24	32.33	34.66	19.28	15.36
Ash ^b	31.05	48.39	44.44	56.56	59.04
Ultimate Analysis (wt%): ^b					
Hydrogen	1.10	0.88	0.97	0.64	0.66
Carbon	60.53	47.06	51.49	40.26	37.71
Nitrogen	0.80	0.51	0.60	0.43	0.29
Sulfur	0.67	0.36	0.39	0.43	0.56
Oxygen (by diff.)	5.82	2.78	2.09	1.69	1.73
Ash	31.05	48.39	44.44	56.56	59.04
Fines Production Rate, lb/hr	2.52	4.75	4.34	4.60	3.65
Mass Mean Diameter (MMD), microns	128	115	113	118	108

^a As-received

^b Moisture-free

occurred was an increase in freeboard pressure in the gasifier due to a build-up of organic residue in the glycol-cooled heat exchanger of the gas quench system.

3.1.2.2 Stream Analyses

Typical proximate and ultimate analyses of the feed coals for the limestone test matrix are listed in Table 3-4. Velva lignite was highest in moisture content and lowest in ash content of the test coals. The three coals had similar elemental compositions based on the ultimate analyses.

The product gas compositions measured by gas chromatography for the limestone test matrix are shown in Table 3-5. The hydrogen content of the product gas ranged from 41.6 to 47.9 mol% for the entire matrix and, in general, decreased with increasing temperature and decreasing steam:carbon ratio for the Velva and Martin Lake coal runs. The hydrogen composition for the Wyodak runs behaved similarly at the 1:1 steam:carbon ratio (decreasing

TABLE 3-3
EXPERIMENTAL DESIGN FOR CPU LIMESTONE TEST MATRIX

Test	Run Order	X ₁	X ₂	X ₃
1	14	-1	-1	0
2	4	1	-1	0
3	10	-1	1	0
4	6	1	1	0
5	7	-1	0	-1
6	5	1	0	-1
7	13	-1	0	1
8	9	1	0	1
9	3	0	-1	-1
10	1	0	1	-1
11	15	0	-1	1
12	11	0	1	1
13	2	0	0	0
14	8	0	0	0
15	12	0	0	0

Where:

X₁ Bed Temperature

-1 = 700°C
0 = 750°C
1 = 800°C

X₂ Steam:Carbon Molar Ratio

-1 = 1:1
0 = 2:1
1 = 3:1

X₃ Coal

-1 = Martin Lake lignite
0 = Wyodak Subbituminous Coal
1 = Velva lignite

with increasing temperatures), but increased in hydrogen content with increasing steam:carbon ratio at 800°C. The carbon dioxide composition of the product gas ranged from 35.9 to 42.9 mol% for the entire matrix and also displayed the general trend of increasing with lower temperatures and higher steam:carbon ratios. Carbon monoxide composition ranged from 7.1 to 20.1 mol% and decreased with lower temperatures and higher steam:carbon ratios, which was the reverse of the carbon dioxide composition trend.

The proximate and ultimate analyses of the cyclone fines from the limestone test matrix are shown in Table 3-6. The fines production rate did not vary greatly for the Wyodak subbituminous coal, but did show a decrease with increasing temperature and steam:carbon ratio for the Velva and Martin

TABLE 3-4
PROXIMATE AND ULTIMATE ANALYSES OF FEED COALS

Coal	<u>Velva</u>	<u>Martin Lake</u>	<u>Wyodak</u>
Proximate Analysis (wt%): ^a			
Moisture	34.55	31.60	29.88
Volatile Matter	28.15	30.11	30.55
Fixed Carbon (by diff.)	31.49	30.65	33.63
Ash	5.80	7.62	5.93
Ultimate Analysis (wt%): ^b			
Hydrogen	4.54	4.74	4.65
Carbon	63.95	63.28	64.29
Nitrogen	0.93	1.10	0.91
Sulfur	0.32	1.02	0.42
Oxygen (by diff.)	21.35	18.72	21.23
Heating Value, BTU/lb ^a	6975	7568	7728

^a As-received

^b Moisture-free

Lake lignites. The carbon content of the fines generally decreased with increasing bed temperature and ranged from 65 to 47 wt% for all the test coals. The MMD of the Wyodak fines ranged from 78 to 151 microns over the test matrix and decreased with increasing temperature. The MMD of the Wyodak fines also decreased with increasing steam:carbon ratio at 800°C, but remained relatively constant with increasing steam:carbon ratio at 700°C. The MMD for the Velva fines ranged from 113 to 146 microns and decreased with increasing steam:carbon ratio, but remained constant with changing temperature. The MMD for the Martin Lake fines ranged from 109 to 138 microns and decreased with increasing temperature and steam:carbon ratio.

The analyses of the process condensates from the first-stage gas/liquid separation vessel for the limestone matrix are listed in Table 3-7. The condensates were alkaline, with pH's greater than 8.5. The alkaline pH is due to the high concentration of free ammonia in the condensate. The ammonia concentration generally decreases with higher steam:carbon ratios, due to dilution of the condensate with larger quantities of unreacted steam. Total carbon contents of the condensates decreased with lower temperatures and higher steam:carbon ratios and were all above 1700 mg/l. A majority of the carbon in the condensate was inorganic, as the total organic carbon (TOC) was typically less than 650 mg/l. Chemical oxygen demand (COD) and biochemical

TABLE 3-5

PRODUCT GAS COMPOSITIONS FOR CPU LIMESTONE TEST MATRIX

Run No.	14	4	2	2R	12	12R	10R	6
Coal	Wyodak	Wyodak	Wyodak	Wyodak	Wyodak	Wyodak	Wyodak	Wyodak
Bed Temp., °C	699	696	751	746	743	750	806	802
Steam:Carbon	1.57	3.51	2.50	2.10	2.31	2.35	1.28	3.41
Molar Ratio								
Bed Material	Limestone	Limestone	Limestone	Limestone	Limestone	Limestone	Limestone	Limestone
Product Gas Composition (mol%):								
H ₂	44.94	46.88	46.76	45.93	46.81	44.23	44.98	44.60
CO ₂	39.00	42.04	38.38	38.31	36.16	34.21	33.84	40.94
CO	11.28	7.13	10.79	11.47	14.37	12.72	17.92	10.55
CH ₄	3.75	2.69	2.85	3.07	2.02	3.00	2.40	2.70
C ₂ H ₄	0.37	0.57	0.78	0.84	0.31	0.62	0.61	0.67
C ₂ H ₆	0.15	0.02	0.02	0.20	0.01	0.17	0.01	0.17
C ₃ H ₆	0.46	0.63	0.39	0.08	0.29	0.02	ND	0.39
C ₃ H ₈	ND	ND	ND	ND	ND	ND	ND	ND
C ₄ H ₈	ND	ND	ND	ND	ND	ND	ND	ND
C ₄ H ₁₀	ND	ND	ND	ND	ND	ND	ND	ND
H ₂ S	0.06	0.05	0.05	0.05	0.03	0.04	0.08	0.15

ND = Not Detected

TABLE 3-5 (Cont.)

PRODUCT GAS COMPOSITIONS FOR CPU LIMESTONE TEST MATRIX

Run No.	15	13	9	11	3	7	5	1
Coal	Velva	Velva	Velva	Velva	Martin Lake	Martin Lake	Martin Lake	Martin Lake
Bed Temp., °C	698	744	750	802	699	741	752	801
Steam:Carbon Molar Ratio	2.34	1.37	3.31	2.38	2.44	1.04	3.40	2.23
Bed Material	Limestone	Limestone	Limestone	Limestone	Limestone	Limestone	Limestone	Limestone
Product Gas Composition (mol%):								
H ₂	45.69	43.22	45.91	43.65	47.89	43.89	46.06	44.75
CO ₂	42.08	38.82	42.88	41.63	40.14	36.94	40.18	37.34
CO	9.00	14.69	8.24	12.11	8.53	14.08	9.55	13.30
CH ₄	2.44	2.47	2.27	2.17	3.09	3.61	2.70	3.19
C ₂ H ₄	0.30	0.45	0.51	0.34	0.61	0.78	0.95	0.91
C ₂ H ₆	0.08	0.01	0.01	0.05	0.02	0.03	0.02	0.01
C ₃ H ₆	0.37	0.31	0.12	0.08	0.49	0.51	0.48	0.38
C ₃ H ₈	ND	ND	ND	ND	ND	ND	ND	ND
C ₄ H ₈	ND	ND	ND	ND	ND	ND	ND	ND
C ₄ H ₁₀	ND	ND	ND	ND	ND	ND	ND	ND
H ₂ S	0.03	0.04	0.03	0.05	0.16	0.17	0.07	0.11

ND = Not Detected

TABLE 3-6

PROXIMATE AND ULTIMATE ANALYSES OF CYCLONE FINES FOR CPU LIMESTONE TEST MATRIX

Run No.	14	4	2	2R	12	12R	10R	6
Coal	Wyodak	Wyodak	Wyodak	Wyodak	Wyodak	Wyodak	Wyodak	Wyodak
Bed Temperature, °C	699	696	751	746	743	750	806	802
Steam:Carbon Molar Ratio	1.57	3.51	2.50	2.10	2.31	2.35	1.28	3.41
Bed Material	Limestone	Limestone	Limestone	Limestone	Limestone	Limestone	Limestone	Limestone
Fines Production Rate, lb/hr	3.67	2.59	2.85	3.75	2.80	2.52	2.57	2.30
Proximate Analysis (wt%):								
Moisture ^a	1.50	2.70	1.80	2.50	1.80	4.40	6.50	4.70
Volatile Matter ^b	14.67	14.70	12.83	14.28	15.53	14.71	15.87	20.40
Fixed Carbon (by diff.) ^b	52.28	60.55	61.04	59.84	47.84	54.24	46.30	36.58
Ash ^b	33.05	24.75	26.13	25.88	36.63	31.05	37.83	43.02
Ultimate Analysis (wt%): ^b								
Hydrogen	1.33	1.53	1.31	1.29	1.25	1.10	0.70	0.82
Carbon	64.15	64.97	63.39	63.82	60.39	60.53	52.08	47.11
Nitrogen	0.91	1.00	0.93	0.91	0.85	0.80	0.65	0.59
Sulfur	0.56	0.66	0.43	0.55	0.71	0.67	0.71	0.52
Oxygen	0.00	7.07	7.79	7.53	0.15	5.82	8.01	7.93
Ash	33.05	24.75	26.13	25.88	36.63	31.05	37.83	43.02
Mass Mean Diameter (μ m), microns	144	151	137	135	151	128	93	78

^a As-Received^b Moisture-Free

TABLE 3-6 (Cont.)

PROXIMATE AND ULTIMATE ANALYSES OF CYCLONE FINES FOR CPU LIMESTONE TEST MATRIX

Run No.	15	13	9	11	3	7	5	1
Coal	Velva	Velva	Velva	Velva	Martin Lake	Martin Lake	Martin Lake	Martin Lake
Bed Temperature, °C	698	744	750	802	699	741	752	801
Steam:Carbon Molar Ratio	2.34	1.37	3.31	2.38	2.44	1.04	3.40	2.23
Bed Material	Limestone	Limestone	Limestone	Limestone	Limestone	Limestone	Limestone	Limestone
Fines Production Rate, lb/hr	4.10	4.75	2.50	2.18	3.28	7.90	2.29	2.39
Proximate Analysis (wt%):								
Moisture ^a	1.30	1.00	2.90	2.50	2.20	1.00	2.90	1.10
Volatile Matter ^b	19.31	18.63	19.51	18.94	13.97	14.84	15.65	13.58
Fixed Carbon (by diff.) ^b	50.83	50.44	42.65	38.18	54.55	51.11	40.95	41.32
Ash ^b	29.86	30.93	37.84	42.88	31.48	34.05	43.40	45.10
Ultimate Analysis (wt%): ^b								
Hydrogen	1.44	1.27	1.07	0.82	1.30	0.97	0.86	0.68
Carbon	65.36	60.56	51.95	48.18	58.87	56.39	47.36	47.82
Nitrogen	0.91	0.89	0.75	0.63	1.04	0.94	0.73	0.71
Sulfur	0.51	0.42	0.54	0.31	0.73	0.83	1.10	1.48
Oxygen	1.91	5.90	7.83	7.16	6.56	6.79	6.53	4.19
Ash	29.86	30.93	37.84	42.88	31.48	34.05	43.40	45.10
Mass Mean Diameter (MMD), microns	125	146	117	113	137	138	109	120
^a As-Received								
^b Moisture-free								

TABLE 3-7

WASTEWATER ANALYSIS FOR CPU LIMESTONE TEST MATRIX

Run No.	14	4	2	2R	12	12R	10R	6
Coal	Wyodak	Wyodak	Wyodak	Wyodak	Wyodak	Wyodak	Wyodak	Wyodak
Bed Temp., °C	699	696	751	746	743	750	806	802
Steam:Carbon Molar Ratio	1.57	3.51	2.50	2.10	2.31	2.35	1.28	3.41
Bed Material	Limestone	Limestone	Limestone	Limestone	Limestone	Limestone	Limestone	Limestone
Wastewater Analysis, (mg/L):								
pH	9.04	9.06	9.12	9.22	8.94	9.05	9.15	8.91
Ammonia, Free	5870	2480	3330	3530	3880	3370	3520	2900
Ammonia, Total	5870	2580	3550	3530	3880	3370	3600	2990
Total Carbon	3110	1720	2080	2180	2590	2180	2440	1720
TOC	448	422	449	1980	646	1980	2180	88
COD	2270	1800	1880	1880	2940	1640	2730	460
BOD	1040	842	987	1250	1380	871	1330	168
Total Solids	5200	2120	2590	8150	3750	1660	1950	800
Total Suspended Solids	4480	1730	1540	756	3380	919	1240	604

TABLE 3-7 (Cont.)

WASTEWATER ANALYSIS FOR CPU LIMESTONE TEST MATRIX

Run No.	15	13	9	11	3	7	5	1
Coal	Velva	Velva	Velva	Velva	Martin Lake	Martin Lake	Martin Lake	Martin
Bed Temp., °C	698	744	750	802	699	741	752	801
Steam:Carbon Molar Ratio	2.34	1.37	3.31	2.38	2.44	1.04	3.40	2.23
Bed Material	Limestone	Limestone	Limestone	Limestone	Limestone	Limestone	Limestone	Limestone
Wastewater Analysis, (mg/L):								
pH	8.95	9.03	8.65	8.70	9.34	9.27	9.08	9.21
Ammonia, Free	3570	4970	2820	3690	4290	7990	3450	5330
Ammonia, Total	3570	4970	2940	3690	3400	7990	3610	5330
Total Carbon	2180	2920	1740	2290	2300	4000	2040	2680
TOC	353	466	222	644	498	592	432	155
COD	1790	2680	880	680	2420	2840	1930	1060
BOD	1060	846	474	118	1340	1060	935	348
Total Solids	5590	2720	1800	1850	3050	10860	1690	1880
Total Suspended Solids	4870	2170	1350	1580	1980	10353	653	1440

oxygen demand (BOD) of the condensate usually decreased with increasing temperature and steam:carbon ratio. The total solids concentration of the condensate exhibited a trend similar to the COD and BOD of the wastewater.

The proximate and ultimate analyses for the post-run bed materials for the limestone test matrix are shown in Table 3-8. The carbon content of the post-run bed material decreased with increasing temperature and steam:carbon ratio for the Wyodak and Velva coal runs. The results of the Martin Lake runs indicated a decrease in bed carbon content with temperature, but not with steam:carbon ratio. The MMD of the post-run bed material for the Wyodak runs ranged from 1000 to 1465 microns, and decreased with increasing temperature and decreasing steam:carbon ratio. The MMD of the post-run bed material for the Velva runs ranged from 985 to 1355 microns and decreased with increasing temperature and steam:carbon ratio. The change in MMD for the post-run bed material for the Martin Lake runs was similar to the Velva runs, decreasing in size with increasing temperature and steam:carbon ratio. The MMD of the bed material for the Martin Lake runs ranged from 855 to 1315 microns.

3.1.2.3 Statistical Analysis

Although the product gas composition shows some trends with respect to steam:carbon ratio and temperature, it is not a good indication of the production rates of the gases as was demonstrated in the operability testing (5). A more appropriate way to show changes in gas production rates with changing operating conditions is on a volumetric basis per unit mass of maf coal utilizing the material balance results. Material balances were performed and analyzed for all the test runs during which on-line operation of the gas quench system was sustained. The material balances were normalized for the sake of comparison by forcing the overall mass balance to be equal using the elemental balance as the primary criterion. This allows for comparison of gas production rates and carbon conversion to gas at different test conditions with different coals. Tabulated summaries of the unadjusted and adjusted material balances for the limestone parametric test matrix are presented in Appendixes A and B.

A detailed statistical analysis of data from the parametric tests was conducted. Data and variables that were evaluated are listed in Table 3-9. An averaged analysis was used for the composition of Wyodak coal because of the excessive variability of analyses of that coal between runs.

Statistical analyses were performed using each of the four X_2 variables listed in Table 3-9. Evaluation of the data using the steam:carbon ratio as X_2 resulted in good correlations for several responses; however, using the total water:carbon molar ratio as X_2 yielded similar results with better correlations. The oxygen:steam molar ratio did not produce correlations that were as good as the previous X_2 's, but was included due to its similarity with the steam:oxygen ratio, which is commonly used commercially. The statistical analysis using the oxygen:carbon ratio resulted in very poor correlations.

TABLE 3-8

PROXIMATE AND ULTIMATE ANALYSES OF BED MATERIAL BLOWDOWN FOR CPU LIMESTONE TEST MATRIX

Run No.	14	4	2	2R	12	12R	10R	6
Coal	Wyodak	Wyodak	Wyodak	Wyodak	Wyodak	Wyodak	Wyodak	Wyodak
Bed Temperature, °C	599	696	751	746	743	750	806	802
Steam:Carbon Molar Ratio	1.57	3.51	2.50	2.10	2.31	2.35	1.28	3.41
Bed Material	Limestone	Limestone	Limestone	Limestone	Limestone	Limestone	Limestone	Limestone
Proximate Analysis (wt%):								
Moisture ^a	0.40	0.30	0.00	0.00	0.00	0.00	0.00	0.00
Volatile Matter ^b	38.31	41.53	36.42	32.09	32.41	30.52	11.33	12.62
Fixed Carbon (by diff.) ^b	0.61	0.37	0.00	0.00	0.00	0.00	0.00	0.00
Ash ^b	61.08	58.10	63.58	67.91	67.65	69.48	88.67	87.38
Ultimate Analysis (wt%): ^b								
Hydrogen	0.17	0.09	0.02	0.12	0.10	0.29	0.53	0.94
Carbon	19.63	13.65	8.62	8.63	9.50	8.35	3.01	0.72
Nitrogen	0.16	0.14	0.28	0.06	0.16	0.06	0.06	0.08
Sulfur	0.08	0.14	0.02	0.34	0.01	0.02	0.16	0.00
Oxygen	18.87	27.87	27.48	22.94	22.58	21.80	7.57	0.00
Ash	61.08	58.10	63.58	67.91	67.65	69.48	88.67	87.38
Mass Mean Diameter (MMD), microns	1025	1310	1035	1020	1465	1260	1000	1225

^a As-Received^b Moisture-Free

TABLE 3-8 (Cont.)

PROXIMATE AND ULTIMATE ANALYSES OF BED MATERIAL BLOWDOWN FOR CPU LIMESTONE TEST MATRIX

Run No.	15	13	9	11	3	7	5	1
Coal	Velva	Velva	Velva	Velva	Martin Lake	Martin Lake	Martin Lake	Martin Lake
Bed Temperature, °C	698	744	750	802	699	741	752	801
Steam:Carbon Molar Ratio	2.34	1.37	3.31	2.38	2.44	1.04	3.40	2.23
Bed Material	Limestone	Limestone	Limestone	Limestone	Limestone	Limestone	Limestone	Limestone
Proximate Analysis (wt%):								
Moisture ^a	0.40	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Volatile Matter ^b	22.62	30.59	24.25	16.39	36.43	31.83	35.24	16.41
Fixed Carbon (by diff.) ^b	12.16	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ash ^b	65.22	69.41	75.75	83.61	63.21	68.17	64.76	83.59
Ultimate Analysis (wt%): ^b								
Hydrogen	0.11	0.02	0.46	0.27	0.00	0.10	0.06	0.01
Carbon	11.16	9.54	5.11	0.78	9.50	6.50	7.94	4.68
Nitrogen	0.16	0.18	0.01	0.04	0.26	0.16	0.26	0.18
Sulfur	0.09	0.06	0.01	0.13	0.21	0.79	0.24	0.43
Oxygen	23.24	20.79	18.66	15.17	0.00	24.28	26.74	11.11
Ash	65.22	69.41	75.75	83.61	63.21	68.17	64.76	83.59
Mass Mean Diameter (MMD), microns	1355	1020	985	1225	1190	1315	1070	855

^a As-Received^b Moisture-Free

TABLE 3-9
CPU RESULTS OF LIMESTONE TEST MATRIX

Run #	1-M280L	3-M270L	5-M375L	7-M175L	9-V375L	11-V280L	13-V175L	15-V270L
VARIABLES								
X1: Average Bed Temperature (C)	801	699	752	741	750	802	744	698
X2A: Steam/Carbon Molar Ratio	2.23	2.44	3.40	1.04	3.31	2.38	1.37	2.34
X2B: Total Water/Carbon Molar Ratio	2.54	2.74	3.73	1.34	3.72	2.75	1.73	2.69
X2C: Oxygen/Steam Molar Ratio	0.17	0.14	0.11	0.29	0.12	0.20	0.25	0.16
X2D: Oxygen/Carbon Molar Ratio	0.39	0.34	0.36	0.30	0.39	0.48	0.34	0.36
X3: Coal Type	Mrttn.Lake	Mrttn.Lake	Mrttn.Lake	Mrttn.Lake	Velva	Velva	Velva	Velva
RESPONSES								
Y1: H2 (scfh)/maf Coal (lb/hr)	14.82	14.32	14.88	12.08	14.36	13.72	12.70	13.27
Y2: CO (scfh)/maf Coal (lb/hr)	4.40	2.17	3.09	3.88	2.57	3.81	4.32	2.61
Y3: CO2(scfh)/maf Coal (lb/hr)	12.36	12.90	12.98	10.17	13.41	13.09	11.40	12.22
Y4: Carbon in Fines (lb/hr)/maf Coal (lb/hr)	0.08	0.14	0.10	0.17	0.11	0.09	0.13	0.18
Y5: Carbon in Condensate (lb/hr)/maf Coal (lb/hr)	0.0069	0.0065	0.0077	0.0052	0.0065	0.0065	0.0049	0.0061
Y6: Condensate (lb/hr)/maf Coal (lb/hr)	2.57	2.75	3.78	1.31	3.74	2.83	1.69	2.81
Y14: Carbon in Bed (lb)/Carbon Fed (lb/hr)	0.072	0.321	0.297	0.094	0.195	0.017	0.152	0.331
Y15: H2 (scfh)/O2 Fed (lb/hr)	20.02	21.86	21.54	21.39	19.89	15.62	19.98	18.83
Y16: CO (scfh)/O2 Fed (lb/hr)	5.95	3.31	4.47	6.86	3.57	4.33	6.79	3.71
Y17: CO2(scfh)/O2 Fed (lb/hr)	16.71	19.69	18.79	18.00	18.57	14.89	17.95	17.34
Y18: Carbon in Fines (lb/hr)/O2 Fed (lb/hr)	0.10	0.21	0.15	0.30	0.15	0.10	0.20	0.26
Y19: Carbon in Condensate (lb/hr)/O2 Fed (lb/hr)	0.0093	0.0099	0.0112	0.0093	0.0090	0.0074	0.0078	0.0087
Y20: Condensate (lb/hr)/O2 Fed (lb/hr)	3.48	4.20	5.47	2.31	5.18	3.23	2.66	3.99
Y22: H2 (scfh)/Steam Fed (lb/hr)	6.23	5.47	4.09	10.89	4.19	5.56	8.86	5.21
Y23: CO (scfh)/Steam Fed (lb/hr)	1.85	0.83	0.85	3.49	0.75	1.54	3.01	1.03
Y24: CO2 (scfh)/Steam Fed (lb/hr)	5.20	4.93	3.57	9.16	3.91	5.30	7.96	4.80
Y25: Carbon in Fines (lb/hr)/Steam Fed (lb/hr)	0.032	0.054	0.028	0.155	0.032	0.036	0.089	0.071
Y26: Carbon in Condensate (lb/hr)/Steam Fed (lb/hr)	0.0029	0.0025	0.0021	0.0047	0.0019	0.0026	0.0034	0.0024
Y27: Condensate (lb/hr)/Steam Fed (lb/hr)	1.08	1.05	1.04	1.18	1.09	1.15	1.18	1.10
Y30: Percent Carbon in Fines	47.30	59.95	45.99	55.84	50.47	46.98	59.95	64.49
Y32: H2 (lb/hr)/Hydrogen Fed (lb/hr)	0.22	0.20	0.16	0.29	0.16	0.20	0.26	0.19
Y33: Carbon in Gas (lb/hr)/Carbon Fed (lb/hr)	0.88	0.79	0.85	0.75	0.83	0.86	0.81	0.74
Y34: Free NH3 (lb/hr)/maf Coal (lb/hr) x 10e4*	136	102	128	102	104	103	77	98
Y35: Total NH3 (lb/hr)/maf Coal (lb/hr) x 10e4*	136	102	134	102	109	103	77	98
Y36: Total Carbon (lb/hr)/maf Coal (lb/hr) x 10e4*	68	61	76	51	64	64	45	60
Y37: Total Organic Carbon (lb/hr)/maf Coal (lb/hr) x 10e4*	4	13	16	8	8	18	7	10
Y38: Chemical Oxygen Demand (lb/hr)/maf Coal (lb/hr) x 10e4*	27	64	72	36	33	19	42	49
Y39: Biological Oxygen Demand (lb/hr)/maf Coal (lb/hr) x 10e4*	9	36	35	14	18	3	13	29

* 1st Stage Condensate

TABLE 3-9 (cont.)
CPU RESULTS OF LIMESTONE TEST MATRIX

Run #	11R-V280L	4-W370L	6-W380L	12-W275L	14-W170L	2R-W275L	10R-W180L	12R-W275L
VARIABLES								
X1: Average Bed Temperature (C)	799	696	802	743	699	746	806	750
X2A: Steam/Carbon Molar Ratio	2.50	3.51	3.41	2.31	1.57	2.10	1.28	2.35
X2B: Total Water/Carbon Molar Ratio	2.91	3.79	3.69	2.59	1.95	2.38	1.56	2.63
X2C: Oxygen/Steam Molar Ratio	0.17	0.09	0.13	0.14	0.20	0.16	0.29	0.16
X2D: Oxygen/Carbon Molar Ratio	0.42	0.32	0.44	0.32	0.32	0.34	0.37	0.38
X3: Coal Type	Velva	Wyodak	Wyodak	Wyodak	Wyodak	Wyodak	Wyodak	Wyodak
RESPONSES								
Y1: H2 (scfh)/maf Coal (lb/hr)	13.61	13.76	14.20	14.62	13.72	13.71	15.62	14.18
Y2: CO (scfh)/maf Coal (lb/hr)	3.25	2.09	3.36	3.46	3.44	3.42	6.22	4.08
Y3: CO2(scfh)/maf Coal (lb/hr)	12.70	12.34	13.03	12.86	11.91	11.43	11.75	12.57
Y4: Carbon in Fines (lb/hr)/maf Coal (lb/hr)	0.12	0.16	0.10	0.11	0.13	0.15	0.07	0.10
Y5: Carbon in Condensate (lb/hr)/maf Coal (lb/hr)	0.0053	0.0065	0.0065	0.0063	0.0054	0.0052	0.0034	0.0056
Y6: Condensate (lb/hr)/maf Coal (lb/hr)	2.96	3.79	3.77	2.43	1.74	2.37	1.41	2.59
Y14: Carbon in Bed (lb)/Carbon Fed (lb/hr)	0.016	0.576	0.017	0.226	0.437	0.172	0.034	0.223
Y15: H2 (scfh)/O2 Fed (lb/hr)	17.79	22.58	17.24	24.18	22.91	21.13	22.05	19.92
Y16: CO (scfh)/O2 Fed (lb/hr)	4.25	3.43	4.08	5.72	5.75	5.28	8.78	5.73
Y17: CO2(scfh)/O2 Fed (lb/hr)	16.60	20.25	15.82	21.27	19.88	17.63	16.59	17.66
Y18: Carbon in Fines (lb/hr)/O2 Fed (lb/hr)	0.15	0.26	0.12	0.18	0.21	0.24	0.10	0.14
Y19: Carbon in Condensate (lb/hr) O2 Fed (lb/hr)	0.0069	0.0107	0.0079	0.0104	0.0090	0.0080	0.0049	0.0079
Y20: Condensate (lb/hr)/O2 Fed (lb/hr)	3.87	6.23	4.57	4.02	2.90	3.65	2.00	3.64
Y22: H2 (scfh)/Steam Fed (lb/hr)	5.24	3.72	3.92	5.96	8.22	6.14	11.27	5.67
Y23: CO (scfh)/Steam Fed (lb/hr)	1.25	0.56	0.93	1.41	2.06	1.53	4.49	1.63
Y24: CO2 (scfh)/Steam Fed (lb/hr)	4.89	3.33	3.59	5.24	7.13	5.13	8.48	5.03
Y25: Carbon in Fines (lb/hr)/Steam Fed (lb/hr)	0.045	0.043	0.027	0.044	0.077	0.068	0.050	0.039
Y26: Carbon in Condensate (lb/hr)/Steam Fed (lb/hr)	0.0020	0.0018	0.0018	0.0026	0.0032	0.0023	0.0025	0.0023
Y27: Condensate (lb/hr)/Steam Fed (lb/hr)	1.14	1.02	1.04	0.99	1.04	1.06	1.02	1.04
Y30: Percent Carbon in Fines	48.54	63.24	44.92	59.28	66.80	62.24	48.71	57.87
Y32: H2 (lb/hr)/Hydrogen Fed (lb/hr)	0.18	0.15	0.16	0.22	0.27	0.22	0.34	0.21
Y33: Carbon in Gas (lb/hr)/Carbon Fed (lb/hr)	0.82	0.77	0.85	0.84	0.81	0.78	0.90	0.85
Y34: Free NH3 (lb/hr)/maf Coal (lb/hr) x 10e4*	82	93	93	92	96	80	41	84
Y35: Total NH3 (lb/hr)/maf Coal (lb/hr) x 10e4*	84	97	95	92	96	80	42	84
Y36: Total Carbon (lb/hr)/maf Coal (lb/hr) x 10e4*	50	64	55	61	51	49	29	54
Y37: Total Organic Carbon (lb/hr)/maf Coal (lb/hr) x 10e4*	46	16	3	15	7	45	26	49
Y38: Chemical Oxygen Demand (lb/hr)/maf Coal (lb/hr) x 10e4*	13	67	15	70	37	42	32	41
Y39: Biological Oxygen Demand (lb/hr)/maf Coal (lb/hr) x 10e4*	4	32	5	33	17	28	16	22

* 1st Stage Condensate

Total water:carbon ratio and oxygen:steam ratio were therefore selected as being most useful to describe the system within the scope of the test matrix. Regression summaries for the total water:carbon ratio and oxygen:steam ratio scenarios are listed in Tables 3-10 and 3-11, respectively. A description of the terms used in Tables 3-10 and 3-11 is in Appendix C.

To illustrate important findings and yet limit the amount of material, the plots and comments presented will deal primarily with gas production. The labels for units of variables on the plots have in some cases been altered to delete "hours" where they are redundant. Table 3-12 provides definitions of variables used in the equations that describe the plotted curves. The Z rather than X indicates that the X variable has been converted to a form compatible with the statistical method for evaluation of data from a Box-Behnken experimental design. Due to the relatively small number of data points available, the relationships indicated by the statistical analysis are best thought of as indicators rather than definitive descriptions of the process.

The production rate of hydrogen per unit maf coal did not correlate with either total water:carbon ratio or bed temperature, as shown in Figure 3-2, and was essentially constant over the range of variables tested. The production rate for carbon monoxide per unit maf coal decreased with increasing total water:carbon ratio, as shown in Figure 3-3, and increased with temperature. The production rate for carbon dioxide per unit maf coal increased with increasing total water:carbon ratio, as shown in Figure 3-4, but showed no correlation with temperature.

Another way to approach the data analysis is to look at the gas production rates versus oxygen:steam ratio. The oxygen:steam ratio increases when the steam:carbon ratio decreases, as less sensible heat for the superheated steam is available to maintain reaction temperature. The hydrogen production rate is relatively constant at the higher bed temperatures, but decreases with temperature for increasing oxygen:steam ratio, as shown in Figure 3-5. Carbon monoxide production rates increase with both bed temperature and oxygen:steam ratio (Figure 3-6). The production rates for carbon dioxide, Figure 3-7, increase with increasing bed temperature, but decrease with increasing oxygen:steam ratio.

These gas production rate results indicate that more hydrogen is produced via the water-gas shift reaction at higher steam:carbon ratios and lower bed temperatures, as expected. At lower steam:carbon ratios and higher bed temperatures, more gas is produced via the gasification reaction. In the case of the higher bed temperatures, the carbon conversion kinetics increase with temperature, whereas for the lower steam:carbon ratios, more oxidation reactions occur to maintain temperature and less steam is available for shifting.

In the case of hydrogen produced per unit maf coal as a function of oxygen:steam ratio (Figure 3-5), higher bed temperatures maintained hydrogen production with increasing oxygen:steam ratio. This indicates that less hydrogen is being produced at the higher oxygen:steam ratio (lower steam:carbon ratio) via the water-gas shift reaction.

Table 3-10

Regression Summary -- LIMESTONE Test Matrix
(Case B: Using [Total Water]/Carbon, Mole Ratio)

Responses	Equation *	Conf.	R ²	s	C.V.
Y ₁ : H ₂ / maf Coal	14.0	-	0.00	0.833	5.96%
Y ₂ : CO / maf Coal	3.71 + 0.81Z ₁ - 0.81Z ₂ - 0.35Z ₁ Z ₂ - 0.39Z ₃ ²	99.99%	0.89	0.388	11.1%
Y ₃ : CO ₂ / maf Coal	12.59 + 0.84Z ₂ - 0.48Z ₂ ²	99.99%	0.74	0.451	3.66%
Y ₄ : Fines Carbon / maf Coal	0.122 - 0.030Z ₁	99.94%	0.58	0.022	17.8%
Y ₅ : (Cond C / maf Coal) × 10 ³	5.56 + 0.99Z ₂ - 0.44Z ₃ + 0.63Z ₃ ²	99.95%	0.76	0.547	9.26%
Y ₆ : Condensate / maf Coal	2.59 + 1.06Z ₂ + 0.09Z ₃ ²	99.99%	0.996	0.054	2.04%
Y ₁₄ : Bed Carbon / C In	0.188 - 0.149Z ₁ + 0.073Z ₂ - 0.094Z ₁ Z ₂	99.99%	0.96	0.035	19.1%
Y ₁₅ : H ₂ / O ₂ In	21.40 - 1.32Z ₁ - 1.25Z ₃ - 1.49Z ₃ ²	99.18%	0.61	1.57	7.67%
Y ₁₆ : CO / O ₂ In	5.20 + 0.70Z ₁ - 1.53Z ₂ - 0.48Z ₁ Z ₃ + 0.56Z ₂ ² - 0.66Z ₃ ²	99.99%	0.91	0.566	11.0%
Y ₁₇ : CO ₂ / O ₂ In	18.03 - 1.59Z ₁	99.92%	0.56	1.17	6.51%
Y ₁₈ : Fines Carbon / O ₂ In	0.182 - 0.062Z ₁	99.97%	0.63	0.040	22.4%
Y ₁₉ : (Cond C / O ₂ In) × 10 ³	8.73 - 1.06Z ₁ + 0.94Z ₂ - 0.92Z ₃	99.91%	0.73	0.912	10.6%
Y ₂₀ : Condensate / O ₂ In	3.83 - 0.39Z ₁ + 1.36Z ₂ - 0.21Z ₁ Z ₂	99.99%	0.97	0.212	5.53%
Y ₂₂ : H ₂ / Steam In	5.67 + 0.33Z ₁ - 2.80Z ₂ - 0.37Z ₁ Z ₂ + 1.12Z ₂ ²	99.99%	0.990	0.271	4.32%
Y ₂₃ : CO / Steam In	1.37 + 0.42Z ₁ - 1.20Z ₂ - 0.34Z ₁ Z ₂ + 0.57Z ₂ ²	99.99%	0.98	0.186	10.9%
Y ₂₄ : CO ₂ / Steam In	5.07 - 2.17Z ₂ + 0.77Z ₂ ²	99.99%	0.98	0.270	4.93%

* Statistical significance of regression coefficients:

Not Significant: 1.23 (15% < α)

Significant: 1.23 (1% < α < 5%)

1.23 (10% < α < 15%)

1.23 (0.1% < α < 1%)

1.23 (5% < α < 10%)

1.23 (α < 0.1%)

Table 3-10 (Continued)

Regression Summary -- LIMESTONE Test Matrix
(Case B: Using [Total Water]/Carbon, Mole Ratio)

Responses	Equation *	Conf.	R ²	s	C.V.
Y ₂₅ : Fines Carbon / Steam In	$0.046 - 0.014Z_1 - 0.030Z_2 + 0.018Z_2^2$	99.95%	0.76	0.018	31.9%
Y ₂₆ : (Cond C / Steam In)x10 ³	$2.16 - 0.77Z_2 + 0.31Z_2^2 + 0.41Z_3^2$	99.98%	0.80	0.371	14.5%
Y ₂₇ : Condensate / Steam In	$1.030 - 0.029Z_2 + 0.025Z_3 - 0.081Z_3^2$	99.93%	0.75	0.033	3.07%
Y ₃₀ : Fines Carbon	$58.6 - 8.1Z_1 - 3.0Z_2 + 1.7Z_3 - 2.0Z_2^2 - 3.6Z_3^2$	99.99%	0.97	1.60	2.91%
Y ₃₂ : H Gas Out / H In	$0.215 - 0.063Z_2 + 0.015Z_2^2 - 0.014Z_3^2$	99.99%	0.93	0.015	7.23%
Y ₃₃ : C Gas Out / Carbon In	$0.819 - 0.043Z_1$	99.92%	0.57	0.031	3.79%
Y ₃₄ : (Free NH ₃ /maf Coal)x10 ³	$8.3 + 1.2Z_2 - 1.3Z_3 + 2.2Z_3^3$	99.46%	0.64	1.43	15.1%
Y ₃₅ : (Total NH ₃ /maf Coal)x10 ³	$8.4 + 1.4Z_2 - 1.3Z_3 + 2.2Z_3^3$	99.73%	0.68	1.38	14.5%
Y ₃₆ : (TC / maf Coal)x10 ³	$5.2 + 1.0Z_2 - 0.5Z_3 + 0.8Z_3^3$	99.82%	0.70	0.667	11.8%
Y ₃₇ : (TOC / maf Coal)x10 ³	1.82	-	0.00	1.48	81.4%
Y ₃₈ : (COD / maf Coal)x10 ³	$4.87 - 1.38Z_1 + 0.44Z_2 - 0.71Z_3 - 1.16Z_1Z_2$ $- 1.02Z_2Z_3 - 1.00Z_1^2$	99.92%	0.89	0.825	20.0%
Y ₃₉ : (BOD / maf Coal)x10 ³	$2.00 - 1.02Z_1$	99.84%	0.52	0.816	41.6%

* Statistical significance of regression coefficients:

Not Significant: 1.23 (15% < α)

Significant: 1.23 (1% < α < 5%)

1.23 (10% < α < 15%)

1.23 (0.1% < α < 1%)

1.23 (5% < α < 10%)

1.23 (α < 0.1%)

Table 3-11

Regression Summary -- LIMESTONE Test Matrix
(Case C: Using X_2 = Oxygen/Steam, Mole Ratio)

Responses	Equation *	Conf.	R ²	s	C.V.
Y_1 : H ₂ / maf Coal	$13.83 + 0.53Z_1 - 0.58Z_2 + 0.77Z_1Z_2$	97.51%	0.53	0.661	4.73%
Y_2 : CO / maf Coal	$3.83 + 0.58Z_1 + 0.90Z_2 - 0.57Z_3^2$	99.99%	0.85	0.432	12.3%
Y_3 : CO ₂ / maf Coal	$12.29 + 0.40Z_1 - 0.93Z_2$	99.94%	0.68	0.506	4.11%
Y_4 : Fines Carbon / maf Coal	$0.122 - 0.030Z_1$	99.94%	0.58	0.022	17.8%
Y_5 : (Cond C / maf Coal) × 10 ³	$5.45 - 1.10Z_2 - 0.34Z_3 + 0.82Z_3^2$	99.99%	0.82	0.472	8.00%
Y_6 : Condensate / maf Coal	$2.24 + 0.28Z_1 - 1.32Z_2 + 0.18Z_3 + 0.40Z_2^2 + 0.30Z_3^2$	99.99%	0.95	0.221	8.31%
Y_{14} : Bed Carbon / C In	$0.180 - 0.141Z_1 - 0.078Z_2 + 0.085Z_1Z_2$	99.99%	0.93	0.045	24.6%
Y_{15} : H ₂ / O ₂ In	$21.40 - 1.32Z_1 - 1.25Z_3 - 1.49Z_3^2$	99.18%	0.61	1.57	7.67%
Y_{16} : CO / O ₂ In	$5.71 - 1.75Z_2 - 0.99Z_3^2$	99.99%	0.79	0.748	14.6%
Y_{17} : CO ₂ / O ₂ In	$18.03 - 1.59Z_1$	99.92%	0.56	1.17	6.51%
Y_{18} : Fines Carbon / O ₂ In	$0.182 - 0.062Z_1$	99.97%	0.63	0.040	22.4%
Y_{19} : (Cond C / O ₂ In) × 10 ³	$8.27 - 0.84Z_1 - 1.07Z_2 - 0.88Z_3 + 0.78Z_3^2$	99.91%	0.80	0.833	9.64%
Y_{20} : Condensate / O ₂ In	$3.26 - 1.86Z_2 + 0.15Z_3 + 0.75Z_2^2 + 0.27Z_3^2$	99.99%	0.992	0.122	3.19%
Y_{22} : H ₂ / Steam In	$6.71 - 0.41Z_1 + 3.16Z_2 - 0.44Z_3 - 0.59Z_3^2$	99.99%	0.97	0.466	7.41%
Y_{23} : CO / Steam In	$1.77 + 1.27Z_2 + 0.28Z_2^2 - 0.35Z_3^2$	99.99%	0.95	0.263	15.5%
Y_{24} : CO ₂ / Steam In	$5.53 - 0.46Z_1 + 2.43Z_2$	99.99%	0.97	0.349	6.38%

* Statistical significance of regression coefficients:

Not Significant: 1.23 (15% < α)

Significant: 1.23 (1% < α < 5%)

1.23 (10% < α < 15%)

1.23 (0.1% < α < 1%)

1.23 (5% < α < 10%)

1.23 (α < 0.1%)

Table 3-11 (Continued)
Regression Summary -- LIMESTONE Test Matrix
(Case C: Using X_2 = Oxygen/Steam, Mole Ratio)

Responses	Equation *	Conf.	R ²	s	C.V.
Y ₂₅ : Fines Carbon / Steam In	$0.060 - 0.023Z_1 + 0.037Z_2 - 0.017Z_1Z_2$	99.99%	0.83	0.015	27.0%
Y ₂₆ : (Cond C / Steam In)x10 ³	$2.67 - 0.31Z_1 + 0.89Z_2 - 0.26Z_3 - 0.47Z_1Z_2$	99.99%	0.89	0.291	11.4%
Y ₂₇ : Condensate / Steam In	$1.033 + 0.034Z_2 + 0.022Z_3 + 0.075Z_3^2$	99.97%	0.78	0.031	2.86%
Y ₃₀ : Fines Carbon	$59.8 - 8.8Z_1 + 4.6Z_2 - 3.5Z_2^2 - 4.3Z_3^2$	99.99%	0.93	2.24	4.06%
Y ₃₂ : H Gas Out / H In	$0.231 + 0.067Z_2 - 0.011Z_3 - 0.026Z_3^2$	99.99%	0.92	0.017	7.84%
Y ₃₃ : C Gas Out / Carbon In	$0.819 - 0.043Z_1$	99.92%	0.57	0.031	3.79%
Y ₃₄ : (Free NH ₃ /maf Coal)x10 ³	$8.1 - 1.5Z_2 - 1.2Z_3 + 2.4Z_3^3$	99.84%	0.71	1.29	13.6%
Y ₃₅ : (Total NH ₃ /maf Coal)x10 ³	$8.2 - 1.6Z_2 - 1.2Z_3 + 2.5Z_3^3$	99.91%	0.73	1.26	13.2%
Y ₃₆ : (TC / maf Coal)x10 ³	$5.1 - 1.1Z_2 - 0.4Z_3 + 1.0Z_3^3$	99.98%	0.80	0.548	9.72%
Y ₃₇ : (TOC / maf Coal)x10 ³	1.82	-	0.00	1.48	81.4%
Y ₃₈ : (COD / maf Coal)x10 ³	$4.18 - 1.63Z_1$	99.71%	0.48	1.42	34.4%
Y ₃₉ : (BOD / maf Coal)x10 ³	$2.34 - 0.77Z_1 - 0.54Z_2 - 0.40Z_3 + 0.97Z_1Z_2 - 0.78Z_1^2$	99.97%	0.88	0.487	24.8%

* Statistical significance of regression coefficients:

Not Significant: 1.23 (15% < α)

Significant: 1.23 (1% < α < 5%)

1.23 (10% < α < 15%)

1.23 (0.1% < α < 1%)

1.23 (5% < α < 10%)

1.23 (α < 0.1%)

TABLE 3-12

KEY TO VARIABLES USED TO DESCRIBE RESPONSES

-
- Z_1 - linear effect of average bed temperature (X_1)
 Z_2 - linear effect of the X_2 variable
 Z_3 - indicates that the lignites differ (X_3)
 $Z_1 * Z_2$ - effect of X_1 depends on X_2
 $Z_1 * Z_3$ - effect of X_1 differs for lignites
 $Z_2 * Z_3$ - effect of X_2 differs for lignites
 $Z_1 * Z_1$ - indicates curvature in X_1 response
 $Z_2 * Z_2$ - indicates curvature in X_2 response
 $Z_3 * Z_3$ - indicates that Wyodak differs from lignites tested
-

Figure 3-2. Hydrogen Production per maf Coal Versus Total Water:Carbon Ratio.

CO / maf Coal (Y2)

$$F2 = 3.71 + 0.81 \cdot Z1 - 0.81 \cdot Z2 - 0.35 \cdot Z1 \cdot Z2 - 0.39 \cdot Z3 \cdot Z3$$

Figure 3-3. Carbon Monoxide Production per maf Coal Versus Total Water:Carbon Ratio.

CO2 / maf Coal (Y3)

$$F3 = 12.59 + 0.84 \cdot Z2 - 0.48 \cdot Z2 \cdot Z2$$

Figure 3-4. Carbon Dioxide Production per maf Coal Versus Total Water:Carbon Ratio.

Figure 3-5. Hydrogen Production per maf Coal Versus Oxygen:Steam Ratio.

Figure 3-6. Carbon Monoxide Production per maf Coal Versus Oxygen:Steam Ratio.

CO₂ / maf Coal (Y3)

$$F3 = 12.29 + 0.40 \cdot Z1 - 0.93 \cdot Z2$$

Figure 3-7. Carbon Dioxide Production per maf Coal Versus Oxygen:Steam Ratio.

The conversion of hydrogen fed (coal and water) to the reactor is improved by reducing the amount of water fed to the reactor per unit carbon, as shown by Figure 3-8. The quantity of hydrogen produced in the gas decreases with the hydrogen fed, due to the lower conversion of steam at the higher steam:carbon ratios. The type of coal used also has some effect, as less moisture was contained in the Wyodak coal than in the Martin Lake and Velva coals.

The conversion of carbon to gas relative to the total water:carbon ratio is dependent entirely on temperature, as shown in Figure 3-9. This is expected, as the gasification reaction kinetics increase with temperature. Total water:carbon ratio had an insignificant effect, although it was the only X_2 variable for which there was a significant correlation.

From this and other information derived from the statistical analysis several inferences can be made. Higher operating temperature generally improves utilization of feed streams for gas production. Lower steam:carbon ratios would again improve gas production and reduce what is evidently an unnecessary excess of steam. The results were generally the same for both the Wyodak subbituminous coal and the Velva and Martin Lake lignites.

Figure 3-8. Hydrogen in Product Gas per Hydrogen in Reactants Versus Total Water:Carbon Ratio.

Figure 3-9. Carbon in Product Gas per Carbon Fed Versus Average Bed Temperature.

3.1.3 Extended Test Runs

A 72-hour test run using a limestone bed material was attempted in late October with Wyodak subbituminous coal at a bed temperature of 750°C and a 2:1 steam:carbon molar ratio to determine the effects of extended CPU operation. Material balance periods were planned at 24, 48, and 72 hours of steady-state operation. No additional limestone was added to the bed over the duration of the test. Because of problems with the gasification tower ventilation system, the run was shortened to 48 hours. No problems were encountered with the CPU during the 48 hours of operation. No degradation of the bed occurred as a nominal 4-foot bed was consistently observed throughout the run. Material balances were obtained at 24 and 48 hours of steady-state operation.

3.1.3.1 Product Gas

The product gas compositions for the two material balance periods at 24 and 48 hours are given in Table 3-13. The product gas composition for an 8-hour CPU test done previously is included in the table for comparison. The product gas compositions after 8, 24, and 48 hours of steady-state operation did not differ significantly, indicating that the system reached equilibrium within 8 hours. Hydrogen, carbon monoxide, and carbon dioxide production rates per pound maf coal fed for each material balance period are shown in Figure 3-10. As shown in Figure 3-10, gas production rates were relatively constant with time. Hydrogen production rates were nominally 14.5 scf/lb maf coal, with carbon dioxide and carbon monoxide production rates at 13 scf/lb maf coal and 3.5 scf/lb maf coal, respectively. The carbon conversion to gas was nominally 85% for the extended test runs.

3.1.3.2 Cyclone Fines

Table 3-14 gives the proximate and ultimate analyses of the cyclone fines, along with the fines production rates, for the two material balance periods and also for the previous 8-hour CPU test. The fines production rate was approximately 2.5 lb/hr for the extended CPU runs. As shown in Table 3-14, the proximate and ultimate analyses of the fines were similar for the different material balance periods. The carbon content of the fines was typically 59%. However, the ash content of the fines varied between the material balance periods for some unknown reason. Mass mean diameters of the fines ranged from 117 to 135 microns.

3.1.3.3 Wastewater Analysis

Table 3-15 gives the analysis of the process condensate from the first-stage gas/liquid separator for the extended CPU runs. The results of the wastewater analysis from the 8-hour CPU run are also included. The alkaline nature of the condensate is due to the high concentration of free ammonia. Because nearly all of the ammonia in the process condensate is free ammonia, it can be removed easily by steam stripping. The total carbon, TOC, COD, and BOD for the 48-hour test were similar for the samples taken at the 24-hour and 48-hour material balance periods. COD and BOD for the 24- and 48-hour samples were double those of the 8-hour test, which may be due to differences in sample handling between the two test runs. Total solids and total suspended solids varied considerably for all three samples.

TABLE 3-13

PRODUCT GAS COMPOSITIONS FOR EXTENDED CPU RUNS

Time at Steady-State	8 Hours ^a	24 Hours	48 Hours
Product Gas Composition (mol%):			
H ₂	45.23	44.36	43.41
CO ₂	39.19	41.42	40.30
CO	11.66	10.58	12.26
CH ₄	2.93	2.77	3.06
C ₂ H ₄	0.71	0.63	0.69
C ₂ H ₆	0.18	0.18	0.21
C ₃ H ₆	0.03	0.00	0.00
C ₃ H ₈	0.00	0.00	0.00
C ₄ H ₈	0.01	0.00	0.00
C ₄ H ₁₀	0.00	0.00	0.00
H ₂ S	0.04	0.06	0.07
% carbon conv. to gas	82.31	86.02	84.80

^a Previous CPU Test Run

Figure 3-10. Gas Production Rates for Extended CPU Test Runs.

TABLE 3-14
PROXIMATE AND ULTIMATE ANALYSES OF CYCLONE FINES
FOR EXTENDED CPU RUNS

Time at Steady-State	8 Hours ^a	24 Hours	48 Hours
Proximate Analysis (wt%):			
Moisture ^b	2.90	3.30	3.60
Volatile Matter ^c	14.84	14.26	13.70
Fixed Carbon (by diff.) ^c	53.97	50.76	55.44
Ash ^c	31.19	34.98	30.85
Ultimate Analysis (wt%): ^c			
Hydrogen	1.21	1.20	1.16
Carbon	61.58	58.52	59.10
Nitrogen	0.85	0.80	0.79
Sulfur	0.64	0.39	0.39
Oxygen (by diff.)	4.53	4.08	7.68
Ash	31.19	34.98	30.86
Fines Production Rate, lb/hr	2.72	2.20	2.49
Mass Mean Diameter (MMD), microns	135	117	123

^a Previous CPU Test Run

^b As-Received

^c Moisture-Free

3.1.3.4 Bed Material

The ultimate analyses and ESCA results for the bed material after 8, 24, and 48 hours of steady-state operation with the CPU are given in Table 3-16. All three samples were from different CPU test runs with Wyodak subbituminous coal at 750°C and a 2:1 steam:carbon ratio using a limestone bed material. No bed material sample was obtained during the extended CPU test run for the 24-hour material balance period. The carbon content of the bed remained constant at an average of 8.7 wt% for the three tests. However, the sulfur content of the bed material was higher for the 8-hour test run. The ESCA results show that the calcium concentration remained constant with extended operation. The ESCA results also indicate that there was no sulfur on the surface of the limestone bed material. The absence of sulfur on the surface of the limestone is probably due to the low concentration of CaO, as indicated by the low CaO/CaCO₃ ratio in Table 3-16. The sulfur in the post-run bed material is due to the coal char remaining in the bed.

The mass mean diameters of the bed material are also given in Table 3-16. The particle size distributions showed that very little attrition of the bed material occurred even after 48 hours of steady-state operation.

TABLE 3-15
WASTEWATER ANALYSIS FOR EXTENDED CPU RUNS

Time at Steady-State	8 Hours ^a	24 Hours	48 Hours
pH	9.07	8.78	8.88
Wastewater Analysis, mg/l:			
Ammonia, Free	3580	3520	3470
Ammonia, Total	3600	3520	3640
Total Carbon	2320	2620	2820
TOC	1540	1100	1140
COD	2150	4060	4100
BOD	1170	2310	2510
Total Solids	4520	1990	2740
Total Suspended Solids	1690	1160	3840

^a Previous CPU Test Run

3.1.4 Reactor Testing

3.1.4.1 Bed Probe Testing

Four CPU runs were made using a probe to sample the bed during operation. The objective of the bed sampling was to determine the carbon content and particle size distributions of the bed at one-foot intervals above the distributor plate. Two runs were made with Wyodak subbituminous coal and one run each was made with Velva and Martin Lake lignites at 750°C and a 2:1 steam:carbon ratio.

A schematic of the bed probe is shown in Figure 3-11. The bed sampling probe consisted of a 20-foot length of one-half inch 316 stainless steel tubing inserted at the top of the gasifier through a Conax fitting. The tube was marked to indicate the 1-, 2-, 3-, and 4-foot levels above the distributor plate. A cyclone, also constructed of 316 stainless steel, was used to separate the bed material from the gas. A gas ejector vacuum system was used to increase the differential pressure between the gasifier and the bed probe to draw bed material from the reactor. The probe was configured to allow for a nitrogen purge to clear the line into the gasifier and to provide a nitrogen purge over the bed sample. The procedure used to sample the bed was as follows:

The nitrogen purge to the probe was opened. Then the Conax fitting at the top of the gasifier was loosened and the probe was lowered to the appropriate mark. The vacuum was turned on and the cyclone and sample collection pot were purged with nitrogen. Then the valve to the sampling system was opened and the nitrogen purges were shut off. After sampling for approximately 10 seconds, the valve to the sampling system was closed

TABLE 3-16
BED MATERIAL ANALYSES FOR EXTENDED CPU RUNS

Time at Steady-State	8 Hours ^a	24 Hours ^a	48 Hours
Ultimate Analysis (wt%): ^b			
Hydrogen	0.17	0.08	0.09
Carbon	8.83	8.63	8.90
Nitrogen	0.09	0.03	0.04
Sulfur	0.13 ^c	0.02	0.02
Oxygen (by diff.)	22.44	23.96	23.14
Ash	68.35	67.28	67.80
ESCA Analysis (atomic %):			
Carbon	31.6	29.6	25.5
Oxygen	52.0	53.1	54.8
Sulfur	0.0	0.0	0.0
Calcium	16.0	15.6	15.4
Aluminum	0.1	0.0	2.4
Silicon	0.0	1.4	1.6
XRD Analysis			
CaO/CaCO ₃ Ratio	0.28	0.30	0.21
Mass Mean Diameter, microns	1020	925	1005

^a Previous CPU Test Runs

^b Moisture-Free

^c Higher than expected

and the nitrogen purge to the probe was opened. The probe was then pulled up above the bed and the Conax fitting was tightened. The cyclone and sample collection pot were removed and the inlet and outlet to the cyclone were plugged to minimize exposure of the sample to the atmosphere. The sample was allowed to cool and then transferred to a one-half pint sample jar in a glove bag purged with nitrogen. The sample jar was sealed for later analysis.

Bed sampling at the one-foot level was discontinued after the sample probe plugged during the first two attempts. No problems were encountered with sampling at the 2-, 3-, and 4-foot levels.

In addition to the bed sampling, samples of the first- and second-stage condensate and the cryogenic trap were combined to give a composite gasifier wastewater sample. The samples were analyzed by qualitative gas chromatography/mass spectrometry to determine the relative quantities of organic compounds present in the wastewater.

The carbon content of the bed remained relatively constant at the various bed heights, as indicated by Table 3-17. The carbon content was nominally 11% over the 2- to 4-foot bed height range for all three test coals. This

Figure 3-11. Schematic of Bed Probe.

TABLE 3-17

CPU BED PROBE TEST RUNS, CARBON CONTENT OF BED (WT%)

Bed Height	Wyodak	Wyodak	Martin Lake	Velva
4 ft	12.73	9.76	10.90	11.18
3 ft	11.34	10.54	11.24	--
2 ft	10.14	10.40	10.68	10.53

indicates that the coal char was uniformly distributed throughout the bed, as expected in a well-mixed fluid-bed reactor.

3.1.4.2 Kinetic Effects of Bed Temperature and Steam:Carbon Ratio

Based on the results of the bed probe testing, the reactor kinetics were estimated using the assumption that the fluid-bed reactor behaves similarly to a continuously stirred reactor (CSTR). The rate of reaction for carbon consumption and gas production for the limestone test matrix did not correlate

with bed temperature, but correlated with steam:carbon molar ratio. As shown in Figure 3-12, the rates of reaction for H_2 , CO , and CO_2 followed the carbon consumption as expected, indicating that the more carbon converted to gas, the higher the production of gases. The rate of reaction has an exponential relationship with steam:carbon ratio, and increases with decreasing steam:carbon ratio. No coal-specific relationships were observed.

The reactivity constants were calculated from the kinetic data for the limestone test matrix and are shown in Table 3-18. As shown in the table, the reactivity constant increases with temperature for all three test coals. The reactivity constant typically doubled as the temperature increased from 700°C to 750°C, and increased tenfold from 750°C to 800°C for Velva and Wyodak coals, but only increased fivefold for Martin Lake coal. This compares with the reactivity parameters calculated from TGA laboratory experiments shown in Table 3-19 for the coals over the same temperature range and with a K_2CO_3 catalyst. This implies that the TGA can be used to predict the behavior of a coal in the fluid-bed gasifier.

3.1.4.3 Bed Height Testing

Several runs were performed in November with Wyodak subbituminous coal and Martin Lake lignite to determine the effect of bed height on CPU operation. All runs were made with limestone as the bed material at 750°C and a steam:carbon ratio of 2:1. The gasifier typically is operated with a 4-foot expanded bed. In this series of runs, the operation of the gasifier was

Figure 3-12. Rates of Reaction for Carbon Consumption and Gas Production Versus Steam:Carbon Ratio.

TABLE 3-18

CARBON CONSUMPTION RATE CONSTANTS FOR CPU LIMESTONE TEST MATRIX

<u>Run No.</u>	<u>Coal</u>	<u>Bed Temp., °C</u>	<u>Stm/C Ratio</u>	<u>C Consumed Rate Constant k, hr⁻¹</u>
1-M280L	M Lake	801	2.23	12.17
5-M375L	M Lake	752	3.40	2.86
7-M175L	M Lake	741	1.04	7.94
3-M270L	M Lake	699	2.44	2.92
11-V280L	Velva	802	2.38	49.13
9-V375L	Velva	750	3.31	4.27
13-V175L	Velva	744	1.37	5.45
15-V270L	Velva	698	2.34	2.24
6-W380L	Wyodak	802	3.41	51.13
10R-W180L	Wyodak	806	1.28	26.82
12-W275L	Wyodak	743	2.31	3.71
2R-W275L	Wyodak	746	2.10	4.53
12R-W275L	Wyodak	750	2.35	3.81
4-W370L	Wyodak	696	3.51	1.33
14-W170L	Wyodak	699	1.57	1.86

evaluated at expanded bed heights of 1, 2, 3, and 4 feet. The variation in bed height should help to determine the effect of solids residence time on gas production.

The different bed heights had little effect on the product gas composition, as shown by the product gas compositions in Tables 3-20 and 3-21 for the Martin Lake lignite and Wyodak subbituminous coal CPU test runs. The gas production rates were not significantly affected by bed height, as shown in Figures 3-13 and 3-14 for the Martin Lake and Wyodak runs, respectively. Only Martin Lake showed a slight increase in hydrogen production with lower bed heights. Although gas composition and production rates were not significantly altered by variations in bed height, the bed temperature became more difficult to control as the bed height decreased.

The rate of reaction for carbon consumption showed a power relationship with bed height, and increased with decreasing bed height as shown in Figure 3-15. As shown in Figure 3-15, the rate of reaction for carbon consumption for the Martin Lake and Wyodak coals behaved similarly with respect to bed height. The results of this testing indicate that expanded bed heights below 4 feet can be used with no adverse effects on gas production. However, the lower limit for bed height will be determined based on operability of the gasifier.

TABLE 3-19
LABORATORY REACTIVITY PARAMETERS (TGA)

Coal	Catalyst	Temp., °C	k, hr ⁻¹
Velva	None	700	0.30
Velva	None	750	1.35
Velva	None	800	2.10
Velva	10 wt% K ₂ CO ₃	700	4.06
Velva	10 wt% K ₂ CO ₃	750	8.17
Velva	10 wt% K ₂ CO ₃	800	34.8
Velva	20 wt% CaCO ₃	700	5.00
Velva	20 wt% CaCO ₃	750	8.76
Velva	20 wt% CaCO ₃	800	15.00
Martin Lake	10 wt% K ₂ CO ₃	700	2.40
Martin Lake	10 wt% K ₂ CO ₃	750	4.60
Martin Lake	10 wt% K ₂ CO ₃	800	5.30
Wyodak	10 wt% K ₂ CO ₃	700	4.30
Wyodak	10 wt% K ₂ CO ₃	750	8.24
Wyodak	10 wt% K ₂ CO ₃	800	13.48

TABLE 3-20
PRODUCT GAS COMPOSITIONS FOR CPU BED HEIGHT TEST RUNS
WITH MARTIN LAKE COAL

Bed Height, feet	1	2	3	4
Product Gas Composition (mol%):				
H ₂	45.80	45.13	44.26	44.19
CO ₂	37.86	38.16	38.46	39.04
CO	12.75	12.70	13.23	12.38
CH ₄	2.77	2.90	2.85	3.01
C ₂ H ₄	0.50	0.16	0.66	0.65
C ₂ H ₆	0.20	0.22	0.22	0.23
C ₃ H ₆	0.00	0.16	0.11	0.39
C ₃ H ₈	0.00	0.00	0.00	0.00
C ₄ H ₈	0.00	0.00	0.00	0.00
C ₄ H ₁₀	0.00	0.00	0.00	0.00
H ₂ S	0.12	0.14	0.20	0.12

TABLE 3-21

PRODUCT GAS COMPOSITIONS FOR CPU BED HEIGHT TEST RUNS
WITH WYODAK COAL

Bed Height, feet	1	2	3	4
Product Gas Composition (mol%):				
H ₂	43.66	45.66	42.58	45.23
CO ₂	41.61	39.28	41.46	39.19
CO	10.69	11.13	11.23	11.66
CH ₄	2.97	2.78	3.41	2.93
C ₂ H ₄	0.72	0.64	0.94	0.71
C ₂ H ₆	0.18	0.20	0.24	0.18
C ₃ H ₆	0.10	0.26	0.10	0.03
C ₃ H ₈	0.00	0.00	0.00	0.00
C ₄ H ₈	0.00	0.00	0.01	0.01
C ₄ H ₁₀	0.00	0.00	0.00	0.00
H ₂ S	0.07	0.07	0.03	0.04

Figure 3-13. Gas Production Versus Bed Height for Martin Lake CPU Test Runs.

Figure 3-14. Gas Production Versus Bed Height for Wyodak CPU Test Runs.

Figure 3-15. Rate of Reaction for Carbon Consumption Versus Bed Height.

3.1.5 CPU Bench-Scale Support Studies

3.1.5.1 Bed Material Testing

Lean taconite is a plentiful spoil of the mining of iron ore in the Minnesota iron range. Largely hematite (Fe_2O_3) and goethite ($\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$), the taconite contains silicates in excess of that of acceptable ore. Liberating the excess silicates from the iron-rich ore requires extraordinary crushing and chemical treatment before magnetic separation. The added cost of cleaning the ore results in unfavorable economics, thus currently making it a waste material.

The oxidized taconite was tested as a bed material in seven CPU tests previously described. The tests resulted in some interesting observations concerning mineral transformations within the bed material under the gasifier conditions. Optical microscopic examination by the University of Minnesota-Duluth Natural Resources Research Institute found the following:

- Conversion of hematite to magnetite (Fe_3O_4) was relatively high under the gasification conditions.
- Conversion to magnetite took place with no modification of original mineral structure.
- Little evidence of reaction between magnetite and the surrounding quartz matrix was observed.
- More wustite (FeO) was found in the bed material following Tests 3 and 4 than in Tests 1 and 2, indicating that the reduction potential of the gas in the first two tests was greater than that of the latter two tests.
- Reaction rims on siliceous particles imply that in Tests 3 and 4, which were carried out at the same temperatures as Tests 1 and 2, fluxing with trona had occurred.
- Fayalite (Fe_2SiO_4) appears to be present in the reaction rims.
- Large, relatively pure iron oxide phases consisting of magnetite centers and wustite peripheries were present.

The varying operational results for the different bed materials used in the CPU testing with the trona catalyst posed an interesting question as to why some of the bed materials did not agglomerate to the same extent as others. One postulation was that there may be differences in heat capacities among the materials. Three bed materials used in the CPU testing, gabbro, oxidized taconite, and limestone, and a 50:50 wt:wt mixture of limestone:trona were analyzed by Differential Scanning Calorimetry (DSC). Each was heated at $20^\circ\text{C}/\text{min}$ under flowing argon to 550°C (essentially the temperature limit of the instrument) in the same sample container. Heat flow was measured against temperature, and the heat capacity at constant pressure (C_p) was calculated at

200°, 300°, 400°, 500°, and 550°C. Figure 3-16 is a plot of C_p versus temperature for each of the bed materials and the standard, a sapphire lens. Table 3-22 shows the C_p values at each of the temperatures.

The sapphire standard showed a steady increase in C_p with temperature. The bed materials, however, varied in their temperature effects. Decomposition of limestone/trona resulted in a decrease in C_p when the temperature was increased from 200°C to 350°C, followed by a steady increase in C_p . Gabbro also showed a decrease in C_p until approximately 500°C, and then began to increase. Gabbro is a rock consisting of a variety of minerals, which may be responding to the increase in temperature by mineral transformation. The taconite also underwent an apparent decrease in C_p until the temperature reached 500°C. However, a large increase in C_p occurred between 300°C and 400°C (not noted on the figure), followed by a decrease to 500°C, and then an increase. The limestone C_p reached a low at ~400°C and then increased steadily. At 550°C the C_p 's, in order of increasing magnitude, were taconite < sapphire < gabbro < limestone < limestone/trona. These data may indicate that a knowledge of the heat capacity of the bed material coupled with experience with the behavior of a few bed materials, could be useful in predicting heat transfer phenomena such as agglomeration.

Figure 3-16. Heat Capacity Versus Temperature for Various Bed Materials.

TABLE 3-22
HEAT CAPACITIES OF BED MATERIALS AT VARIOUS TEMPERATURES

Temp, °C	C_p , J/g-deg ^a				
	Sapphire	Gabbro	Limestone	Taconite	LS ^b /Trona
200	1.12	1.44	1.45	1.44	1.55
300	1.13	1.49	1.33	1.39	1.15
400	1.15	1.24	1.25	1.11	1.30
500	1.17	1.18	1.40	0.97	1.52
550	1.19	1.39	1.45	1.16	1.64

^a Corrected to Standard Sapphire C_p = 1.171 at 500°C.

^b Limestone.

Another question that arose from the CPU testing with limestone is the mechanism of the catalytic effect that limestone has on the char-steam reaction. The dispersion of limestone on the coal surface during catalytic gasification is directly related to the rate of conversion. Scanning Electron Microscopy/Energy Dispersive Spectroscopy (SEM/EDS) was used to examine the occurrence of limestone on the coal before feeding to the reactor and after heating to 750°C under steam and argon.

The catalyzed feed coal was prepared by admixing 20 wt% limestone to Velva coal. The mixture was analyzed by SEM/EDS, which showed that the limestone was spread non-uniformly over the coal surface. An elemental map of the calcium showed large areas where the element was not deposited. A sample of the mixture was heated to reaction temperature under argon and steam, cooled, and analyzed by SEM/EDS. In this sample, the limestone was spread more uniformly, and larger particles of the limestone showed signs of melting. However, unlike trona-catalyzed samples where the sodium carbonate was no longer particulate, the limestone in these samples was still particulate, indicating that melting was far from complete. The presence of lower-melting material and/or partial dissolution of the calcium carbonate by the lower melting material or moisture must be responsible for the dispersion that does occur. More complete dispersion of the added limestone or increasing the concentration of limestone catalyst (by using it as a bed material) should enhance reactivity.

3.1.5.2 Wastewater Treatment

Preliminary bench-scale wastewater treatment studies were performed to assess the treatability of the wastewater produced in the CPU. In late February, a total of approximately 550 gallons of first-stage condensate from all of the hydrogen production CPU runs were steam stripped to remove ammonia in preparation for wastewater treatment by the activated sludge process. The samples were thoroughly mixed prior to stripping to obtain a uniform feed. The goal of the stripping process was to reduce the total ammonia

concentration in a composite sample of the wastewater from 3518 mg/l to 500 mg/l or less. The compositions of the steam stripper feed and final product are given in Table 3-23.

Approximately 61 gallons per hour of wastewater were fed to the stripping column. After slightly more than 3 hours of operation, the total ammonia concentration of the steam stripper wastewater product dropped to 518 mg/l and remained at less than 500 mg/l for the remainder of the stripping operation. Approximately 1.2 pounds of steam were required per gallon of wastewater. The average temperature of the water entering the ammonia stripping column was 200°F. The final product was thoroughly mixed in a 1000-gallon tank to provide a uniform feed for the activated sludge unit, and then stored in epoxy-lined 55-gallon barrels. The final total ammonia concentration was 419 mg/l.

A bench-scale activated sludge unit was set up to determine the treatability of the hydrogen production CPU wastewater. The bioreactor was seeded with approximately 4 gallons of cooling water from the cooling tower basin at the Great Plains Gasification Plant (GPGP) in Beulah, North Dakota. The bioreactor was also seeded with biomass from the EMRC Deep Column Reactor, which is fed with a synthetic gasification wastewater.

TABLE 3-23
STEAM STRIPPER FEED AND FINAL PRODUCT COMPOSITIONS

	Steam Stripper Feed	Steam Stripper Product
pH	9.10	8.97
Wastewater Analysis, mg/l:		
Ammonia, Free	3518	380
Ammonia, Total	3518	419
TOC	415	292
COD	1540	1180
BOD	1020	800
Phenolics	--	277
PO ₄	--	<1
CN	--	18.9

A schematic of the bioreactor is shown in Figure 3-17. A reactor volume of 10 gallons was selected and a standpipe was included so that the reactor volume could be varied if necessary. The reactor was aerated with compressed air, which also stirred the reactor contents to provide complete mixing. Solids were settled in a clarifier and recycled back to the reactor. The clarifier effluent was suitable for disposal to the city sewer system.

For approximately one week, until the wastewater could be steam stripped for use in the bench-scale wastewater treatment work, a dilute solution of unstripped hydrogen production wastewater was used as feed to the reactor to acclimate the biomass to the wastewater. For the first two weeks, the draw-and-fill method was used. The sludge was allowed to settle and a volume of supernatant equal to the amount fed per day was withdrawn from the reactor. After the first two weeks, the reactor effluent was allowed to overflow to the clarifier. The feedrate was increased from 5 gallons per day to 10 gallons per day over a 5-day period to achieve a 1-day hydraulic retention time (HRT). A sludge retention time (SRT) of 20 days was selected to see if nitrification of the ammonia could be accomplished. When sludge loss in the clarifier effluent was considered, the actual SRT was 15.6 days. The food to microorganism ratio based on COD was 0.68.

Data from the first 3 weeks of treatment indicate a removal rate of 99% of the phenolics and 79% of the COD. Nitrifying bacteria were present in the sludge obtained from the EMRC Deep Column Reactor and preliminary data indicate that some nitrification of the ammonia is occurring. More data is required before a definite conclusion can be reached.

Figure 3-17. Schematic of Bench-Scale Wastewater Treatment Unit.

A 24-hour batch reactor test was performed to determine reactor kinetics. The data was used to determine the rate of substrate removal in the activated sludge process. The kinetic coefficients obtained can be used for design and comparison purposes.

3.2 Coal Properties and Reactivity Analysis

3.2.1 Thermogravimetric Analysis

The bench-scale study of catalyst effects on the coal char gasification reaction was continued with emphasis on the catalysis by natural mineral matter. Taconite, taconite and trona, and limestone were tested in the temperature range of 700°-800°C. Table 3-24 shows the results of gas analyses from some of the experiments. All hydrogen results were acceptable and carbon monoxide compositions were temperature dependent as in previous experiments (5).

The reactivities shown in Table 3-25 indicate the relative effectiveness of the catalyst in converting the initial 25% of the char carbon to gas. Taconite and taconite-with-trona affected catalytic activity on the Velva char-steam gasification reaction, with the taconite-trona combination having a greater effect. Calcium acetate was also tested with Velva char and produced only slight catalysis at the higher temperatures. Limestone at four different concentrations was tested on the gasification reaction of Zap (Indian Head), North Dakota, lignite. The rates of gasification at the two highest catalyst loadings (10 and 15 wt%) were not significantly different from one another. The reactivity parameters (k) for the higher limestone loading are included in Table 3-25.

Agglomeration of bed material was observed when using trona as a catalyst. Both limestone and taconite bed materials agglomerated when trona was included in the test; but, at the relatively mild temperatures of the gasification experiments, limestone alone did not agglomerate.

3.2.2 Active Site Measurement

A gravimetric method, similar to a method proposed by Ratcliffe and Vaughn (6), was used to determine the number of CO₂ active sites on the catalyzed and uncatalyzed low rank coal char used in the production of hydrogen gas. The procedure and results of this method have been previously reported (5).

An alternate method of reactive site determination using ¹³C nuclear magnetic resonance (NMR) suggested by Mims and Pabst was carried out on Velva chars containing varying amounts of added potassium (7,8). The procedure is as follows:

Ten-gram samples of -100 mesh as-received coal was dry-mixed with 5, 10, and 20 wt% K₂CO₃. Approximately two grams of each mixture was heated rapidly under argon in the large TGA to 750°C, held there for 10 minutes, and cooled to room temperature. The char thus formed was methylated with ¹³CH₃I by mixing it in a ten-to-one ratio of ¹³CH₃I (dissolved in THF) to potassium in the char in an

TABLE 3-24

PRODUCT GAS ANALYSES FOR LABORATORY-SCALE TGA EXPERIMENTS (MOL%)

SAMPLE	TEMP., °C	H ₂	CO ₂	CO	CH ₄	C ₂ H ₆
Velva/ 10% Tac. w/steam	800	59.0	24.0	17.0	--	--
Velva/ 10% Tac. w/steam	750	62.7	32.5	12.7	--	--
Velva/ 10% Tac. w/steam	700	56.8	34.5	8.63	--	--
Velva/ Tac + Tr	800	60.8	19.2	20.0	--	--
Velva/ Tac + Tr	750	55.4	32.4	12.2	--	--
Velva/ Tac + Tr	700	63.1	29.1	7.9	--	--
Velva/ CaAcet	800	60.0	21.6	18.8	--	--
Velva/ CaAcet	750	63.2	23.7	13.2	--	--
Velva/ CaAcet	700	63.2	29.9	6.93	--	--
Indhd/ 15% L.S.	800	62.1	22.5	15.4	--	--
Indhd/ 10% L.S.	800	59.5	22.5	18.0	--	--
Indhd/ 5% L.S.	800	61.1	20.8	18.1	--	--
Indhd 2% L.S.	800	52.4	30.6	17.0	--	--

TABLE 3-25
REACTIVITY PARAMETER (k) AT 25% CARBON CONVERSION

SAMPLE	CATALYST	Temperature, °C		
		700	750	800
Velva/Taconite	Trona	1.46	2.70	3.84
Velva/Taconite	None	1.33	1.63	2.85
Velva/Limestone	Trona	5.20	8.94	13.31
Velva	CaAcetate	1.49	1.47	1.74
Zap	None	1.00	0.74	1.07
Zap	K ₂ CO ₃	2.30	3.21	3.96
Zap	Limestone	1.42	2.24	3.33

ultrasonic bath overnight at room temperature. The reaction was quenched using methanolic HCl, followed by washing to remove excess ¹³CH₃I. Each sample was analyzed by solid ¹³C NMR using H/C cross polarization and magic angle spinning, and was compared 1) with spectra obtained by the Bloch Decay method, and 2) with gravimetric CO₂ chemisorption data.

Table 3-26 shows some of the active site data acquired by CO₂ adsorption along with the reactivity parameter for the char-steam reaction previously reported (5). Also shown on this table is the correlation coefficient for the plot of k versus active sites for several samples. The chars investigated included catalyzed and uncatalyzed Velva and Martin Lake lignites and were prepared under argon in the temperature range of 650°-750°C at 50°C intervals. Potassium carbonate and trona were the catalysts used in the char-steam reactions, and coals containing the catalyst, along with the uncatalyzed coal, were analyzed for active sites. As expected, the active site number generally followed the reactivity parameter and plots of C/active site versus reactivity parameter had correlation coefficients of > 0.80. Both catalyzed samples of Martin Lake lignite gave excellent correlation between active sites and reactivity parameter in the temperature range between 650° and 750°C. Martin Lake containing no catalyst gave the poorest correlation.

If it is assumed that the reaction involved in preparing the ¹³C-enriched samples for determining active sites by the method of Mims and Pabst is as follows:

then the difference between natural abundance ¹³C and that of the enriched sample should be a measure of the number of (potassium) active sites. Figure 3-18 shows a plot of normalized peak integration versus wt% K₂CO₃ for natural abundance and enriched coal char. The difference gives active site numbers shown in Table 3-27.

TABLE 3-26

C/ACTIVE SITE AND REACTIVITY PARAMETER FOR CATALYZED AND
UNCATALYZED VELVA LIGNITE

<u>Coal</u>	<u>Catalyst</u>	<u>Temp., °C</u>	<u>k*</u>	<u>C/Active Site</u>	<u>r²**</u>
Velva	None	650	0.30	206	0.97
		700	1.40	159	
		750	2.44	47	
Velva	K ₂ CO ₃	650	1.43	43	0.83
		700	3.50	32	
		750	7.04	31	
Velva	Trona	650	1.28	68	0.99
		700	3.23	52	
		750	5.81	37	
M. Lake	None	650	0.36	272	0.80
		700	0.70	160	
		750	1.62	140	
M. Lake	K ₂ CO ₃	650	0.45	113	1.00
		700	1.41	92	
		750	3.55	39	
M. Lake	Trona	650	1.05	97	1.00
		700	2.37	72	
		750	3.50	48	

* Reactivity Parameter in (g/hr)/g.

** Correlation Coefficient for C/Active Site vs k.

The results of this NMR technique indicate that the methylation of the active sites on the char is independent of the amount of potassium carbonate originally added to the coal. As indicated by Table 3-27 and Figure 3-18, the enrichment in ¹³C in the char is the same in the three samples within experimental error. A comparison between C/active site by this method and that of the gravimetric procedure (Table 3-26) for Velva/K₂CO₃ char prepared in vitro at 750°C show them to be consistent.

3.2.3 Surface Analysis

3.2.3.1 Surface Area

The question arises as to the possibility of increased surface area on carbonization of the coal as the major factor in exposing more active sites and thus increasing reactivity. Brunauer-Emmett-Teller (BET) surface area analyses were carried out at EMRC and by a commercial laboratory on selected samples. Table 3-28 shows the results of these surface analyses. Based on the variability of the results, it is inconclusive as to whether a surface area effect was observed.

Figure 3-18. Atom % Aliphatic ¹³C Versus wt% K₂CO₃ for Velva/K₂CO₃ Char Reacted with ¹³CH₃I as Determined by Solid ¹³C NMR Spectroscopy.

3.2.3.2 ESCA Analysis of Char Surface

Electron Spectroscopy for Chemical Analysis (ESCA) was used to investigate carbon-silicon behavior during the devolatilization of coal. The method involved acquiring spectra of hexaphenyldisiloxane, tetraphenylsilane, chlorotriphenylsilane, and silicon carbide and then comparing spectra of char with the standard spectra. Preliminary study of the data yielded no well-defined information. The data is to be re-plotted and spectra deconvoluted for additional study.

3.2.4 Topical Report

The final draft of the char properties and reactivity topical report was completed and submitted to the DOE-COTR.

3.3 Hydrogen Market Assessment

A detailed hydrogen market assessment was subcontracted to J.E. Sinor Consultants, Inc., of Niwot, Colorado, in May. The objective of the market assessment was to determine the optimum market for hydrogen produced by the EMRC hydrogen production process. A meeting was held in June with J. E. Sinor Consultants to discuss the preliminary findings of the market

TABLE 3-27

POTASSIUM ACTIVE SITES ON VELVA CHAR PREPARED AT 750°C AS
DETERMINED BY ENRICHED ^{13}C NMR SPECTROSCOPY

Peak Area % Normalized to the Aromatic Peak			
	wt% K_2CO_3		
Natural Abundance	2	10	15
Carbonyl/o-sub. aromatic	46.99	22.92	25.20
Aromatic	100.00	100.00	100.00
Ether/o-sub. Aliph.	15.78	24.18	18.66
Aliphatic	14.72	9.73	15.63
Enriched			
Carbonyl/o-sub. aromatic	46.91	22.98	25.19
Aromatic	100.00	100.00	100.00
Ether/o-sub. Aliph.	15.84	24.26	18.56
Aliphatic	43.00	36.76	45.45
NMR ACTIVE SITE DETERMINATIONS - Difference in ^{13}C Concentrations - normalized to aromatic peak carbon atom %			
Change in carbonyl	-0.07	0.06	-0.01
Change in aromatics	0.00	0.00	0.00
Change in ether/o-sub aliph	0.06	0.09	-0.10
Change in aliphatics	28.29	27.03	29.82
Enhancement in aliphatic ^{13}C	2.92	3.78	2.91
Carbons/active site	565.00	523.00	482.00

TABLE 3-28

BET SURFACE AREAS OF VELVA LIGNITE AND CHAR WITH AND WITHOUT CATALYST

SAMPLE	AREA, m ² /g	ADSORBATE
VELVA	1.58	Nitrogen
VELVA/TRONA	56.31	Nitrogen
VELVA/ K_2CO_3	0.98	Nitrogen
" " CHAR	1.54	Nitrogen
" " CHAR	2.41	Nitrogen
" " CHAR (MM*)	7.07	Krypton
VELVA CHAR	16.84	Nitrogen
VELVA CHAR (MM*)	110.85	Nitrogen

MM* - Analysis performed by Micromeritics, Inc.

assessment. The final report for the hydrogen market assessment was submitted to the EMRC project manager in August of 1988. The following items summarize the highlights of the market assessment report:

- Methanol production represents the best near-term market opportunity from a technical standpoint. A fuel methanol market (M-85 of 85% methanol, 15% gasoline) will appear in California, but slowly. Methanol from coal is close to being competitive with methanol from natural gas in the United States, but will have to compete with methanol from overseas natural gas.
- The most attractive methanol market niche for coal gasification is coproduction with electricity. However, it is not clear whether the EMRC process will have a competitive advantage in coproducing methanol and electricity.
- The ideal long-term market niche for catalyzed gasification of low-rank coal is to provide hydrogen for molten carbonate fuel cells. If molten carbonate fuel cells are successful, they are certain to be widely adopted. Fuel cells to produce electricity represent a larger potential market than any other hydrogen-from-coal application.
- The widely discussed "Hydrogen Economy" is still at least one generation in the future. Hydrogen from renewable resources is not likely to be competitive with hydrogen from coal in the near future. The carbon dioxide "Greenhouse Effect" will create a non-economic driving force to reduce combustion of fossil fuels.
- Markets for merchant hydrogen will not expand dramatically in the near future. Oil refineries in general will not need large amounts of hydrogen from the outside. Also, ammonia does not represent an attractive market niche for hydrogen from the catalytic gasification of low-rank coal.

3.4 Economic Assessment

A request for proposals (RFP) on performing an economic assessment for the EMRC hydrogen production process was sent to various architectural and engineering firms in early July. The RFP was also listed in the Commerce Business Daily. The deadline for submitting proposals to EMRC was August 7. The proposals received were reviewed by Rod Sears and Warrack Willson of EMRC. Black & Veatch Engineers-Architects was selected as the firm to conduct the economic assessment.

Once the subcontract was agreed upon, copies of the past two annual project reports, along with the final report for the detailed market assessment were sent to Black & Veatch for review. A kickoff meeting for the economic assessment was held at EMRC on September 29. The purpose of the kickoff meeting was to agree on the direction of the assessment and to exchange as much information as possible on the CPU test results.

The scope of work for the economic assessment was expanded to include the design and economic evaluation of two additional scenarios: 1) methanol/electricity coproduction, and 2) fuel cell electricity generation, in addition to the production of high purity hydrogen. The design and economics guidelines document was expanded to include the two additional scenarios. A draft of the design and economics guidelines document was transmitted to EMRC for review in November. Comments by EMRC on the document were received and incorporated by Black & Veatch. Tables 3-29 and 3-30 summarize the design and economic bases.

Design of the gasifier was initiated based on material balances provided by EMRC. Gasifier heat and mass balances and process flow diagrams were developed on a commercial scale. Additional information was supplied by EMRC to estimate carbon conversion with the addition of fines recycle in the gasifier design. Rough estimates of system heat rates by Black & Veatch suggest that emphasis must be on hydrogen or methanol production rather than electrical production using combined cycle.

The process design for the production of high purity hydrogen utilized a pressure swing adsorption (PSA) process for hydrogen purification. Figure 3-19 is the block flow diagram for the hydrogen production plant. The process off-gas from the PSA unit will be used to cogenerate electricity. The use of membrane diffusion as an alternative approach to hydrogen concentration was investigated and eliminated.

The process design for the cogeneration of methanol and electricity utilized the ICI methanol synthesis process with a gas turbine for power generation. Figure 3-20 is the block flow diagram for the methanol/electricity coproduction plant. The off-gas from the methanol synthesis step will be used to fire the gas turbine.

A molten carbonate fuel cell design was used in the integration of fuel cells with the gasifier. Figure 3-21 is the block flow diagram for the fuel cell plant. Design information for the molten carbonate fuel cell was supplied to EMRC and Black & Veatch by George Steinfeld of the Energy Research Corporation of Danbury, Connecticut.

A review meeting was held at Black & Veatch with the EMRC project manager on December 16, 1988. The design of the commercial-scale gasifier and the process flow diagrams for the three process scenarios were reviewed. The preliminary configuration of the economic model was also reviewed at the meeting. The economic assessment was completed in April and the final report was submitted to EMRC in May.

TABLE 3-29

COMMON PLANT DESIGN CRITERIA AND ASSUMPTIONS

-
- Northeast Colorado Site
 - Ambient Temperature: Dry Bulb 50°F
Wet Bulb 38°F
 - 1995 Commercial Operation
 - Oxygen Purity: 98%
 - Fluidized Bed Combustor for CaS
 - Baseload Operations
 - Nominally Based on Experimental Run 12-W275L
 - Wyodak Subbituminous Coal
 - Limestone Bed Material
 - Reaction Gas Temperature at 1,370°F
 - Gasifier Pressure: 26 psia
 - Steam:Carbon Ratio: 2:1
 - Carbon Conversion: 94%
 - (As a Result of Fines Recycle)
 - Commercial Scale Gasifier Based on UND-EMRC Gasifier
 - 27 Feet Diameter
 - 29 Feet Tall
 - 4 Feet Expanded Bed Height
 - 9 Inches of Refractory
 - Nominal 2 Feet/Second Superficial Velocity
 - One GE Frame 6 Combustion Turbine and Purge Gas Composition Sets Plant Size
-

TABLE 3-30

ECONOMIC EVALUATION APPROACH

-
- Use Proforma Spreadsheet Model of Plant Financial Performance
 - Key Assumptions
 - Book Life: 30 years
 - Tax Life: 20 Years
 - Debt/Equity
 - Preferred Share: 6.1%
 - Common Share: 43.9%
 - Debt Share: 50%
 - Discount Rate: 10.2%
-

Figure 3-19. Simplified Flow Diagram for Hydrogen Plant.

Figure 3-20. Simplified Flow Diagram for Methanol Plant.

Figure 3-21. Simplified Flow Diagram for Fuel Cell Plant.

4.0 CONCLUSIONS

- The trona catalyst caused agglomeration of the bed material in the CPU test runs. The degree of agglomeration varied with bed material and steam:carbon ratio, with less agglomeration at higher steam:carbon ratios.
- The results of the limestone test matrix indicated that hydrogen production was not significantly affected by temperature or steam:carbon ratio. Hydrogen production rates are maintained at lower temperatures and steam:carbon ratios due to the water-gas shift reaction. At higher temperatures and steam:carbon ratios, hydrogen production is maintained due to higher carbon conversion via the gasification reaction, which produces more raw gas.
- The rate of reaction for carbon conversion correlated only with steam:carbon ratio, increasing with decreasing steam:carbon ratio. The rate of reaction for carbon conversion also increased with decreasing bed height.

- The reactivity constants increased with increasing temperature and were similar to the results obtained from the laboratory TGA study. TGA is a good method of predicting the behavior of a coal in the fluid-bed gasifier.
- Active sites correlated well with the reactivity parameter over the temperature range of 650° to 750°C. Also, methanation of the active sites on the char is independent of the amount of K_2CO_3 originally added to the coal.
- Methanol production represents the best near-term market opportunity for hydrogen and the most attractive market niche for coal gasification is coproduction with electricity. The ideal long-term market niche for catalyzed gasification of low-rank coal is to provide hydrogen for molten carbonate fuel cells.

5.0 PRESENTATIONS AND PUBLICATIONS

The following is a list of publications and presentations that were prepared and/or given during this project year:

Mohs, T.R., R.C. Timpe, R.E. Sears, (1988), Proc. N.D. Acad. Sci., 42, 78.

Sears, R.E. and R.C. Timpe, "Production of Hydrogen from Low-Rank Coals," Proceedings of the Eighth Annual Gasification and Gas Stream Cleanup Systems Contractors Review Meeting, DOE/METC, Morgantown, WV, May 10-12, 1988.

Sears, R.E., R.C. Timpe, M.A. Musich, S.J. Cisney, "Production of Hydrogen from Low-Rank Coal," Annual Report, DOE Contract DE-FC21-86MC10637-T3, May 1988.

Timpe, R.C., and R.E. Sears, (1988), ACS Div. Fuel Preprints, 33, No. 2, 359-367.

Timpe, R.C., R.E. Sears, and G.G. Montgomery, Journal of Coal Quality, 8, No. 1, 27-31 (1989).

6.0 REFERENCES

1. Pohani, B.P., J. Japan. Petrol. Inst., 27, 1, (1984).
2. "Low-Rank Coal Research," University of North Dakota Energy Research Center, Quarterly Technical Progress Report, January-March 1986, DOE/UNDERC/QTR-86/1.
3. Galegher, S.J., R.C. Timpe, W.G. Willson, and S.A. Farnum, "Kinetics of Catalyzed Steam Gasification of Low-Rank Coals To Produce Hydrogen," Final Report, June 1986, DOE/FE/60181-2034.

4. "CO₂ Acceptor Process Gasification Pilot Plant," Final Report, Volume 12, DOE Contract EX-76-C-01-1734, Nov. 1978.
5. Sears, R.E., Timpe, R.C., Musich, M.A., and Cisney, S.J., "Production of Hydrogen From Low-Rank Coals," Annual Technical Report, April 1, 1987 through March 31, 1988, DOE Contact No.DE-FC21-86MC10637, April 1988.
6. Ratcliffe, C.T., and Vaughn, S.N., ACS Div. Fuel Preprints, 30, No. 1, 304 (1985).
7. Mims, C.A., and Pabst, J.K., Fuel, 1983, 62, 176-179.
8. Mims, C.A., and Pabst, J.K., "Proceedings of the International Conference on Coal Science," 1981, 730, Verlag Gluckauf GmbH, Essen.

APPENDIX A

UNADJUSTED MATERIAL BALANCES FOR CPU LIMESTONE TEST MATRIX

TABLE A-1

UNADJUSTED MATERIAL BALANCES FOR WYODAK PARAMETRIC TESTS

Run No.	2	4	6	12	14	2R	10R	12R
Coal	Wyodak	Wyodak	Wyodak	Wyodak	Wyodak	Wyodak	Wyodak	Wyodak
Bed Material	Limestone	Limestone	Limestone	Limestone	Limestone	Limestone	Limestone	Limestone
AvgFrbrdP (psia)	21.83	19.08	22.70	26.22	25.70	22.46	29.21	25.73
Avg Bed T (C)	751.06	695.96	801.70	743.02	698.59	745.98	806.36	749.95
O ₂ :Stm Ratio	0.19	0.10	0.13	0.14	0.22	0.16	0.25	0.17
Stm:C Ratio	2.43	3.32	3.17	2.27	1.14	2.23	1.16	2.33
O ₂ :C Ratio	0.45	0.32	0.42	0.32	0.24	0.35	0.30	0.40
In (lb/hr)								
Coal	21.70	16.49	16.36	23.74	38.34	22.89	30.39	23.25
Steam	36.26	37.19	36.72	37.00	29.91	35.10	24.84	37.15
Oxygen	12.05	6.29	8.55	9.25	11.45	9.91	11.24	11.45
Nitrogen	4.26	4.26	5.44	5.12	5.46	4.62	4.75	3.75
Out (lb/hr)								
Fines Acc	2.85	2.59	2.30	2.80	3.67	3.75	2.57	2.52
Cond Acc	39.95	39.18	39.09	37.24	33.27	36.17	25.32	38.48
Prod Gas	23.16	18.83	20.89	30.46	36.06	27.73	32.82	29.75
Nitrogen	4.26	4.26	5.44	5.12	5.46	4.62	4.75	3.75
Mass Closure (%)	94.55	100.97	100.95	100.68	92.13	99.65	91.91	98.55
In (lb/hr)								
Carbon	9.94	7.46	7.72	10.87	17.56	10.48	14.25	10.65
Hydrogen	5.45	5.24	5.16	5.67	5.83	5.40	4.81	5.65
Oxygen	53.20	46.15	47.67	51.89	53.79	50.51	45.60	54.02
Sulfur	0.06	0.05	0.05	0.06	0.10	0.06	0.06	0.06
Ash	1.23	0.97	0.90	1.33	2.17	1.30	1.54	1.32
Out (lb/hr)								
Carbon	8.87	7.27	7.36	10.85	13.57	10.84	11.55	10.54
Hydrogen	5.64	5.33	5.32	5.61	5.51	5.45	4.41	5.67
Oxygen	50.55	47.33	48.48	52.87	52.57	50.24	43.69	53.62
Sulfur	0.03	0.04	0.05	0.03	0.06	0.05	0.06	0.04
Ash	0.73	0.62	0.94	1.01	1.10	0.95	0.91	0.75
C - In (lb/hr)	9.94	7.46	7.72	10.87	17.56	10.48	14.25	10.65
C - Gas	7.01	5.56	6.26	9.09	11.01	8.42	10.24	9.00
C - Fines	1.77	1.63	1.03	1.66	2.45	2.33	1.25	1.46
C - Condensate	0.08	0.07	0.07	0.10	0.10	0.08	0.06	0.08
C - Recovery (%)	89.27	97.36	95.34	99.77	77.27	103.37	81.05	99.02
S - In (lb/hr)	0.06	0.05	0.05	0.06	0.10	0.06	0.06	0.06
S - Gas	0.02	0.01	0.04	0.01	0.03	0.02	0.04	0.02
S - Fines	0.01	0.02	0.01	0.02	0.02	0.02	0.02	0.02
S - Condensate	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
S - Bed	0.00	0.01	0.00	0.00	0.01	0.01	0.00	0.00
S - Recovery (%)	49.33	77.58	110.70	54.59	54.58	80.91	100.26	57.06

TABLE A-1 (Cont.)

UNADJUSTED MATERIAL BALANCES FOR WYODAK PARAMETRIC TESTS

Run No.	2	4	6	12	14	2R	10R	12R
Coal Bed Material	Wyodak Limestone	Wyodak Limestone	Wyodak Limestone	Wyodak Limestone	Wyodak Limestone	Wyodak Limestone	Wyodak Limestone	Wyodak Limestone
AvgFrbrdP (psia)	21.83	19.08	22.70	26.22	25.70	22.46	29.21	25.73
Avg Bed T (C)	751.06	695.96	801.70	743.02	698.59	745.98	806.36	749.95
O ₂ :Stm Ratio	0.19	0.10	0.13	0.14	0.22	0.16	0.25	0.17
Stm:C Ratio	2.43	3.32	3.17	2.27	1.14	2.23	1.16	2.33
O ₂ :C Ratio	0.45	0.32	0.42	0.32	0.24	0.35	0.30	0.40
Prod Gas (mol%)								
H ₂	46.76	46.88	44.60	45.54	44.94	45.93	44.98	44.23
CO	10.79	7.13	10.55	10.78	11.28	11.47	17.92	12.72
CO ₂	38.38	42.04	40.94	40.06	39.00	38.31	33.84	39.21
CH ₄	2.85	2.69	2.70	2.73	3.75	3.07	2.40	3.00
C ₂ H ₄	0.78	0.57	0.67	0.61	0.37	0.89	0.61	0.62
C ₂ H ₆	0.02	0.02	0.01	0.18	0.15	0.20	0.17	0.17
C ₃ H ₆	0.39	0.63	0.39	0.01	0.46	0.08	0.00	0.01
C ₃ H ₈	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00
C ₄ H ₈	0.00	0.00	0.00	0.03	0.00	0.00	0.00	0.00
C ₄ H ₁₀	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
H ₂ S	0.05	0.05	0.15	0.03	0.06	0.05	0.08	0.04
Prod Gas (scfh)	383.11	303.11	330.47	491.40	583.93	455.87	549.66	476.42
H ₂ (scfh)	179.14	142.10	147.39	223.80	262.43	209.38	247.26	210.73
H ₂ (scfh)/ maf Coal (lb/hr)	12.79	13.40	13.71	14.59	10.60	14.17	12.49	14.04
CO (scfh)/ maf Coal (lb/hr)	2.95	2.04	3.24	3.45	2.66	3.54	4.98	4.04
CO ₂ (scfh)/ maf Coal (lb/hr)	10.50	12.01	12.58	12.83	9.20	11.82	9.40	12.45
H ₂ out (lb)/ H in (lb) (%)	18.31	15.12	15.91	22.00	25.05	21.60	28.63	20.77
Norm C>Gas Conv	79.05	76.57	85.06	83.83	81.17	77.73	88.62	85.37
H ₂ O - In (lb/hr)	42.72	42.10	41.44	44.07	41.33	41.92	33.89	44.07
H ₂ O - Out	39.76	39.18	39.03	37.08	33.06	36.08	25.35	38.40
H ₂ O - Conv (%)	6.94	6.94	5.81	15.86	20.01	13.93	25.20	12.87

TABLE A-2

UNADJUSTED MATERIAL BALANCES FOR MARTIN LAKE AND VELVA PARAMETRIC TESTS

Run No.	1	3	5	7	9	11	13	15
Coal	Martin Lake	Martin Lake	Martin Lake	Martin Lake	Velva	Velva	Velva	Velva
Bed Material	Limestone	Limestone	Limestone	Limestone	Limestone	Limestone	Limestone	Limestone
AvgFrbrdP (psia)	21.81	25.03	21.73	30.89	21.66	27.18	26.44	22.48
Avg Bed T (C)	800.80	699.22	752.31	740.90	750.21	802.03	744.25	698.43
O ₂ :Stm Ratio	0.18	0.14	0.13	0.27	0.11	0.19	0.27	0.14
Stm:C Ratio	2.17	2.14	3.35	1.11	3.74	2.36	1.21	2.33
O ₂ :C Ratio	0.38	0.31	0.43	0.30	0.43	0.44	0.32	0.32
In (lb/hr)								
Coal	24.72	25.59	17.40	41.98	16.22	24.16	40.18	24.44
Steam	34.90	36.12	37.35	30.36	35.19	34.91	30.10	37.08
Oxygen	10.90	9.15	8.55	14.48	7.19	11.60	14.25	9.15
Nitrogen	7.04	5.70	4.33	5.33	5.08	4.59	4.81	5.35
Out (lb/hr)								
Fines Acc	2.39	3.28	2.29	9.05	2.18	2.50	4.75	4.10
Cond Acc	37.89	38.41	38.79	33.48	37.25	37.41	37.96	40.97
Prod Gas	29.90	26.78	20.51	43.52	19.66	26.64	41.69	26.65
Nitrogen	7.04	5.70	4.33	5.33	5.08	4.59	4.81	5.35
Mass Closure (%)	99.55	96.87	97.45	99.16	100.79	94.54	99.85	101.38
In (lb/hr)								
Carbon	10.70	11.25	7.43	18.16	6.28	9.85	16.59	10.60
Hydrogen	5.53	5.73	5.35	6.16	5.03	5.50	6.09	5.82
Oxygen	52.01	51.54	49.02	58.54	46.17	53.78	59.22	52.63
Sulfur	0.17	0.18	0.13	0.28	0.03	0.04	0.08	0.06
Ash	1.88	1.97	1.25	3.34	1.00	1.36	2.32	1.40
Out (lb/hr)								
Carbon	10.49	10.00	7.32	18.81	6.88	9.12	15.69	10.57
Hydrogen	5.67	5.65	5.33	5.92	5.05	5.29	6.09	5.83
Oxygen	52.68	51.60	47.80	57.78	46.24	50.94	60.93	53.92
Sulfur	0.09	0.09	0.06	0.23	0.02	0.03	0.05	0.04
Ash	1.06	1.00	0.96	3.05	0.80	1.05	1.45	1.21
C - In (lb/hr)	10.70	11.25	7.43	18.16	6.28	9.85	16.59	10.60
C - Gas	9.26	7.95	6.19	13.62	5.71	7.86	12.73	7.83
C - Fines	1.13	1.96	1.05	5.05	1.10	1.17	2.85	2.64
C - Condensate	0.10	0.09	0.08	0.13	0.06	0.09	0.11	0.09
C - Recovery (%)	98.02	88.92	98.47	103.54	109.56	92.65	94.59	99.71
S - In (lb/hr)	0.17	0.18	0.13	0.28	0.03	0.04	0.08	0.06
S - Gas	0.05	0.06	0.02	0.10	0.01	0.02	0.03	0.01
S - Fines	0.03	0.01	0.02	0.07	0.01	0.01	0.02	0.02
S - Condensate	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
S - Bed	0.01	0.02	0.02	0.05	0.00	0.00	0.00	0.01
S - Recovery (%)	54.13	51.48	48.05	82.71	71.27	79.15	58.87	68.10

TABLE A-2 (Cont.)

UNADJUSTED MATERIAL BALANCES FOR MARTIN LAKE AND VELVA PARAMETRIC TESTS

Run No.	1	3	5	7	9	11	13	15
Coal Bed Material	Martin Lake Limestone	Martin Lake Limestone	Martin Lake Limestone	Martin Lake Limestone	Velva Limestone	Velva Limestone	Velva Limestone	Velva Limestone
AvgFrbrdP (psia)	21.81	25.03	21.73	30.89	21.66	27.18	26.44	22.48
Avg Bed T (C)	800.80	699.22	752.31	740.90	750.21	802.03	744.25	698.43
O ₂ :Stm Ratio	0.18	0.14	0.13	0.27	0.11	0.19	0.27	0.14
Stm:C Ratio	2.17	2.14	3.35	1.11	3.74	2.36	1.21	2.33
O ₂ :C Ratio	0.38	0.31	0.43	0.30	0.43	0.44	0.32	0.32
Prod Gas (mol%)								
H ₂	44.75	46.35	46.06	43.89	45.91	43.65	43.22	45.69
CO	13.30	7.02	9.55	14.08	8.23	12.11	14.69	9.00
CO ₂	37.34	41.76	40.18	36.94	42.88	41.63	38.82	42.08
CH ₄	3.19	3.52	2.70	3.61	2.27	2.17	2.47	2.44
C ₂ H ₄	0.91	0.54	0.95	0.78	0.51	0.34	0.45	0.30
C ₂ H ₆	0.01	0.26	0.02	0.03	0.01	0.05	0.01	0.08
C ₃ H ₆	0.38	0.30	0.48	0.51	0.15	0.00	0.31	0.37
C ₃ H ₈	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00
C ₄ H ₈	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C ₄ H ₁₀	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
H ₂ S	0.11	0.16	0.07	0.17	0.04	0.05	0.04	0.03
Prod Gas (scfh)	487.67	431.48	331.74	705.43	311.41	414.96	658.82	423.16
H ₂ (scfh)	218.26	200.01	152.80	309.58	142.98	181.14	284.71	193.35
H ₂ (scfh)/ maf Coal (lb/hr)	14.52	12.73	14.65	12.08	15.73	12.71	12.01	13.24
CO (scfh)/ maf Coal (lb/hr)	4.32	1.93	3.04	3.88	2.82	3.53	4.08	2.61
CO ₂ (scfh)/ maf Coal (lb/hr)	12.12	11.47	12.78	10.17	14.69	12.12	10.79	12.19
H ₂ out (lb)/ H in (lb) (%)	21.97	19.44	15.91	27.99	15.85	18.35	26.04	18.50
Norm C>Gas Conv	88.28	79.46	84.55	72.42	83.04	86.19	81.14	74.14
H ₂ O - In (lb/hr)	42.72	44.03	43.08	43.38	41.32	43.46	44.25	45.51
H ₂ O - Out	37.64	38.28	38.66	33.21	37.16	37.27	37.74	40.82
H ₂ O - Conv (%)	11.87	13.06	10.26	23.44	10.07	14.23	14.72	10.32

APPENDIX B

ADJUSTED MATERIAL BALANCES FOR CPU LIMESTONE TEST MATRIX

B.1 Material Balances

Material balances for hydrogen production runs are based on information collected while the product gas stream is diverted to the gas quench system. The coal feed rate is initially set by calibration of the coal feed system. Due to inconsistencies in feeding, the observed coal feed rate is determined by measuring the difference in weight of the coal hopper over the period that coal is fed. The sulfur in the bed material is assumed to accumulate linearly during the time that coal is fed to the reactor.

Standard temperature and pressure are, in this case, 0°C and 14.7 psi. The average bed temperature at point 3 is the temperature of the bed approximately 1.5 feet above the distributor plate. The average bed temperature for points 3 through 6 is the averaged temperatures at 1.5, 2, 2.5, and 3 feet above the distributor plate. The oxygen:steam, steam:carbon, and oxygen:carbon ratios are on a molar basis.

The normalized conversion of carbon to gas is the percentage of carbon observed to exit the reactor in a gaseous form. Nitrogen indicated as being fed to and exiting from the reactor is determined by the analysis of the product gas. It is introduced as purge gas. Only that nitrogen contained in the structure of the coal seems to undergo chemical reaction in this environment.

Adjustments to the material balances are made on the bases of elemental and mass closures. First, the carbon in is adjusted to equal the carbon out, typically by adjusting the coal feed rate. The coal feed rate is evidently inconsistent with time, which makes it relatively reasonable to adjust it to compensate for changes during the run period.

The mass closure is then usually balanced by adjusting the steam feed rate. The indicated steam feed rate is dependent on instrumentation which, although calibrated, tends to drift. Compensation for zero drift is made but is inadequate.

Whether steam or oxygen or another stream is adjusted is dependent on the elemental balance. However good mass and/or elemental balances may be prior to adjustment, an unreasonable final elemental balance, which is inconsistent with data for similar runs, indicates a run that should be repeated.

TABLE B-1

ADJUSTED MATERIAL BALANCES FOR WYODAK PARAMETRIC TESTS

Run No.	2	4	6	12	14	2R	10R	12R
Coal	Wyodak	Wyodak	Wyodak	Wyodak	Wyodak	Wyodak	Wyodak	Wyodak
Bed Material	Limestone	Limestone	Limestone	Limestone	Limestone	Limestone	Limestone	Limestone
AvgFrbrdP (psia)	21.83	19.08	22.70	26.22	25.70	22.46	29.21	25.73
Avg Bed T (C)	751.06	695.96	801.70	743.02	698.59	745.98	806.36	749.95
O ₂ :Stm Ratio	0.20	0.09	0.13	0.14	0.20	0.16	0.29	0.16
Stm:C Ratio	2.50	3.51	3.41	2.31	1.57	2.10	1.28	2.35
O ₂ :C Ratio	0.51	0.32	0.44	0.32	0.32	0.34	0.37	0.38
In (lb/hr)								
Coal	20.63	16.06	16.08	23.68	29.63	23.66	27.51	23.02
Steam	33.28	38.25	37.64	37.56	31.92	34.08	24.84	37.15
Oxygen	12.05	6.29	8.55	9.25	11.45	9.91	12.69	10.58
Nitrogen	4.26	4.26	5.44	5.12	5.46	4.62	5.37	3.75
Out (lb/hr)								
Fines Acc	2.85	2.59	2.30	2.80	3.67	3.75	2.57	2.52
Cond Acc	39.95	39.18	39.09	37.24	33.27	36.17	25.32	38.48
Prod Gas	23.16	18.83	20.89	30.46	36.06	27.73	37.15	29.75
Nitrogen	4.26	4.26	5.44	5.12	5.46	4.62	5.37	3.75
Mass Closure (%)	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
In (lb/hr)								
Carbon	8.87	7.27	7.36	10.85	13.57	10.84	12.90	10.54
Hydrogen	5.12	5.32	5.24	5.72	5.49	5.34	4.62	5.64
Oxygen	50.15	46.91	48.62	52.37	52.00	49.92	45.89	53.06
Sulfur	0.19	0.05	0.04	0.06	0.08	0.06	0.05	0.06
Ash	1.51	0.95	0.91	1.33	1.68	1.34	1.40	1.30
Out (lb/hr)								
Carbon	8.87	7.27	7.36	10.85	13.57	10.84	12.90	10.54
Hydrogen	5.64	5.32	5.32	5.61	5.51	5.45	4.62	5.67
Oxygen	50.55	47.25	48.48	52.87	52.57	50.24	46.46	53.62
Sulfur	0.03	0.04	0.05	0.03	0.06	0.05	0.06	0.04
Ash	0.73	0.62	0.94	1.01	1.10	0.95	0.91	0.75
C - In (lb/hr)	8.87	7.27	7.36	10.85	13.57	10.84	12.90	10.54
C - Gas	7.01	5.56	6.26	9.09	11.01	8.42	11.59	9.00
C - Fines	1.77	1.63	1.03	1.66	2.45	2.33	1.25	1.46
C - Condensate	0.08	0.07	0.07	0.10	0.10	0.08	0.06	0.08
C - Recovery (%)	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
S - In (lb/hr)	0.19	0.05	0.04	0.06	0.08	0.06	0.05	0.06
S - Gas	0.02	0.01	0.04	0.01	0.03	0.02	0.04	0.02
S - Fines	0.01	0.02	0.01	0.02	0.02	0.02	0.02	0.02
S - Condensate	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
S - Bed	0.00	0.01	0.00	0.00	0.01	0.01	0.00	0.00
S - Recovery (%)	15.57	79.68	125.19	54.72	70.63	78.27	120.34	57.63

TABLE B-1 (Cont.)

ADJUSTED MATERIAL BALANCES FOR WYODAK PARAMETRIC TESTS

Run No.	2	4	6	12	14	2R	10R	12R
Coal	Wyodak	Wyodak	Wyodak	Wyodak	Wyodak	Wyodak	Wyodak	Wyodak
Bed Material	Limestone	Limestone	Limestone	Limestone	Limestone	Limestone	Limestone	Limestone
AvgFrbrdP (psia)	21.83	19.08	22.70	26.22	25.70	22.46	29.21	25.73
Avg Bed T (C)	751.06	695.96	801.70	743.02	698.59	745.98	806.36	749.95
O ₂ :Stm Ratio	0.20	0.09	0.13	0.14	0.20	0.16	0.29	0.16
Stm:C Ratio	2.50	3.51	3.41	2.31	1.57	2.10	1.28	2.35
O ₂ :C Ratio	0.51	0.32	0.44	0.32	0.32	0.34	0.37	0.38
Prod Gas (mol%)								
H ₂	46.76	46.88	44.60	45.54	44.94	45.93	44.98	44.23
CO	10.79	7.13	10.55	10.78	11.28	11.47	17.92	12.72
CO ₂	38.38	42.04	40.94	40.06	39.00	38.31	33.84	39.21
CH ₄	2.85	2.69	2.70	2.73	3.75	3.07	2.40	3.00
C ₂ H ₄	0.78	0.57	0.67	0.61	0.37	0.89	0.61	0.62
C ₂ H ₆	0.02	0.02	0.01	0.18	0.15	0.20	0.17	0.17
C ₃ H ₆	0.39	0.63	0.39	0.01	0.46	0.08	0.00	0.01
C ₃ H ₈	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00
C ₄ H ₈	0.00	0.00	0.00	0.03	0.00	0.00	0.00	0.00
C ₄ H ₁₀	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
H ₂ S	0.05	0.05	0.15	0.03	0.06	0.05	0.08	0.04
Prod Gas (scfh)	383.11	303.11	330.47	491.40	583.93	455.87	622.15	476.42
H ₂ (scfh)	179.14	142.10	147.39	223.80	262.43	209.38	279.87	210.73
H ₂ (scfh)/ maf Coal (lb/hr)	14.59	13.76	14.20	14.62	13.72	13.71	15.62	14.18
CO (scfh)/ maf Coal (lb/hr)	3.37	2.09	3.36	3.46	3.44	3.42	6.22	4.08
CO ₂ (scfh)/ maf Coal (lb/hr)	11.98	12.34	13.03	12.86	11.91	11.43	11.75	12.57
H ₂ out (lb)/ H in (lb) (%)	19.49	14.87	15.68	21.77	26.64	21.86	33.77	20.83
Norm C>Gas Conv	79.05	76.57	85.06	83.83	81.17	77.73	89.81	85.37
H ₂ O - In (lb/hr)	40.13	43.03	42.43	44.62	40.74	41.12	33.04	44.01
H ₂ O - Out	39.76	39.10	39.03	37.08	33.06	36.08	25.35	38.40
H ₂ O - Conv (%)	0.92	9.14	8.02	16.90	18.86	12.27	23.26	12.74

TABLE B-2

ADJUSTED MATERIAL BALANCES FOR MARTIN LAKE AND VELVA PARAMETRIC TESTS

Run No.	1	3	5	7	9	11	13	15
Coal	Martin Lake	Martin Lake	Martin Lake	Martin Lake	Velva	Velva	Velva	Velva
Bed Material	Limestone	Limestone	Limestone	Limestone	Limestone	Limestone	Limestone	Limestone
AvgFrbrdP (psia)	21.81	25.03	21.73	30.89	21.66	27.18	26.44	22.48
Avg Bed T (C)	800.80	699.22	752.31	740.90	750.21	802.03	744.25	698.43
O ₂ :Stm Ratio	0.17	0.14	0.11	0.29	0.12	0.20	0.25	0.16
Stm:C Ratio	2.23	2.44	3.40	1.04	3.31	2.38	1.37	2.34
O ₂ :C Ratio	0.39	0.34	0.36	0.30	0.39	0.48	0.34	0.36
In (lb/hr)								
Coal	24.23	22.75	17.14	41.98	17.77	22.38	38.00	24.37
Steam	35.04	36.56	37.35	28.44	34.14	32.57	32.15	37.08
Oxygen	10.90	9.15	7.09	14.48	7.19	11.60	14.25	10.27
Nitrogen	7.04	5.70	4.33	5.33	5.08	4.59	4.81	5.35
Out (lb/hr)								
Fines Acc	2.39	3.28	2.29	7.90	2.18	2.50	4.75	4.10
Cond Acc	37.89	38.41	38.79	33.48	37.25	37.41	37.96	40.97
Prod Gas	29.90	26.78	20.51	43.52	19.66	26.64	41.69	26.65
Nitrogen	7.04	5.70	4.33	5.33	5.08	4.59	4.81	5.35
Mass Closure (%)	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
In (lb/hr)								
Carbon	10.49	10.00	7.32	18.16	6.88	9.12	15.69	10.57
Hydrogen	5.52	5.59	5.33	5.95	5.02	5.12	6.17	5.82
Oxygen	51.93	50.79	47.45	56.83	45.98	50.88	60.05	53.71
Sulfur	0.17	0.16	0.12	0.28	0.03	0.03	0.08	0.06
Ash	1.84	1.75	1.23	3.34	1.09	1.26	2.20	1.40
Out (lb/hr)								
Carbon	10.49	10.00	7.32	18.16	6.88	9.12	15.69	10.57
Hydrogen	5.67	5.65	5.33	5.90	5.05	5.29	6.09	5.83
Oxygen	52.68	51.60	47.80	57.69	46.24	50.94	60.93	53.92
Sulfur	0.09	0.09	0.06	0.22	0.02	0.03	0.05	0.04
Ash	1.06	1.00	0.96	2.66	0.80	1.05	1.45	1.21
C - In (lb/hr)	10.49	10.00	7.32	18.16	6.88	9.12	15.69	10.57
C - Gas	9.26	7.95	6.19	13.62	5.71	7.86	12.73	7.83
C - Fines	1.13	1.96	1.05	4.41	1.10	1.17	2.85	2.64
C - Condensate	0.10	0.09	0.08	0.13	0.06	0.09	0.11	0.09
C - Recovery (%)	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
S - In (lb/hr)	0.17	0.16	0.12	0.28	0.03	0.03	0.08	0.06
S - Gas	0.05	0.06	0.02	0.10	0.01	0.02	0.03	0.01
S - Fines	0.03	0.01	0.02	0.06	0.01	0.01	0.02	0.02
S - Condensate	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
S - Bed	0.01	0.02	0.02	0.05	0.00	0.00	0.00	0.01
S - Recovery (%)	55.22	57.90	48.80	79.29	65.01	85.43	62.24	68.30

TABLE B-2 (Cont.)

ADJUSTED MATERIAL BALANCES FOR MARTIN LAKE AND VELVA PARAMETRIC TESTS

Run No.	1	3	5	7	9	11	13	15
Coal	Martin Lake	Martin Lake	Martin Lake	Martin Lake	Velva	Velva	Velva	Velva
Bed Material	Limestone	Limestone	Limestone	Limestone	Limestone	Limestone	Limestone	Limestone
AvgFrbrdP (psia)	21.81	25.03	21.73	30.89	21.66	27.18	26.44	22.48
Avg Bed T (C)	800.80	699.22	752.31	740.90	750.21	802.03	744.25	698.43
O ₂ :Stm Ratio	0.17	0.14	0.11	0.29	0.12	0.20	0.25	0.16
Stm:C Ratio	2.23	2.44	3.40	1.04	3.31	2.38	1.37	2.34
O ₂ :C Ratio	0.39	0.34	0.36	0.30	0.39	0.48	0.34	0.36
Prod Gas (mol%)								
H ₂	44.75	46.35	46.06	43.89	45.91	43.65	43.22	45.69
CO	13.30	7.02	9.55	14.08	8.23	12.11	14.69	9.00
CO ₂	37.34	41.76	40.18	36.94	42.88	41.63	38.82	42.08
CH ₄	3.19	3.52	2.70	3.61	2.27	2.17	2.47	2.44
C ₂ H ₄	0.91	0.54	0.95	0.78	0.51	0.34	0.45	0.30
C ₂ H ₆	0.01	0.26	0.02	0.03	0.01	0.05	0.01	0.08
C ₃ H ₆	0.38	0.30	0.48	0.51	0.15	0.00	0.31	0.37
C ₃ H ₈	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00
C ₄ H ₈	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C ₄ H ₁₀	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
H ₂ S	0.11	0.16	0.07	0.17	0.04	0.05	0.04	0.03
Prod Gas (scfh)	487.68	431.48	331.74	705.43	311.41	414.96	658.82	423.16
H ₂ (scfh)	218.26	200.01	152.80	309.58	142.98	181.14	284.71	193.35
H ₂ (scfh)/ maf Coal (lb/hr)	14.82	14.32	14.88	12.08	14.36	13.72	12.70	13.27
CO (scfh)/ maf Coal (lb/hr)	4.40	2.17	3.09	3.88	2.57	3.81	4.32	2.61
CO ₂ (scfh)/ maf Coal (lb/hr)	12.36	12.90	12.98	10.17	13.41	13.09	11.40	12.22
H ₂ out (lb)/ H in (lb) (%)	22.04	19.93	15.96	29.00	15.88	19.71	25.71	18.52
Norm C>Gas Conv	88.28	79.46	84.55	74.99	83.04	86.19	81.14	74.14
H ₂ O - In (lb/hr)	42.70	43.59	42.99	41.45	40.86	40.49	45.53	45.49
H ₂ O - Out	37.64	38.28	38.66	33.20	37.16	37.27	37.74	40.82
H ₂ O - Conv (%)	11.84	12.18	10.08	19.90	9.05	7.95	17.11	10.27

APPENDIX C

DEFINITION OF TERMS USED IN REGRESSION SUMMARY TABLES

C.1 REGRESSION SUMMARY TABLES

The regression summary tables contain not only the best equations to describe the data, but also information on each response so that the reliability of the conclusions can be assessed.

- a. Equation -- The best regression equation that describes the data is given in this column. It is a "pruned" equation, in that a full quadratic equation for three factors was fit to the data, and then any terms which were not significant were dropped. The only exception was that if a second order term (i.e., a squared term or a cross-product term) was found to be significant for any factor, then the linear term for that factor was automatically included in the model whether it was significant or not. The degree of confidence for each term in the equation is also indicated by the typeface used for the coefficient. For example, if a coefficient is bold (not underlined) it implies that the term is significant at the 1-5% level. This means that the chances of the measured coefficient for that term being as big as it is (or bigger) are only between 1% and 5% if the actual coefficient for the term is zero. (The chance of that happening is usually given the symbol, α , in statistics literature.)
- b. Confidence (conf.) -- This column indicates our confidence that something is going on at all. In other words, it indicates how confident we are that at least one of the terms in the equation (other than the constant term) is not zero. The closer the confidence level is to 100% the better.
- c. R^2 -- The multiple correlation coefficient, R^2 , indicates how much of the variability in the data is explained by the equation (expressed as a fraction). Therefore, if R^2 were 1.00, the equation would be a perfect fit to the data. If R^2 is small, there is a large amount of scatter of the data around the equation.
- d. Standard Deviation (s) -- The amount of inherent variability in the data is usually characterized by the standard deviation, s. It is calculated as the square root of the average squared difference between the data, y_i , and the predicted (equation) value, f_i .

$$s = \sqrt{\sum (y_i - f_i)^2 / (n - p)}$$

where: n = the number of data points
 p = the number of terms in the equation
(including the intercept)

- e. Coefficient of Variation (C.V.) -- The inherent variability in the data is often expressed as a percentage of the mean value. This is called the coefficient of variation.

$$C.V. = (s/\bar{y}) \times 100\%$$

U.S. DEPARTMENT OF ENERGY
FEDERAL ASSISTANCE MANAGEMENT SUMMARY REPORT

Page ____ of ____

1. Program/Project Identification No.		2. Program/Project Title Hydrogen Production of Low-Rank Coals		3. Reporting Period 4/1/88 through 5/30/89	
4. Name and Address University of North Dakota Energy and Mineral Research Center Box 8213, University Station Grand Forks, North Dakota 58202				5. Program/Project Start Date 4/1/86	
				6. Completion Date 3/31/92	
Milestone ID. No.	Description	Planned Completion Date	Actual Completion Date	Comments	
a.1	Complete design and construction of CPU	02/01/87	03/01/87		
a.2	Shakedown testing	05/01/87	06/01/87		
b.1	CPU test plan preparation	04/30/87	05/15/87		
b.2	CPU performance evaluation	01/01/89	03/30/89		
b.3	Bed material testing	09/01/88	05/01/89	Change to 05/01/89	
b.4	Technical report	03/01/89		06/01/89	
b.5	Wastewater Treatment	05/01/89	05/15/89		
c.1	Properties and reactivity test plan preparation	06/01/86	05/15/86		
c.2	Property and reactivity testing	07/01/88	09/15/88		
c.3	Technical report	10/01/88	05/31/89		
d.1	Selection of subcontractor for economic feasibility study	07/01/88	08/15/88		
d.2	Economic feasibility study	01/01/89	05/15/89	05/01/89	
e.1	Gas and water treatment assessment	09/01/88	01/01/89		
e.2	Identification of end-use applications	11/01/89	09/01/88		
e.3	Systems approach paper	03/31/89		06/30/89	

6.2 Advanced Wastewater Treatment

ADVANCED WASTEWATER TREATMENT

Final Technical Report for the Period
April 1, 1988 - June 30, 1989
including the Quarterly Technical Progress Report
for the Period April through June, 1989

By

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and
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July 1989

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TABLE OF CONTENTS

	<u>Page</u>
LIST OF FIGURES.....	ii
LIST OF TABLES.....	vi
NOMENCLATURE.....	viii
1.0 GOALS AND OBJECTIVES.....	1
1.1 Objectives.....	1
1.2 Background.....	1
2.0 DEEP COLUMN REACTOR.....	2
2.1 Background.....	2
2.2 Literature Review.....	3
2.3 Design Considerations.....	5
2.3.1 Hydrostatic Pressure.....	5
2.3.2 Oxygen Content.....	6
2.3.3 Temperature.....	7
2.4 Wastewater Composition.....	7
2.5 Deep Column Reactor Process.....	9
2.5.1 Design Considerations.....	9
2.5.2 Process Configuration.....	14
2.5.3 Flow Analysis.....	14
2.5.4 Aeration Testing.....	23
2.6 Data Acquisition.....	24
2.7 Process Performance.....	26
2.7.1 Operation.....	26
2.7.2 Performance.....	28
2.8 Kinetics.....	40
2.8.1 Continuous Kinetics.....	40
2.8.2 Batch Kinetics.....	43
2.8.2.1 Batch Test with Nitrification.....	43
2.8.2.2 Batch Test without Nitrification.....	51
2.9 Microbial Ecology.....	62
2.9.1 Allozymes.....	64
2.9.1.1 Introduction.....	64
2.9.1.2 Materials and Methods.....	65
2.9.1.3 Results.....	66
2.9.1.4 Discussion.....	67
2.9.2 Growth Rate Comparisons.....	67
2.9.2.1 Introduction.....	67
2.9.2.2 Materials and Methods.....	70
2.9.2.3 Results and Discussion.....	70
2.9.3 Summary.....	74
2.10 Conclusions.....	75
3.0 ACKNOWLEDGEMENTS.....	75
4.0 REFERENCES.....	75
APPENDIX A - COMPUTER PROGRAMS FOR KINETIC ANALYSIS.....	A-1

LIST OF FIGURES

<u>Figure</u>	<u>Page</u>
1 Dissolved oxygen concentration of 20°C water at saturation with air or 100% oxygen as a function of pressure.....	8
2 Hydraulic retention time (HRT) versus biomass concentrations for a range of influent BOD (S_0) based on the design equation for a complete mix stirred tank reactor (CSTR).....	12
3 Hydraulic retention time (HRT) versus biomass concentrations for plug flow kinetics at an influent BOD of 1000 mg/l, and effluent BOD of 25 mg/l and a K of 0.021 l/mg-day.....	13
4 Process flow schematic of the pilot scale Deep Column reactor.....	15
5 Plot of time versus absorbance at 610 nm for the dye injected into the Deep Column reactor during the first tracer study.....	18
6 Plot of time versus absorbance at 610 nm for the dye injected into the Deep Column reactor during the second tracer study.....	18
7 Plot of the $F(t)$ function versus time for the second Deep Column reactor dye tracer study.....	19
8 Plot of the $E(t)$ (point distribution) function versus time for the second Deep Column dye tracer study.....	20
9 Plot of the $F(t)$ function versus dimensionless time for a variety of dispersion numbers (after Grady and Lim, 1980).....	22
10 Plot of the $F(t)$ function versus dimensionless time for the Deep Column reactor.....	22
11 Results of the aeration test in the Deep Column reactor.....	24
12 Variation in mixed liquor temperature during the pilot-scale Deep Column reactor operations.....	29
13 Variation in mixed liquor pH during the pilot-scale Deep Column reactor operations.....	29
14 Buffer usage, as a solution of sodium bicarbonate (160 g/l) during the period of operation.....	30
15 Variation in dissolved oxygen concentration at the top of the pilot scale Deep Column reactor.....	31
16 Variation in the feed rate to the pilot-scale Deep Column reactor during the period of operation.....	31

LIST OF FIGURES (continued)

<u>Figure</u>	<u>Page</u>
17 Variation in the hydraulic retention time (HRT) for the pilot-scale Deep Column reactor during the period of operations.....	32
18 Variation in the fluid velocity through the reactor column of the pilot-scale Deep Column reactor during the period of operations....	33
19 Variation in the recycle ratio of the pilot-scale Deep Column reactor during the period of operations.....	33
20 Variation in the oxygen uptake rate of the mixed liquor in the pilot-scale Deep Column reactor during the period of operations....	35
21 Variation in the mixed liquor settleable solids concentration in the pilot-scale Deep Column reactor during the period of operations.....	35
22 Variation in the sludge volume index (SVI) of the mixed liquor in the pilot-scale Deep Column reactor during the period of operations.....	36
23 Variation in the mixed liquor volatile suspended solids (MLVSS) concentrations in the pilot-scale Deep Column reactor during the period of operations.....	36
24 Variation in the effluent or clarified volatile suspended solids concentrations (CVSS) in the pilot-scale Deep Column reactor during the period of operations.....	37
25 Variation in the effluent settleable solids concentrations in the pilot-scale Deep Column reactor during the period of operations....	38
26 Variation in the solids retention time (SRT) in the pilot-scale Deep Column reactor during the period of operations.....	39
27 Variation in the chemical oxygen demand (COD) concentrations in the influent and effluent of the pilot-scale Deep Column reactor during the period of operations.....	39
28 Variation in removal of chemical oxygen demand (COD) in the pilot-scale Deep Column reactor during the period of operations.....	41
29 Sludge settling curve for the pilot-scale Deep Column reactor.....	41
30 Change in COD concentration with reactor height at the 2.2-h HRT in the Deep Column reactor.....	42
31 Plot of the oxygen uptake rate through the 24-h reaction period for the batch kinetic reactor operated at an F/M of 0.32.....	45

LIST OF FIGURES (continued)

<u>Figure</u>		<u>Page</u>
32	Plot of the oxygen uptake rate through the 24-h reaction period for the batch kinetic reactor operated at an F/M of 0.37.....	45
33	Plot of the oxygen uptake rate through the 24-h reaction period for the batch kinetic reactor operated at an F/M of 0.56.....	46
34	Plot of the oxygen uptake rate through the 24-h reaction period for the batch kinetic reactor operated at an F/M of 1.11.....	46
35	Maintenance plot for the determination of Y_g , the biomass yield coefficient, and K_d , the endogenous decay coefficient, based on COD.....	48
36	Maintenance plot for the determination of Y_g , the biomass yield coefficient, and K_d , the endogenous decay coefficient, based on TOC.....	48
37	Maintenance plot for the determination of Y_g , the biomass yield coefficient, and K_d , the endogenous decay coefficient, based on NH_3	49
38	Oxygen plot for the determination of Y' , the oxygen coefficient, and K_e' , the endogenous oxygen coefficient, based on COD.....	49
39	Oxygen plot for the determination of Y' , the oxygen coefficient, and K_e' , the endogenous oxygen coefficient, based on TOC.....	50
40	Oxygen plot for the determination of Y' , the oxygen coefficient, and K_e' , the endogenous oxygen coefficient, based on NH_3	50
41	Plot of the oxygen uptake rate through the 24-h reaction period for the batch kinetic reactor operated at an F/M of 0.336.....	53
42	Plot of the oxygen uptake rate through the 24-h reaction period for the batch kinetic reactor operated at an F/M of 0.460.....	53
43	Plot of the oxygen uptake rate through the 24-h reaction period for the batch kinetic reactor operated at an F/M of 0.672.....	54
44	Plot of the oxygen uptake rate through the 24-h reaction period for the batch kinetic reactor operated at an F/M of 0.863.....	54
45	Plot of the oxygen uptake rate through the 24-h reaction period for the batch kinetic reactor operated at an F/M of 0.986.....	55
46	Plot of the oxygen uptake rate through the 24-h reaction period for the batch kinetic reactor operated at an F/M of 1.240.....	55

LIST OF FIGURES (continued)

<u>Figure</u>	<u>Page</u>
47 Maintenance plot for the determination of Y_g , the biomass yield coefficient, and K_d , the endogenous decay coefficient, based on COD.....	57
48 Maintenance plot for the determination of Y_g , the biomass yield coefficient, and k_d , the endogenous decay coefficient, based on TOC.....	57
49 Oxygen plot for the determination of Y' , the oxygen coefficient, and K_e' , the endogenous oxygen coefficient, based on COD.....	58
50 Oxygen plot for the determination of Y' , the oxygen coefficient, and K_e' , the endogenous oxygen coefficient, based on TOC.....	58
51 Decrease in COD concentrations with incubation time for the batch reactor operating at an F/M of 0.67 per day.....	59
52 Increase in biomass concentrations, as MLVSS, with incubation time for the batch reactor operating at an F/M of 0.67 per day.....	59
53 Plot used for determination of K , the reaction rate constant, for the batch reactor operated at an F/M of 0.67 per day.....	61
54 Eckenfelder-type plot for determination of the reaction rate constant for the batch reactor operating at an F/M of 0.67 per day.....	61
55 Plot of the specific growth rate against the COD concentration for the batch kinetic test with an F/M of 0.67 per day.....	63
56 Plot for the determination of the maximum specific substrate utilization rate, U_{max} , and the Michaelis-Menten half-saturation constant, K_m	63
57 Batch growth curve for Isolate 1 from the Deep Column reactor.....	71
58 Batch growth curve for Isolate 2 from the Deep Column reactor.....	72
59 Batch growth curve for Isolate 3 from the Deep Column reactor.....	72
60 Batch growth curve for Isolate 4 from the Deep Column reactor.....	73
61 Batch growth curve for Isolate 5 from the Deep Column reactor.....	73
62 Batch growth curve for Isolate 7 from the Deep Column reactor.....	74

LIST OF TABLES

<u>Table</u>	<u>Page</u>
1 Saturation of oxygen in water as a function of temperature using air (20.9% O ₂ , at sea level).....	8
2 Composition of Gasification Wastewaters.....	10
3 Composition of the Synthetic Wastewater.....	10
4 Design Characteristics of the Pilot-Scale Deep Column Reactor.....	16
5 System Parameters During the First Deep Column Reactor Tracer Study.....	17
6 Maintenance Schedule for the Deep Column Reactor.....	25
7 Deep Column Reactor Daily Data Collection.....	25
8 Analytical Methods Used for these Investigations.....	27
9 COD and Biomass Changes with Respect to Length in the Deep Column Reactor.....	42
10 Batch Reactor Test 1 Start-Up Composition.....	44
11 Batch Reactor Test 1 Biomass and Substrate Concentrations.....	44
12 Reduced Data from Batch Kinetic Test 1.....	47
13 Kinetic Coefficients from Batch Test 1 Using a Nitrifying Sludge...	51
14 Operating History of the Biomass Used for Non-Nitrifying Batch Kinetic Tests.....	52
15 Biomass and Substrate Concentrations from the Non-Nitrifying Batch Kinetic Tests.....	52
16 Reduced Data from the Batch Kinetic Tests with a Non-Nitrifying Sludge.....	56
17 Kinetic Coefficients from Batch Testing Using a Non-Nitrifying Sludge.....	64
18 Buffer Systems for Electrophoresis of Bacterial Enzymes.....	66
19 Buffer Systems and Enzyme Stains Used.....	67
20 Microbiological Characters of the Isolates.....	68

LIST OF TABLES (continued)

<u>Table</u>		<u>Page</u>
21	Allozyme Profiles for the Bacterial Isolates Using Buffer System A.....	68
22	Allozyme Profiles for the Bacterial Isolates Using Buffer Systems B and C.....	69
23	Relative Lag Periods and Growth Rates for Isolates from the Deep Column Reactor under Batch Conditions.....	71

NOMENCLATURE

A	gas constant
atm	atmosphere
B	Bunsen gas coefficient
BOD ₅	biochemical oxygen demand, five-day
C	concentration
C ₀	initial concentration
CFU	colony forming units
COD	chemical oxygen demand
CSTR	completely-mixed stirred tank reactor
C(t)	concentration as a function of time
d	day
D _l	axial dispersion coefficient
DO	dissolved oxygen
DOE	U.S. Department of Energy
EMRC	Energy and Mineral Research Center
E(t)	fraction of elements with retention times between t and t + dt
F/M	food-to-microorganism ratio
F(t)	fraction of elements with retention times less than time t
gpd	gallons per day
G	gravitational acceleration constant
GPGP	Great Plains Gasification Plant
h	height of water column
HRT	hydraulic retention time
K	reaction rate coefficient
K ₁	Eckenfelder reaction rate constant
K _d	endogenous decay coefficient
K _{e'}	oxygen decay coefficient
K _m	Michaelis-Menten half-saturation constant
kPa	kilopascals
l/d	liters per day
L	length of reactor
mgd	million gallons per day
MLSS	mixed liquor suspended solids
MLVSS	mixed liquor volatile suspended solids
mA	milliamperes
mm	millimeters
nm	nanometers
p	hydrostatic pressure
PDU	process development unit
PFR	plug flow reactor
POAS	pure oxygen activated sludge
PO ₂	partial pressure of oxygen
POTW	publicly-owned treatment works
Ps	standard pressure
psig	pounds per square inch gauge
P _T	total pressure
Q	flow rate

NOMENCLATURE (continued)

R^2	correlation coefficient
ρ	fluid density
S	substrate
S_e	effluent substrate concentration
SGL	stripped gas liquor
SNG	synthetic natural gas
S_0	initial substrate concentration
SRT	solids retention time
SVI	sludge volume index
θ	hydraulic retention time
t	time
T	mean residence time
TOC	total organic carbon
TVSS	total volatile suspended solids
U	specific substrate utilization rate
U_{max}	maximum specific substrate utilization rate
UND	University of North Dakota
V	volume
v	velocity through reactor
W	water vapor pressure
X	mean mixed liquor volatile suspended solids concentration
X_{O_2}	fraction of oxygen in gas phase
Y'	oxygen utilization coefficient
Y_g	biomass yield coefficient

ADVANCED WASTEWATER TREATMENT

Final Technical Report for the Period
April 1, 1988 - June 30, 1989
including the Quarterly Technical Progress Report
for the Period April through June, 1988

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1.0 GOALS AND OBJECTIVES

1.1 Objectives

The overall goal of this research project is to expand the scientific and engineering data base with respect to wastewater treatment for synthetic fuels plants. Specific goals were to: 1) develop a novel method for combined carbon oxidation and nitrogen removal, 2) develop a high-rate biological oxidation reactor, and 3) define potential pretreatment requirements for discharge of synthetic fuels wastewaters to publicly-owned treatment works (POTWs). Goal 1 was accomplished through the use of a pilot-scale research unit--a downflow-coupled fluidized-bed system, which combines the removal of carbonaceous compounds and nitrogen from wastewater from the Great Plains Gasification Plant. Pretreatment requirements for synfuel wastewaters were evaluated via literature search, evaluation of applicable statutes and a case study. Final reporting for these items is in Mayer et al., 1988. A pilot-scale deep column unit was used for the second project goal. This reactor makes use of pure oxygen, high transfer efficiencies and plug flow kinetics to perform as a high-rate biological reactor.

1.2 Background Statement

Synthetic fuels technologies all produce a wastewater that must be treated and/or reused. Some wastewater streams, particularly certain gasification condensates, are highly contaminated with organic and inorganic compounds. These contaminants include ammonia, thiocyanate, cyanide, phenolics, organic acids and numerous other compounds. Treatment scenarios for synfuel technologies with highly contaminated streams often utilize pretreatment by solvent extraction and steam stripping to reduce contents of phenolics, ammonia and acid gases. Following pretreatment, biological treatment is often the most economical option for further treatment of the wastewater.

Conventional biological treatment processes such as activated sludge, are susceptible to upsets in the presence of toxic compounds, and organic or hydraulic shock loads. In addition, the low biomass concentrations and resulting long hydraulic retention times for treatment in the activated sludge process may be economically prohibitive. Improved reactor configurations are needed that can attain high biomass concentrations and are resistant to toxics and other shocks. Fixed-film biological processes typically have much greater

stability to toxics and shocks, due to the immobilization of the biomass on support media. Immobilization of the biomass prevents loss (wash out) when growth is inhibited. Additionally, longer solids retention times (SRTs) can be obtained with fixed-film processes, as opposed to suspended growth processes (activated sludge). Long SRTs correspond to slow microbial growth rates. Thus, fixed-film reactors provide a better environment for the establishment of more stable populations, including nitrifiers.

Fixed-film reactors of several types have been used, including rotating biological contactors, packed bed columns and fluidized bed columns. A specially configured fluidized bed reactor has been tested at the Canadian Wastewater Technology Center (Nutt et al. 1982). This configuration, sometimes called the pre-denitrification process, uses two fluidized beds connected in series. One bed is aerated (oxic), while the other bed is not aerated (anoxic). This process combines, in a single coupled reactor, three conventionally separated operations--carbon oxidation, nitrification and denitrification. The result is reduced capital costs, reduced oxygen requirements, and reduced sludge production.

Limitations with respect to oxygen transfer and oxygen solubility prevent the maintenance of greater than about 3,000 mg/l of biomass in suspended growth biological systems. Pure oxygen activated sludge reactors have been used to obtain higher biomass concentrations. Activated sludge reactors are, however, often configured as complete mix systems, which operate at much less than the maximum substrate removal rate. Plug flow reactors have a gradient of substrate concentration through the reactor length, resulting in a mixture of substrate removal rates ranging from maximum to approximately the same as a complete mix system. The combination of a high dissolved oxygen system and plug flow design provides a significantly greater removal rate potential than traditional biological systems.

2.0 DEEP COLUMN REACTOR

2.1 Background

A plug flow reactor is designed to provide little or no longitudinal mixing between adjacent fluid elements. Each element or small parcel of fluid in a plug flow reactor is analogous to a completely mixed batch reactor moving along a time axis. Plug flow reactors have a number of distinct advantages over continuous complete mix reactors. The most important of these advantages are kinetic in nature. Grady and Lim (1980) state "...if the volumes of the reactors (plug flow and complete mix) are the same, and the effluent concentration is to be kept the same, the PFR (plug flow reactor) can process more fluid than the CSTR (completely mixed stirred tank reactor)." This kinetic advantage is attributed to the fact that the reaction rates are high in the inlet of the PFR and decrease through the reactor length, whereas in the CSTR the reaction rates are uniform. The CSTR reaction rates are slower since the reactor substrate concentration is equal to the effluent concentration. The kinetic advantages of a PFR over a CSTR are negligible under conditions of zero-order kinetics, but increase with increasing reaction order.

PFRs are thought to have fewer sludge settling problems during clarification than CSTRs by virtue of the change in substrate concentration observed in a PFR. At low substrate concentrations microbes with high surface-to-volume ratios, such as filamentous microbes, are favored. At high substrate concentrations, flocculent microbes, with better settling characteristics, are favored (Rensink 1974). Filamentous sludges do not settle as well as non-filamentous sludges.

A factor that limits improved operation in most biological reactors is limitation in the oxygen concentration attainable in the reaction liquid. Reactors designed for high dissolved oxygen concentrations, such as pure oxygen activated sludge (POAS) reactors generally have improved reaction rates. The improvements observed in POAS reactors are usually attributed to the increased concentrations of biomass attainable. While biomass concentrations in conventional air-activated sludge may be in the range of 1000 to 3000 mg/l (mixed liquor suspended solids, MLSS), POAS systems can attain an MLSS in the range of 4000 to 8000 mg/l at solids retention times of 3 to 15 days. POAS systems have not been widely used since they require: 1) a source of pure oxygen and 2) high energy inputs for mixing. Moreover, the POAS system generally involves considerable oxygen wastage and requires greater operator skill for efficient operations.

The Deep Column process takes advantage of plug flow conditions and high reactor dissolved oxygen content, resulting in a reactor that is expected to have considerably higher treatment efficiencies than a conventional activated sludge or similar biological treatment system. The reactor design, discussed in detail later, involves a tall column that takes advantage of increased hydrostatic pressure to maintain high dissolved oxygen concentrations. This type of reactor should be especially useful in the treatment of high-strength wastewaters. In addition, the use of a tall treatment system would be desirable under conditions of space limitations, such as those encountered in industry.

This type of biological treatment reactor is considered to be especially applicable to the synthetic fuels industry. For gasification condensate, where biological pretreatment is required for reuse or discharge, the capital costs of the Deep Column reactor should be lower than for conventional treatment systems. It is expected to be less expensive with regard to capital costs as a result of the improved kinetic rates. Moreover, many synfuels plants would have systems for the production of purified oxygen, thus the capital costs for this requirement are reduced as well.

2.2 Literature Review

The use of hydrostatic pressure for increasing the dissolved oxygen content in a biological treatment reactor was evaluated by Urza and Jackson in 1975. They conducted oxygen transfer tests in a narrow, 55-ft (16.76-m) tall column. Their results showed oxygen transfer efficiency increases of about 1% per foot for columns from 14 to 53 ft in height. Advantages pointed out were lower energy requirements, smaller land area needs, and simplified construction. A disadvantage noted was an increase in pumping costs. Design implications noted were reduced reactor volumes, reduction in process upsets, and a sludge mass that is more reactive and easily suspended.

Jackson, James and Leber (1975) conducted additional oxygen transfer testing using a 23-m (75-ft) column equipped with a diffuser. Oxygen transfer efficiencies were found to be 96% at the 8-m depth. Jackson, Chen and Plopper (1978) reported on the use of a deep tank reactor for treatment of wood pulp paper mill wastewater. The system used a deep tank reactor, 1.83 m (6 ft) in diameter with a 12.8-m (42-ft) liquid depth. Dissolved air flotation was used for solids separation. The reactor was operated on a 24-hour cyclical batch feed, aeration and solids separation schedule. BOD removals of better than 95% were observed.

Jackson (1981) reported additional details on the field test of a deep tank system for pulp mill wastewater treatment. The reactor was 36.6 m (120 ft) in diameter and 21.3 m (70 ft) in height. The flow rate was 29.46×10^7 liters/day (25) with an HRT of 10 hours. The solids retention time was 1.4 days with an MLSS of 1800 to 2000 mg/l. The influent BOD was 430 mg/l and the mean removal was 96 to 97%.

Jackson and Shen (1978) evaluated several variables involved in oxygen transfer in columns ranging in diameter from 76 mm to 7.6 m and in height from 4 to 21 m. Transfer equations were similar and valid over a wide range of variables, including geometry and depths to 21 m. They concluded that performance assessments in narrow-diameter columns could be scaled to larger operations with confidence.

Jackson (1985) evaluated tall tank reactors for thermophilic (40 to 60°C) biological treatment and discussed the operation of the deep tank aeration treatment system with pulping wastewater. The paper pulp mill plant mentioned previously (Jackson, James and Leber 1975), has doubled its capacity and the resulting increased load to the treatment system has produced a dissolved oxygen concentration in the reactor of near zero. In spite of the low dissolved oxygen concentrations, treatment efficiency and performance have not been adversely impacted.

Jackson (1986) evaluated oxygen transfer in a tall tank. Linear relationships were found among the transfer coefficient, holdup, and the superficial gas rise velocity. Equations are provided to scale up laboratory data.

Deep shaft technology was assessed by Gallo and Sandford (1980). This technology was developed by Imperial Chemical Industries of Great Britain (ICI). The deep shaft is a totally encased and grouted shaft 100 to 300 meters in depth, which is divided into downward and riser sections. Air is injected into the downward side and is entrained by the flow. Increasing hydrostatic pressure improves oxygen solubility as depth increases. Sludge is usually removed via dissolved air flotation since the increased pressure often results in the development of bubbles in the floc.

A number of deep shaft pilot plants have been tested, primarily using dairy and brewery wastes. These pilot studies have demonstrated both high removal rates (>95%), under conditions of variable loading, and good stability. Energy requirements were said to be exceptionally low due to the use of dissolved air flotation for solids removal and the decreased requirements for pumping.

2.3 Design Considerations

2.3.1 Hydrostatic Pressure

Oxygen is poorly soluble in water. Oxygen concentration at saturation with air at 25°C and 760 mm Hg is 8.25 mg/l. The oxygen requirement for complete biological oxidation of a quantity of wastewater having a BOD of 1000 mg/l is equal to 1000 mg O₂ plus endogenous oxygen requirements. Therefore, for complete oxidation of the 1000 mg/l BOD wastewater, it will have to be aerated to the equivalent of 121 times saturation. Increases in temperature result in a decrease in oxygen solubility, but increases in hydrostatic pressure result in increases in oxygen solubility.

Hydrostatic pressure can be estimated according to equation 1 (Weast 1974),

$$p = h\rho G \quad (1)$$

where p is the hydrostatic pressure in dynes/cm², h is the height of the water column in cm, ρ is the fluid density in g/cm³ and G is the gravitational acceleration, (equal to 980.621 cm/sec² at 45° latitude). The hydrostatic pressure at 10.333 m (33.9 ft) is calculated as follows:

$$(1033.3 \text{ cm})(1 \text{ g/cm}^3)(980.621 \text{ cm/sec}^2) = 1013276 \text{ g/cm-sec}^2$$

Since one dyne equals one g-cm/sec², the hydrostatic pressure is 1013276 dynes/cm². One atmosphere of pressure is equal to 1.01325 x 10⁶ dynes/cm². Therefore, 1013276 dynes/cm² is equal to 1.0000 atmospheres of hydrostatic pressure.

We can calculate the effect of hydrostatic pressure on oxygen solubility in the following manner (Pagenkopf 1978):

$$P_{O_2} = X_{O_2} \frac{(P_T - W)}{P_S} \quad (2)$$

$$[O_2] = \frac{B P_{O_2}}{A} \quad (3)$$

where P_{O_2} = partial pressure of oxygen, atm,
 X_{O_2} = fraction of oxygen in the gas phase,
 P_T = total pressure, mm Hg,
 W = water vapor pressure, mm Hg
 B = Bunsen gas adsorption coefficient, atm⁻¹
 A = gas constant, 22.414 liters/mole,
 P_S = standard pressure, (760 mm Hg).

At a temperature of 20°C, at sea level and using air, the saturation of oxygen in water is given as:

$$P_{O_2} = 0.209 \frac{(760 - 17.5)}{760} = 0.2042$$

$$[O_2] = \frac{(0.03102)(0.2042)}{22.414} (31998.8 \text{ mg } O_2/\text{mole}) = 9.04 \text{ mg/l.}$$

At a pressure of 1 atm air and a hydrostatic pressure of 1 atm, the dissolved oxygen concentration in water at saturation is:

$$P_{O_2} = 0.209 \frac{(1520 - 17.5)}{760} = 0.4132$$

$$[O_2] = \frac{(0.03102)(0.4132)}{22.414} (31998.8 \text{ mg } O_2/\text{mole}) = 18.3 \text{ mg/l}$$

2.3.2 Oxygen Content

The oxygen content of air is approximately 20.9%. If we increase the oxygen content to 70%, the saturation dissolved oxygen content of water at 20°C and 1 atm air is given by:

$$P_{O_2} = 0.7 \frac{(760 - 17.5)}{760} = 0.6839$$

$$[O_2] = \frac{(0.03102)(0.6839)}{22.414} (31998.8 \text{ mg } O_2/\text{mole}) = 30.3 \text{ mg/l.}$$

Using 70% oxygen at 1 atm air and 1 atm hydrostatic pressure, the dissolved oxygen content in water at saturation is:

$$P_{O_2} = 0.7 \frac{(1520 - 17.5)}{760} = 1.3839$$

$$[O_2] = \frac{(0.03102)(1.3839)}{22.414} (31998.8 \text{ mg } O_2/\text{mole}) = 61.3 \text{ mg/l.}$$

When 100% oxygen is used at 1 atm air, the dissolved oxygen content of water at saturation is:

$$P_{O_2} = 1.0 \frac{(760 - 17.5)}{760} = 0.977$$

$$[O_2] = \frac{(0.03102)(0.977)}{22.414} (31998.8 \text{ mg } O_2/\text{mole}) = 43.26 \text{ mg/l.}$$

Using pure oxygen, 1 atm air and 1 atm hydrostatic pressure, the dissolved oxygen content in water at saturation is:

$$P_{O_2} = 1.0 \frac{(1520 - 17.5)}{760} = 1.977$$

$$[O_2] = \frac{(0.03102)(1.977)}{22.414} (31998.8 \text{ mg } O_2/\text{mole}) = 87.55 \text{ mg/l.}$$

Figure 1 shows the dissolved oxygen content of water at saturation using air and 100% oxygen as a function of pressure. It can be seen that, using air, the maximum dissolved oxygen attainable with 2 atm hydrostatic pressure (3 atm total pressure) is 27.5 mg/l. The advantages of using 100% oxygen are apparent.

2.3.3 Temperature

The effect of temperature on an aerobic biological treatment process is two-fold. Increases in temperature, within a range for a microbial population, result in increases in treatment kinetics. However, increases in temperature also significantly decrease the solubility of oxygen in water.

Generally, an aerobic biological treatment operation is conducted in the mesophilic temperature range, from 20 to 45°C. Increases in temperature above summer ambient are generally not advantageous for wastewater treatment operations. Solubility of oxygen in water, however, is dramatically affected by temperature, as shown in Table 1.

The actual treatment unit temperature would be subject to upstream processing conditions, final treatment design configurations, and climatic conditions. The optimum temperature for pilot plant operations is best chosen as a compromise between the beneficial and detrimental effects of temperature. Normal room temperature, (22 to 24°C) falls within a reasonable range and was used for the pilot operations.

2.4 Wastewater Composition

The intended use of the Deep Column reactor is for the treatment of high-strength industrial wastewater, such as that derived from the production of substitute natural gas. Although the use of an actual gasification wastewater was desirable, the high variability of actual gasification wastewaters would add undesirable complications. Additionally, gasification wastewaters are often extremely difficult to analyze since they are often colored and contain interfering substances for many ion-selective electrode methods. Therefore, a synthetic wastewater was chosen for evaluation of the Deep Column process.

Raw condensates from high-BTU, high temperature processes such as are used at the Great Plains plant (Lurgi dry-ash gasifiers) will require pretreatment prior to biological treatment. Less severe processes result in wastewaters with reduced levels of contamination that would require reduced amounts of pretreatment or none, prior to biological treatment. Pretreatment of gasification wastewaters usually involves solvent extraction to reduce concentrations of phenolics, followed by steam stripping to reduce concentrations of ammonia and the acid gases, hydrogen sulfide and hydrogen cyanide.

Figure 1. Dissolved oxygen concentration of 20°C water at saturation with air or 100% oxygen as a function of pressure. Air pressure at sea level is 760 mm Hg.

TABLE 1

SATURATION OF OXYGEN IN WATER AS A FUNCTION OF TEMPERATURE
USING AIR (20.9% O₂, AT SEA LEVEL).

Temperature (°C)	Bunsen Coefficient (atm ⁻¹)	Dissolved Oxygen (mg/l)	
		Air	100% O ₂
15	0.03415	10.02	47.93
20	0.03102	9.04	43.26
25	0.02831	8.18	39.15
30	0.02608	7.46	35.67
35	0.02306	6.88	32.90

Table 2 shows a comparison of the composition of two pretreated gasification wastewaters, from the Great Plains Lurgi gasifiers and from the KILnGAS rotary kiln pilot gasifier.

The synthetic wastewater was designed to be representative of a pre-treated gasification wastewater. Thus, the primary organic component was phenol. Secondary organic components were cresol, and the fatty acids acetate and formate. Thiocyanate was also added since this component is often formed from cyanide and sulfide after quenching of gasification condensates and is not removed in pretreatment. Ammonia was added to provide a nitrogen source and to simulate the background of gasification wastewater. Phosphorus was added (to meet biological requirements) in the molar, weight ratio of 100:1, BOD to phosphorus. The estimated COD of the synthetic wastewater was 1006 units. Since the organic components are all biodegradable, the BOD should approximate the COD. The composition of the synthetic wastewater is shown in Table 3.

The pH of the synthetic water was adjusted to 7.0 with sodium hydroxide. Batches of the synthetic wastewater were made up to 20X concentration, then diluted with cold tap water into the feed storage tank, as needed. The synthetic wastewater feed tank had a volume of about 2040 liters (540 gal) and was equipped with a nitrogen purge to reduce biological activity. Technical-grade nitrogen gas was added to the headspace of the feed tank at about 2 psig and a flow rate just above that of the feed rate.

2.5 Deep Column Reactor Process

2.5.1 Design Considerations

The Deep Column reactor utilizes a hydrostatic pressure of 1 atm, for a total pressure of 2 atm at the bottom of the reactor, and pure oxygen for oxygenating the reactor. Pure oxygen was chosen due to the wide availability of pure oxygen at synfuel/gasification facilities. Plug flow will take advantage of the inherent kinetic improvements over complete mix kinetics. The operation and design of the Deep Column are discussed below.

In general, the flow pattern is that of an upflow, suspended-solids bioreactor. The water column in the reactor will provide the required hydrostatic pressure to attain a high incoming dissolved oxygen content. The flow of water up through this bioreactor column will entrain the biomass in a plug. The theoretical concentration of dissolved oxygen at the entrance (bottom) of the reactor column should be 80 mg/l. Dissolved oxygen concentrations were controlled to provide about 4 mg/l at the top of the reactor. The high dissolved oxygen concentrations will ensure that the kinetics are limited only by substrate availability.

The initial design assumptions were as follows: 1) the rate of substrate utilization will be equal to or greater than that for the activated sludge treatment of Great Plains' stripped gas liquor ($K = 0.021$ l/mg-day for BOD_5 , Mayer et al. 1986.); 2) the biomass concentrations attainable for the proposed reactor will be in the same range as those for pure oxygen activated sludge (POAS), (4000 to 8000 mg/l MLSS); 3) the settling velocity of the sludge will be similar to conventional activated sludge (about 0.04 cm/sec); and 4) reaction kinetics will be pseudo-first order in nature.

TABLE 2
COMPOSITION OF GASIFICATION WASTEWATERS

Component	Great Plains ^a Stripped Gas Liquor	KILnGAS ^b SSE-3
COD	2770	2980
BOD ₅	1150	560
Phenol	10	92
o-Cresol	7	ND ^c
m,p-Cresol	4	17
Total phenolics	221	198
Acetate	435	76
Formate	110	4
Ammonia	760	150
Thiocyanate	9	150
Cyanide	5	14

^a Mayer et al. 1986.

^b CH2M Hill and EMRC 1988.

^c ND = not detected.

TABLE 3
COMPOSITION OF THE SYNTHETIC WASTEWATER

Constituent	mg/l	mg COD/l	mg TOC/l
Phenol	240	564	185
o-Cresol	30	76	23
Formate	80	28	21
Acetate	200	214	80
Ammonia	100	-	-
Thiocyanate	100	124	21
Phosphate	11	-	-
Total	-	1006	330

One atmosphere of hydrostatic pressure was chosen for the pilot unit in consideration of two factors. Space limitations would severely limit the construction and operation of a reactor at heights greater than about 12 m (40 ft). Secondly, a height of about 10.0 m (32.8 ft) should be sufficient to demonstrate the applicability of the process. Kinetics and performance determined with the pilot plant at a 10.0 m height should be applicable for scaling purposes.

Based on experience at UNDEMRC, a 10-cm (4-in) diameter column for the reactor was considered the minimum optimum diameter for reducing deleterious wall effects. Increasing the diameter above this size would result in significant increases in wastewater usage and sizing of pumps and associated equipment. The effluent BOD concentration was chosen to be 25 mg/l since this is a criteria often used for discharge of wastewater to receiving waters. At an influent BOD of 1000 mg/l and an effluent concentration of 25 mg/l, the required hydraulic retention time (HRT) for a complete mix reactor can be estimated for a range of biomass concentrations. The following equation is used for determination of the substrate utilization rate in CSTRs:

$$\frac{(S_o - S_e)}{\theta X} = K S_e \quad (4)$$

where X is the biomass concentration, θ is the hydraulic retention time in days, S_o is the influent substrate concentration, S_e is the effluent substrate concentration and K is the rate coefficient in l/mg-day. This equation is rearranged as shown in Equation 5 for the determination of the HRT.

$$\theta = \frac{(S_o - S_e)}{K S_e X} \quad (5)$$

Figure 2 shows a plot of biomass concentrations versus hydraulic retention time. From this plot it is apparent that, if a biomass concentration of 5 to 7 g/l can be maintained in the reactor, HRTs should be about 6 to 8 hours. Actual HRTs should be even less since the substrate utilization rate, K, was expected to be larger in the Deep Column reactor than the rate determined for a conventional activated sludge reactor.

Equations 4 and 5 are generally applied to complete mix stirred tank reactors (completely mixed activated sludge); plug flow reactors are subject to different kinetics due to the changes in substrate concentrations with respect to both time and location in the reactor. The following equation is used for a plug flow reactor:

$$\frac{S_e}{S_o} = e^{-KX\theta} \quad (6)$$

where e is the base of the common log. The other terms are identified above. Figure 3 shows Equation 6 plotted for an ideal plug flow reactor and a plug flow reactor with a dispersion factor of 0.2. Dispersion, which ranges from 0 to infinity, is a measure of deviation from ideal plug flow (Reynolds 1982). A completely mixed reactor has a dispersion number of infinity.

Figure 2. Hydraulic retention time (HRT) versus biomass concentrations for a range of influent BOD (S_o) based on the design equation for a complete mix stirred tank reactor (CSTR). Effluent BOD (S_e) is 25 mg/l and the substrate utilization coefficient (K) is 0.021 l/mg-day.

Figure 3 indicates that the required hydraulic retention time, at a biomass concentration of 6 g/l and using the other assumptions, is approximately 50 to 70 minutes. The HRT predicted using complete mix kinetics is 6.8 to 9.6 times greater than those predicted for plug flow kinetics.

Given the settling velocity of the sludge of approximately 0.04 cm/s, and using a safety factor, or design factor, of 3, the required flow velocity for the reactor column is 0.12 cm/sec. For a 10-cm-I.D. column, the required flow rate is 584 ml/min (840 liters/day or 222 gpd). The reactor volume would be 85 liters, resulting in a net cycling of water through the reactor of 9.9 times. The required cycles through the reactor to provide the desired level of treatment is calculated as follows:

BOD in = 1000 mg/l, BOD out = 25 mg/l; therefore, 975 mg/l O_2 are required, neglecting endogenous oxygen requirements.

Plug flow kinetics predict an HRT of about 1 hour. A 2-hour HRT will be used for design purposes.

For an HRT of 2 hours, 1020 liters per day of feed will be required ((24 h/day/2-h HRT) x 85 liters = 1020 liters/day.).

Figure 3. Hydraulic retention time (HRT) versus biomass concentrations for plug flow kinetics at an influent BOD of 1000 mg/l, effluent BOD of 25 mg/l and a K of 0.021 l/mg-day.

1020 liters/day $\times$ 0.975 g O_2 /liter = 994.5 g O_2 /day.

1020 liters feed $\times$ 100% recycle from the clarifier = 2040 l/d

2040 liters/day $\times$ 0.08 g dissolved oxygen/liter = 163.2 g O_2 /day.

One complete cycle through the reactor is 85 liters $\times$ 0.08 g O_2 /liter = 6.8 g O_2 /cycle.

163.2 g O_2 /day required/6.8 g O_2 /cycle = 24 cycles required for complete treatment.

Thus, 9.9 cycles through the reactor are the minimum required for sludge suspension, and 24 cycles are required to provide for sufficient oxygenation. Therefore, the recycle flow rate will be increased from 840 l/d to 2550 l/d (674 gpd or 0.47 gpm). This recycle flow rate will provide 30 cycles through the system, although 24 is the estimated requirement. The extra cycles should ensure that the desired oxygenation can be achieved within the design limitations.

2.5.2 Process Configuration

The pilot-scale reactor is shown in Figure 4 with the column lengths and widths and the clarifier roughly to scale. Design specifications for the system are given in Table 4.

The feed and recycled sludge from the bottom of the clarifier were added to the discharge side of the recycle pump. This arrangement ensures that the highest concentrations of sludge, feed and dissolved oxygen will enter the reactor column together. The liquid flow in the oxygenator is countercurrent to a flow of pure oxygen through a stainless steel fine bubble diffuser; the liquid was pumped into the bottom of the reactor column. The added feed, sludge, and oxygenated water flowed in a plug through the column and then by gravity to the oxygenator column. An effluent stream was drawn off the top of the reactor and flowed to the clarifier. Clarified effluent was removed by gravity, while the thickened sludge was returned to the reactor as described above. A YSI model 56 dissolved oxygen (DO) probe continuously monitored the DO at the top of the reactor. The quantity of oxygen applied to the water in the oxygenator was adjusted to maintain the DO content at the top of the reactor at about 3 to 4 mg/l. This control system ensured that excess oxygen was not added to the water, while preventing oxygen limitations in the reactor.

After a period of operation, the pH of the reactor liquor began to drop below optimal as a result of nitrification. At that time a pH control system was added. The probe was located in the clarifier and the Beckman model 960B pH monitor/controller regulated the addition of a saturated solution of sodium bicarbonate into the clarifier to maintain a system pH of 7.0 ± 0.2 . The dissolved oxygen content was continuously monitored with a YSI model 56 meter, which was connected to an MIC programmable controller. This controller regulated the flow of oxygen via a control valve with an I/P connection. Cylinders of commercial-grade pure oxygen were used with a line pressure of 20 to 25 psig.

2.5.3 Flow Analysis

Tracer studies were conducted to determine the flow pattern through the system in general and the reactor in particular. Since the reactor was designed to test the effects of both pure oxygen and plug flow, it is extremely important that the reactor flow pattern closely simulate plug flow. Two types of tracer studies were conducted.

In the first study, the flow rates of all pumps were set to provide a reactor hydraulic retention time of 24 hours. The flow rates, with an oxygen flow rate representative of expected operation, and volumetric data are shown in Table 5.

In the first tracer test, the system was filled with tap water, the pumps and oxygen flow were all calibrated to the values shown in Table 5, and the system was operated for about one hour for equilibration. Following equilibration, 60 ml of a 1 g/100 ml methylene blue dye solution was pumped into the system via the feed pump. After the dye slug was added, tap water pumping was resumed through the feed pump during the remainder of the test. Samples were taken at each of the sample ports throughout the length of the reactor column (spaced about 1.8 meters apart), at the overflow and the effluent port from the clarifier over a 12 hour period.

Figure 4. Process flow schematic of the pilot-scale Deep Column reactor. The reactor, oxygenation and clarifier are drawn roughly to scale.

TABLE 4
DESIGN CHARACTERISTICS OF THE PILOT-SCALE DEEP COLUMN REACTOR

Item	Specification
Reactor column	
Material	Excelon R-4000 schedule 40 rigid clear plastic pipe
Total height	10.97 m (36 ft)
Liquid level	10.33 m (34 ft)
I.D.	10.226 cm (4.026 in)
O.D.	11.430 cm (4.500 in)
Liquid volume	85.09 liters
Oxygenation column	
Material	Excelon R-4000 schedule 40 rigid clear plastic pipe
Total height	10.97 m (36 ft)
Liquid level	10.33 m (33.9 ft)
I.D.	5.25 cm (2.067 in)
O.D.	6.03 cm (2.375 in)
Liquid volume	22.36 liters
Clarifier	
Material	stainless steel with a plexiglass front
Size	rectangular inverted pyramid, 44.5 cm by 85 cm by 122 cm tall
Liquid volume	45 liters
Pumps	
Feed pump	variable speed, accurate and precise; flow from 60 to 1420 ml/min; maximum head 11 m
Sludge Recycle Pump	variable speed, solids handling positive displacement, flow from 60 to 1420 ml/min, maximum head 11 m
Recycle pump	variable speed, solids handling positive displacement, flows from 390 to 790 ml/min, head approximately 0.6 m

TABLE 5
SYSTEM PARAMETERS DURING THE FIRST DEEP COLUMN REACTOR TRACER STUDY

Reactor volume, liters	85
System volume, liters	137
Recycle flow, mls/min	590
Feed flow, mls/min	60
Overflow rate to clarifier, mls/min	120
Sludge recycle rate, mls/min	60
Oxygen flow rate, mls/min at 14.7 psig	25

The samples were analyzed by reading their absorbance with a spectrophotometer at 610 nm, using tap water as the blank. The results of this analysis for the reactor ports are shown in Figure 5. This figure shows the concentration of the dye at each of the four ports in the reactor as a function of time. Generally, the plot reveals a plug of dye that increasingly disperses as it moves through the reactor, resulting in an essentially completely-mixed system after approximately 480 minutes (8 hours).

A second tracer study was performed, without recycle of column overflow, to analyze the flow pattern within the reactor column. Dye concentrations were measured in the effluent of the reactor column (overflow at the top). The results of this tracer study are shown in Figure 6. Visual inspection of this figure reveals a plug flow reactor with a small amount of dispersion. However, since a detailed kinetic analysis of the performance of this system will be conducted, it is important to determine an axial dispersion coefficient that can be used to modify the ideal plug flow kinetic expressions. This would allow the design engineer to use the derived kinetic coefficients with other reactors for which axial dispersion coefficients are known.

The axial dispersion coefficient encompasses factors such as channeling and short-circuiting that prevent reactors from reaching ideal flow conditions. The deviation of a reactor flow pattern from ideal plug flow can be estimated through the use of the residence time distribution. This is the distribution of times required by elements of fluid to pass through the reactor.

The function $F(t)$ is defined as the fraction of elements in the effluent stream that have residence times less than a given time, t . That function is known as the cumulative distribution, or F curve. An example of this function, based on the second tracer study of the Deep Column reactor, is shown in Figure 7. From this figure, it can be seen that 50 percent of the fluid particles have residence times of less than 2.5 hours, and virtually all of the fluid particles have residence times of less than 4.5 hours. A second function, $E(t)$ is defined by its relationship to the $F(t)$ function:

$$E(t) = dF(t)/dt. \quad (7)$$

Figure 5. Plot of time versus absorbance at 610 nm for the dye injected into the Deep Column reactor as measured at the 4 reactor sample ports (indicated by distance from the bottom of the reactor) during the first tracer study.

Figure 6. Plot of time versus absorbance at 610 nm for the dye injected into the Deep Column reactor during the second tracer study.

Figure 7. Plot of the $F(t)$ function versus time for the second Deep Column reactor dye tracer study. Also known as the cumulative distribution, or F curve.

$E(t)$ is the fraction of effluent that has a residence time between t and $t + dt$. This function is known as the residence time distribution function, or E curve, and is equivalent to the derivative of the $F(t)$ function. An example of the $E(t)$ curve based on the tracer study of the Deep Column reactor is shown in Figure 8.

The distribution functions for a particular reactor and flowrate may be determined by injecting a dye into the input of the reactor and recording the effluent dye concentration versus time. Step and/or impulse signals are easiest to use. An ideal step signal is a sudden application of a continuous flow, and produces a concentration that increases from 0 to the influent concentration, C_0 , at the effluent port in a time equal to one residence time. An impulse signal is a sudden, short application of tracer that ideally occurs in zero time. This results in a dye concentration at the effluent port, at a time equal to one residence time, equal to the concentration initially applied to the reactor.

The ratio of the concentration, C , at any given time, t , to the initial concentration, C_0 , may be related to the cumulative distribution function. Consider a reactor with a step input and let t equal the mean residence time. Divide the effluent stream into two fractions, one which has spent less time than t in the reactor, $F(t)$, and the other, which has spent more time than t

Figure 8. Plot of the $E(t)$, the point distribution function, versus time for the second Deep Column dye tracer study (also known as the residence time distribution function or E curve).

in the reactor, $1 - F(t)$. At time t , the fraction $1 - F(t)$ will not contain any dye, while the fraction $F(t)$ will have the initial concentration of dye, C_0 . The total flow of dye in the effluent will be:

$$F(t)C_0Q + [1 - F(t)](0)Q, \quad (8)$$

which must equal the mass flow of dye at t , or (CQ) , where C equals the effluent dye concentration and Q equals the flow rate through the reactor. At time, t , the right-hand term of equation 3-8 becomes zero because there is no dye in the $[1 - F(t)]$ fraction.

$$F(t)C_0Q = CQ \quad (9)$$

or

$$F(t) = C/C_0 = C(t)/C_0 \quad (10)$$

Equation 10 shows that $F(t)$ is equal to the normalized tracer concentration curve due to a step input of dye and provides a convenient method for determining the $F(t)$ function. The effluent dye concentration expressed as a fraction of the initial feed concentration is the cumulative distribution function $F(t)$.

By definition, the impulse input response is equal to the derivative of the step input response. Consequently:

$$E(t) = dF(t)/dt = d[C(t)/C_0]_{\text{step}}/dt = [C(t)/C_0]_{\text{impulse}}. \quad (11)$$

C_0 may be determined by integrating the area under the curve of $C(t)$ against time.

Similarly, the point distribution function, $E(t)$, is equal to the normalized effluent dye concentration curve resulting from an impulse input. For the tests conducted, impulse dye tracers were used to determine the $E(t)$ curve from equation 11. The initial dye concentration, C_0 , may be determined by determining the area under the curve of the dye concentration at the effluent port, C , against time. Simpson's rule was used to determine this area:

$$C_0 = C(t)_{\text{impulse}} dt. \quad (12)$$

The $F(t)$ curve was then obtained from the $E(t)$ curve by integration using the trapezoidal rule:

$$F(t) = \int_0^{\infty} E(t) dt. \quad (13)$$

The $F(t)$ and $E(t)$ curves determined are shown in Figures 7 and 8.

The dispersion number measures the extent of axial dispersion and is represented by (D_L/vL) where D_L is the axial dispersion coefficient, v is the velocity through the reactor, and L is the axial length of the reactor. Grady and Lim (1980) derive an equation for the inverse of the dispersion number:

$$vL/D_L = 4\pi T^2 [(dF/dt)_{t=T}]^2. \quad (14)$$

The dispersion coefficient can be approximated graphically by a determination of the slope of the F curve at a time equal to one mean residence time and the use of Equation 14. The mean residence time, T , was calculated by use of equation 3-15 (Grady and Lim, 1980):

$$T = \int_0^{\infty} tE(t) dt / \int_0^{\infty} E(t) dt. \quad (15)$$

Using this equation, the mean residence time was calculated to be 2.57 hours. This compares with a residence time of 2.4 hours based on $t = V/Q$ ($V = 85.1$ liters and $Q = 0.59$ liters per minute).

Substituting this mean residence time into Equation 14 and taking the inverse of this result, a dispersion number of 0.0217 was calculated. Figure 9 shows the relationship between the $F(t)$ function and dimensionless time for a series of dispersion numbers ranging from 0 (an ideal plug flow reactor) to infinity (a completely-mixed reactor). This figure may be compared with $F(t)$ versus dimensionless time for the dye test, which is shown in Figure 10. The figures indicate that a reactor having an axial dispersion of 0.0217, while not ideal, approximates plug flow satisfactorily.

Figure 9. Plot of the $F(t)$ function versus dimensionless time for a variety of dispersion numbers (after Grady and Lim, 1980).

Figure 10. Plot of the $F(t)$ function versus dimensionless time for the Deep Column reactor. The function represents a calculated dispersion number of 0.0217.

2.5.4 Aeration Testing

An aeration test was conducted with the Deep Column reactor in order to determine the following: 1) attainable concentrations of dissolved oxygen in the reactor and 2) the rate of oxygenation under the test conditions. On the day of the test the empty reactor was filled with room temperature equilibrated tap water that was deoxygenated. The deoxygenation followed the methodology suggested by Adams, Ford and Eckenfelder (1981). Sodium sulfite was added in a ratio of 7.9 mg Na_2SO_3 /mg dissolved oxygen (a dissolved oxygen content of 9.0 mg/l was assumed for the tap water at the start) with a 20% excess of sodium sulfite. Cobalt chloride was added, as a catalyst, at a concentration of 0.5 mg/l as cobalt ion. This water was mixed and then pumped into the reactor.

A YSI model 56 dissolved oxygen (DO) meter was set up to analyze DO at the top of the reactor column via a stirred probe. This probe was fitted with a 0.002-inch membrane, which doubled the usual range of dissolved oxygen measurement from 0 - 20, to 0 - 40 mg/l. A YSI model 58 DO meter, which was connected to a recorder, was used to measure the DO at the bottom (influent) of the reactor column. This probe was also fitted with a 0.002-inch membrane for increasing the range of the meter. In addition, this meter has an internal switch for membrane thicknesses of 0.0005, 0.001 and 0.002 inches. This switch was set at 0.0005, thus, together with the thicker membrane, effectively quadrupling the range of the meter (YSI, personal communication).

The DO meters were calibrated in humidified air and the pumps were started and run until a steady-state DO concentration was obtained. At this point the flow of oxygen was started at 25 mls/min at 14.7 psig. The time when oxygen flow began in the oxygenation column was designated as time zero. The concentrations of dissolved oxygen versus time for the top and bottom of the column are shown in Figure 11. Oxygen concentrations at the bottom of the column increased quickly to about 40 mg/l. Above the 40-mg/l level, the increase was much slower; gradually reaching approximately 55 mg/l. Oxygen concentrations at the top of the column did not increase until about one retention time (154 minutes) had elapsed and then the DO concentration rose steadily. Oxygen concentrations at the top of the column reached 40 mg/l (the upper limit of the DO meter), which is approximately saturation. Surfaces near the top of the column were covered with bubbles of evolved oxygen.

The actual concentrations of DO achieved are unknown due to the overall poor accuracy of DO meters, which is even poorer when measuring DO levels well above the usual range. The oxygenation rate for the top of the column was estimated at 0.37 mg O_2 /l-minute under the test conditions. This rate is obviously directly related to the rate of flow of oxygenated water from the lower part of the column and reflects some dispersion. There are apparently two rates of oxygenation for the bottom of the column--an initial rate of 1.31 mg O_2 /l-minute and a final rate of 0.065 mg O_2 /l-minute. The oxygenation rate can be controlled by either increasing the flow of oxygen or increasing the recycle of water between the columns.

Figure 11. Results of the aeration test in the Deep Column reactor. Dissolved oxygen concentrations were measured at the top and bottom of the reactor column throughout the test period. Recycle flow = 590 mls/min; oxygen flow = 25 mls/min at 20 psig.

2.6 Data Acquisition

Regular maintenance procedures were instituted to ensure continuous and good operation of the Deep Column reactor. These maintenance procedures and the frequency with which they were performed are shown in Table 6. The reactor and oxygenator columns were cleaned with a polyethylene brush to remove wall growth and reduce the size of the biological floc. As floc size increased, suspension of the floc in the reactor could become difficult and plugging of piping could result. Clarifier walls were also brushed to remove growth. The dissolved oxygen meter and probe required regular cleaning, replacement of membranes and calibration for accurate operation. Readings, as shown in Table 7, were taken to provide needed operating data for the reactor. Feed pump calibration was tested regularly by measuring the rate of effluent accumulation. Feed pump rates varied somewhat as a result of changes in nitrogen purge flows and height of feed in the tank. Recycle pump pressure was monitored to ensure that this pump did not become plugged, as it pumped a large quantity of biological solids.

TABLE 6
MAINTENANCE SCHEDULE FOR THE DEEP COLUMN REACTOR

Item	Frequency
Clean reactor walls	2/day
Clean oxygenator walls	2/week
Clean clarifier	1/day
Calibrate DO meter	2/week
Take readings	1/day
Check feed pump calibration	1/day
Check recycle pump pressure	1/day

TABLE 7
DEEP COLUMN REACTOR DAILY DATA COLLECTION

Item	Units
Date	MMDDYY
Time	0000
Recycle pump rate	hertz
Sludge recycle pump rate	hertz
Feed pump rate	0-10 units
Oxygen cylinder pressure	psig
Oxygen line pressure	psig
Oxygen flow rate	cc/min
DO at reactor top	mg/l
Reactor liquor temperature	°C
Reactor liquor pH	units (0-14)
Buffer usage	liters/day ^a
Settleable solids	ml/l in 30 minutes
Oxygen uptake	mg O ₂ /l-minute

^a Sodium bicarbonate (160 g/l).

A list of the analytical methods used for analysis of feed and effluent wastewater samples and for monitoring the mixed liquor is shown in Table 8. Sampling was performed using grab samples from the feed tank, effluent and reactor. Grab samples for mixed liquor were taken from the lowest port on the reactor column (height of 1.8 m). Analysis of samples from all ports on the column showed that the column was essentially completely mixed with respect to biological solids. Monitoring for pH and dissolved oxygen in the reactor was performed continuously, as described above. Samples were generally taken twice per week during periods of relative stability. For example, if the feed rate had just been changed significantly, sampling might be delayed to allow the system to adjust to the new conditions.

2.7 Process Performance

Process performance defines the operation of the unit, under the operating conditions used, with respect to variables that impact the applicability of this unit for commercial use such as substrate removal, sludge settling, and operational problems. These items are discussed below.

2.7.1 Operation

On March 14, 1988, the Deep Column reactor was filled with biologically treated Great Plains Gasification wastewater and seeded with two liters of mixed liquor from a continuous-flow, completely mixed seed reactor operating with Great Plains wastewater. Four liters of synthetic wastewater was batch-fed to the reactor and the flow of oxygen, and recirculation between the oxygenation and reactor columns was begun. The Deep Column system was operated in a batch mode with additions of increasing quantities of feed and periodic additions of acclimated seed until April 23, 1988. At this time the reactor column was found to have accumulated a large quantity of bio-sludge at the bottom. This sludge should have been suspended in the recycle stream at the 590-ml/min recycle flow. The recycle flow was increased to 890 ml/min, where good suspension of the sludge was found. At this time the addition of feed was begun in a continuous mode at an initial rate of 14 ml/min. The clarifier was put into operation, but sludge wasting, other than for sampling and loss over the clarifier, was not performed.

The rate of sludge return from the clarifier was set at 590 ml/min. This was found to be the minimum rate that returned the sludge, and was slightly in excess of the backflow through the pump. On May 26, 1988, after continual gradual increases in the feed rate, the hydraulic retention time (HRT) was 2.3 days. The biomass, as mixed liquor suspended solids and mixed liquor volatile suspended solids (MLSS and MLVSS) were 1035 ± 59 and 926 ± 59 , respectively. At this time the flow of oxygen was switched from programmable control to continuous. The use of the controller resulted in periodic swings of dissolved oxygen ranging from around 20 mg/l to about 2 mg/l. Continuous addition of oxygen resulted in changes in DO only with a) temperature changes and b) changes in oxygen demand. Daily adjustment of the flow of oxygen was found to be more than adequate to maintain the target 4-mg/l minimum at the top of the reactor.

TABLE 8
ANALYTICAL METHODS USED FOR THESE INVESTIGATIONS

Parameter	Description	Reference ^a
pH	electrode	SM No. 423
Dissolved oxygen	polarographic electrode	SM No. 421F
Solids	gravimetric	SM No. 209
TOC	combustion - infrared	SM No. 505A
COD	digestion - colorimetry	SM No. 508C
Ammonia	distillation - titration	SM No. 505A
Oxygen uptake	polarographic electrode	SM No. 213A
Settleable solids	volumetric	SM No. 213B
Phenols	colorimetric	SM No. 510C

^a SM = Standard Methods (APHA 1985).

On June 1, 1988, a weir was added to the clarifier overflow to reduce the loss of suspended solids. At this time the effluent volatile suspended solids was 518 mg/l. A value of about 50 mg/l would be expected under steady state conditions. The high effluent volatile suspended solids probably resulted from the lack of the weir and the low sludge age in the reactor sludge. Fast growing biomass (low sludge age) results in poor sludge settling.

Between June 30 and September 30, 1988, a series of problems associated largely with periodic power surges and outages occurred. These power problems were generally related to summer thunderstorms common to North Dakota. The surges/outages generally resulted in failure of the column and sludge recycle pumps. The motor controllers for these pumps were very sensitive and required manual re-start. On September 30 a programmable controller was installed that automatically restarted these motor controllers after a surge or outage in normal power. This remedied the problem, as no other pump failures occurred throughout the operation of the system.

On August 7, 1988, the pH of the reactor liquor dropped to 5.7, which was below the normal range of biological activity. This was the result of nitrification, or biological oxidation of ammonia to nitrite and nitrate, with subsequent production of acid. A pH adjustment system was installed at this time that maintained a pH of 7.0 ± 0.1 via the addition of sodium bicarbonate.

On August 19, 1988, the initial target loading of a 1.5-day HRT was attained. On October 6, 1988, the first batch kinetic test was conducted. At this time the F/M was 0.29, the sludge age was about 39 days, and the MLVSS was 2710 mg/l. Data were obtained on the concentrations of biomass and substrate in the reactor column. The data showed that the differences in biomass and substrate were small and not as expected. That is, the concentration of

biomass was expected to increase with reactor length, and the substrate concentration was expected to decrease with reactor length. As a result, the feed rate to the unit was increased to an HRT of 0.5 days with the hope that the predicted differences would be found.

On November 28, 1988, the target HRT of 0.5 days was attained. On December 28, 1988, the concentrations of biomass and substrate were evaluated through the reactor length. The data showed, as before, little differences with respect to biomass or substrate with respect to reactor length (COD was 144 ± 27 units). A second batch kinetic test was performed on February 9, 1989. A third batch kinetic test was conducted on April 17, 1989.

Since the data showed that continuous kinetics on the system could not be obtained as planned, it was decided to determine them via batch methods and continue pilot operations to provide performance and operating data. Accordingly, for the remainder of operations the strategy was to slowly increase the feed rate, while continuing to monitor performance. The HRT was decreased from 0.5 days (12 hrs) to the lowest level attained of 2.13 hours. The system was shut down on May 1, 1989, after operating for over 400 days. The only difficulties associated with operation resulted from power outages/surges, pH drops, and inadequate supply of oxygen.

2.7.2 Performance

The optimum temperature conditions in the Deep Column reactor would be a stable temperature near normal room temperature. Actual temperatures varied according to outside air temperatures and mechanical difficulties in the building housing the reactor. Mixed liquor temperatures, obtained as daily spot measurements, are shown in Figure 12. The mean and standard deviation for temperature were $23.0 \pm 3.2^\circ\text{C}$. The principal effect of variations in temperature within the range noted was a change in oxygen solubility. This change did not adversely impact operations.

Figure 13 shows the variations in pH that occurred in the course of operation. A drastic drop in pH was noted around Day 60. At this time a pH control system was installed that maintained the pH by addition of sodium bicarbonate. The mean and standard deviation for pH were 6.9 ± 0.2 units. This pH would be optimum for most degradative bacteria, but not necessarily optimum for nitrifying bacteria. The drop in pH resulted from biological oxidation of ammonia (nitrification), which results in the production of acid. Nitrification was not a goal of this research, and, as such, was not encouraged.

Buffer, in the form of a solution of sodium bicarbonate, was added to the reactor through the use of a pH controller to maintain a constant, favorable pH. Figure 14 shows the buffer usage, in liters per day of 160 g/l of sodium bicarbonate, during the operating period. A large quantity of the added buffer was used to adjust the pH of the feed to the setpoint of 7.0, since the synwater was only roughly adjusted to 7.0 when made. However, the buffer usage during the period of about Day 60 through Day 170 was primarily for nitrification. After Day 170, nitrification ceased due to a decrease in temperature that was experienced on about Day 186 (Figure 12). Nitrifying bacteria are much more sensitive to low temperatures than are heterotrophic degradative bacteria (EPA 1975). Nitrification did not significantly recover from this episode, and buffer usage subsequent to this time was for feed pH adjustment.

Figure 12. Variation in mixed liquor temperature during the pilot-scale Deep Column reactor operation.

Figure 13. Variation in mixed liquor pH during the pilot-scale Deep Column reactor operation.

Figure 14. Buffer usage, as a solution of sodium bicarbonate (160 g/l) during the period of operation.

The concentration of dissolved oxygen at the top of the reactor was targeted at ≥ 4 mg/l. At this concentration, oxygen would not be limiting, and excess oxygen would not be wasted. Figure 15 shows the variation in dissolved oxygen concentrations in the top of the reactor column throughout operations. Although the primary variable in operations was the feed rate, the fact that the temperature tended to vary a few degrees resulted in some undesirable changes in dissolved oxygen concentrations. Overall, however, oxygen concentrations were adequate to demonstrate the system.

The variations in feed rate to the unit, in liters per day, are shown in Figure 16. This figure shows the initial strategy to attain steady-state with respect to hydraulic and organic loading as well as the solids retention time. Since this strategy did not allow the determination of continuous kinetics, as desired, it was abandoned. The alternative for the pilot unit was to obtain performance data. Thus, the feed rate was periodically increased and the performance monitored. Figure 17 shows the variation in the hydraulic retention time (HRT) during the period of operations. This figure reveals a step-like decline in HRT from about 2.6 to 0.09 days. The mean and standard deviation for HRT were 1.4 ± 0.8 days.

Figure 15. Variation in dissolved oxygen concentrations at the top of the pilot-scale Deep Column reactor.

Figure 16. Variation in the feed rate to the pilot-scale Deep Column reactor during the period of operation.

Figure 17. Variation in the hydraulic retention time (HRT) for the pilot-scale Deep Column reactor during the period of operation.

The variation in fluid velocity in the reactor column over the period of operations is shown in Figure 18. A fluid velocity of about 0.8 cm/sec was found to be necessary to entrain the biomass in the reactor column during initial operations. Thus, the column and sludge recycle pump rates were adjusted to provide this rate. Changes in feed rate were the principal reasons for changes in fluid velocity. However, as the organic loading to the unit increased, the oxygen demand increased. The increased demand for oxygen could only be met by increasing the flow of oxygenated water from the oxygenator column (increasing the column recycle flow). Small increases in the column recycle flow were made to maintain adequate DO concentrations.

Fluid velocities of greater than 0.8 cm/sec are probably required with increases in biomass in order to maintain entrainment of the biomass. The mean and standard deviation for the period of operation were 2.1 ± 2.9 cm/sec.

Figure 19 shows the variation in the recycle ratio during the period of operation. The recycle ratio is the fraction that the sludge recycle flow (clarifier underflow) is of the feed flow. Ideally, the recycle ratio is small; however, with a pilot unit that must be capable of a wide range of operations, the recycle ratio can be expected to be fairly large. This is due to the fact that clarifiers do not scale well. Thus, in order to return sludge appropriately, larger ratios may be needed in pilot- than commercial-scale units. In fact, the recycle ratio was large in this case because the sludge return pump was pumping against about 16 psig of head. Backflow in the pump required a higher than desirable flow rate. The mean and standard deviation for the recycle ratio were 23.6 ± 28.0 .

Figure 18. Variation in the fluid velocity through the reactor column of the pilot-scale Deep Column reactor during the period of operation.

Figure 19. Variation in the recycle ratio of the pilot-scale Deep Column reactor during the period of operation.

The variation in the oxygen uptake rate throughout the operating period is shown in Figure 20. The oxygen uptake rate is often used as a measure of viability or activity of the biomass. This figure shows a gradually increasing rate, somewhat proportional to the increases in feed rate (Figure 16). The mean and standard deviation of the oxygen uptake rate during the operating period were 0.7 ± 0.5 mg O_2 /l-min.

The variation in mixed liquor settleable solids during the operating period is shown in Figure 21. The settleable solids is a measure of the volume of solids in one liter of mixed liquor after settling for 30 minutes. This measure gives an indication of solids stability. A rapidly growing or a sludge experiencing toxicity will tend to have higher settleable solids. Figure 21 shows rather abrupt increases in settleable solids at about Day 220, after which the settleability improved. The rapid increase in settleable solids was probably due to the fact that the reactor temperature dropped to the observed low on Day 187, prompting a low SRT and subsequent fast growth rate and poor settling. The mean and standard deviation for mixed liquor settleable solids were 467 ± 197 .

The variation in sludge volume index (SVI) over the period of operation is shown in Figure 22. The SVI is calculated by dividing the settleable solids by the mixed liquor volatile suspended solids (MLVSS) to give SVI in units of ml/g. Figure 22 shows that the SVI was at a high level when analysis began, but declined to the 130-ml/g level for the remainder of operations. This indicates a stable, well settling sludge, as was expected from the literature (Rensink 1974). The mean and standard deviation of the SVI were 134 ± 51 ml/g during the period of operation.

Biomass can be measured by many diverse methods. The most common method of estimating biomass in the field of wastewater treatment is to use the volatile suspended solids analysis. For this analysis a sample of mixed liquor is filtered through a nominal 0.8- μ m glass fiber filter that has been pre-fired and weighed. The solids accumulated on the filter are dried to determine their moisture content, then fired at 550°C. The use of volatile, rather than just dry solids eliminates the error due to accumulations of mineral matter that often occur in the field. The variation in the mixed liquor volatile suspended solids (MLVSS) concentration during the operating period is shown in Figure 23. Except for a small decline around Day 180-200, the general trend was of continual increase with respect to time. The decline noted occurred at approximately the same time as the previously mentioned low in settleable solids (Figure 21) and likely had the same cause. The mean and standard deviation for MLVSS during the period of operation were 3710 ± 1489 mg/l.

The quantity of biomass lost with the effluent places limits on a biological treatment system. Large losses with the effluent can prevent the attainment of high SRTs and accompanying stability. Figure 24 shows the variation in clarifier volatile suspended solids (CVSS) during the period of operation. CVSS concentrations averaged a relatively low 31 mg/l, but were relatively variable. Since pilot-scale clarifiers do not scale properly, the larger losses of VSS are not troublesome, especially in light of the stable, low values observed for SVI. A commercial scale clarifier would undoubtedly perform much better.

Figure 20. Variation in the oxygen uptake rate of the mixed liquor in the pilot-scale Deep Column reactor during the period of operation.

Figure 21. Variation in the mixed liquor settleable solids concentration in the pilot-scale Deep Column reactor during the period of operation.

Figure 22. Variation in the sludge volume index (SVI) of the mixed liquor in the pilot-scale Deep Column reactor during the period of operation.

Figure 23. Variation in the mixed liquor volatile suspended solids (MLVSS) concentration in the pilot-scale Deep Column reactor during the period of operation.

Figure 24. Variation in the effluent or clarified volatile suspended solids concentration (CVSS) in the pilot-scale Deep Column reactor during the period of operation.

Determination of effluent settleable solids provides a quick measure of the volume of VSS lost in the effluent. Since it is much easier to perform, it was used during the last 45 days of operation to monitor for toxicity or organic or hydraulic overloading. The effluent settleable solids determination was performed using an Imhoff cone with a one-hour settling time. Figure 25 shows the variation in effluent settleable solids observed during the final 45 days of operation. Examination of this figure reveals a slight increase in settleable solids beginning about Day 320. The HRT at this time was decreased from 0.15 to 0.09 days. This increase in settleable solids can be attributed to several causes. The rapid decrease in HRT would result in a large decrease in SRT, as the organic loading would have almost doubled. In addition, the approximate doubling of hydraulic loading may have begun washout. Since the system was at the 0.09-day HRT for only 9 days before shutdown (too short a time for significant acclimation), it is uncertain whether the system was in failure. The mean and standard deviation for these data were 11.5 ± 8.2 ml/l.

The solids retention time (SRT), also known as the sludge age or mean cell retention time, is a key parameter in biological treatment operations. Generally, a much greater stability, with accompanying better effluent quality, results from using high SRTs. The practical limit to increases in SRT comes from the fact that with an increase in SRT there is a proportionate increase in nonviable mass. In addition, there is usually a limit to the mass of solids that a treatment system can handle with respect to pumping and clarification. SRT is a key parameter because it is the inverse of the microbial growth rate. A high SRT equates to a low growth rate (a biomass with a large percentage of cells in mid to late stationary phase), which results in greater stability, settling and, often, metabolic diversity.

Figure 25. Variation in the effluent settleable solids concentration in the pilot-scale Deep Column reactor during the period of operation.

For the purposes of this research, the SRT was not controlled at a particular level. Instead, the level of solids loss over the clarifier was reduced to approximate average levels and the SRT was allowed to reach an equilibrium at those conditions. This approach, along with a minimum of sludge wasting (only for sampling purposes) resulted in a relatively high SRT, as seen in Figure 26. This figure shows that the SRT was variable, but tended to be relatively high. The SRT decreased significantly during the last 60 days of operation. The variability noted in SRT values results in part because these values represent single determinations from periodic analyses rather than averages. The mean and standard deviation for SRT were 31 ± 33 days.

Figure 27 shows the variation in the influent and effluent chemical oxygen demand (COD) concentration for the Deep Column reactor during the period of operation. This figure shows that the influent COD concentration was relatively variable despite efforts to maintain consistency. The feed was made fresh at least weekly, and stored under flow of nitrogen gas to reduce biological oxidation. The mean and standard deviation of the feed COD were 815 ± 203 mg/l. The theoretical COD, confirmed with fresh synwater was 1006 mg/l. Biological degradation, sorption and volatilization reduced the strength of the feed. The effluent COD concentration, as seen in Figure 27, was more consistent and was quite low. Mean and standard deviation for effluent COD were 57.6 ± 70.1 mg/l.

Figure 26. Variation in the solids retention time (SRT) in the pilot-scale Deep Column reactor during the period of operation.

Figure 27. Variation in the chemical oxygen demand (COD) concentration in the influent and effluent of the pilot-scale Deep Column reactor during the period of operation.

The variation in the percent removal of COD during the period of operation are shown in Figure 28. Overall removals are greater than about 85%, with the exception of three values. The mean and standard deviation for percent removal of COD were $93.0 \pm 7.8\%$. These data encompass a period of operation that includes HRTs from 2.6 to 0.09 days (63 to 2.2 hours). Thus, the observed removals are excellent for a pilot unit.

One of the stated advantages of using pure oxygen for a biological treatment system is that sludge settling is excellent (Rensink 1974). The SVI is often used to estimate how well a sludge might settle; however, Benefield and Randall (1980) point out that SVI is only a single point on the sludge settling curve. Thus, a sludge settling curve was determined by settling one liter of mixed liquor in a graduated cylinder and measuring the change in the sludge/water interface height over time. Figure 29 shows the curve for the data taken at a time when the HRT was 0.74 days, the SVI was 200 ml/g, and the MLVSS was 3700 mg/l. A log decay equation was fit to the data with the resulting equation shown in Equation 15 below:

$$Y = -0.196 \log X + 1.264 \quad (15)$$

where Y is the interface height (% of total), and X is the time in minutes. This settling curve will provide a better point of comparison for settling between various sludges.

2.8 Kinetics

2.8.1 Continuous Kinetics

Determination of continuous kinetics is desirable since it provides estimates of the kinetic constants during a pseudo steady-state condition when the biomass is acclimated to a particular loading rate and SRT. Batch kinetics may not be as representative, since the conditions prevalent at the time of sampling the biomass affect the activity of the biomass and the resulting kinetic estimates (Templeton and Grady 1988).

The original research plan called for operating the pilot Deep Column reactor at 3 or 4 hydraulic/organic loading rates. Samples would have been taken through the length of the reactor and kinetic constants would have been estimated. Thus, this method requires that there be measurable differences in substrate and biomass concentrations with respect to reactor length at a minimum of three different loadings. Measurements of biomass and substrate at two different loadings did not result in clear differences in either substrate or biomass with respect to reactor length, until the 2.2-hour HRT was attained (Table 9). Thus, continuous kinetic determinations were abandoned in favor of batch kinetics and process performance evaluations.

The data from the 2.2-hour HRT, as shown in Table 9, are shown plotted in Figure 30. These data were fit with a power curve using GRAPHER, resulting in Equation 16:

$$\text{COD} = h^{-0.656} 190 \quad (16)$$

where h was reactor height and COD was the concentration of COD at height h. At the same time COD analysis was performed over the reactor height, phenol analysis was performed. Phenol concentration at 0.5 m was 4.5 mg/l, at 1.9 m it was 0.2 mg/l, and at greater lengths it was not detectable (<0.1 mg/l).

Figure 28. Variation in removal of chemical oxygen demand (COD) in the pilot-scale Deep Column reactor during the period of operation.

Figure 29. Sludge settling curve for the pilot-scale Deep Column reactor. Conditions were HRT = 0.74 days, SVI = 200 ml/g, and MLVSS = 3700 mg/l.

TABLE 9

COD AND BIOMASS CHANGES WITH RESPECT TO LENGTH IN THE DEEP COLUMN REACTOR

HRT (hrs)	63		18	2.2
Length (m)	COD	MLVSS	COD	COD
1.9	88	936	327	123
3.7	160	830	432	85
7.4	148	951	362	51
9.3	166	988	388	45

Figure 30. Change in COD concentration with reactor height at the 2.2-hour HRT in the Deep Column reactor.

When the reaction rate constant is evaluated for the data in Figure 30 using Computer Program 1 in the Appendix, a K of 49.85 mg/l-hr is obtained for the full length of the column (10.36 m). This value is calculated using Equation A-2, which is designed for a plug flow column with low diffusivity. This rate can be compared to values obtained from batch analysis below.

2.8.2 Batch Kinetics

Batch methods for kinetic evaluations are often used rather than continuous flow methods. In fact, batch methods are often recommended for kinetic determinations of plug flow systems (Grady and Lim 1980). To conduct a batch test, a series of reactors are set up with various food-to-microorganism ratios (F/M). These reactors are stirred and aerated. Data is collected through the reaction period and reduced to arrive at estimates of kinetic coefficients.

Four batch tests were conducted at various times during the operation of the Deep Column reactor. Data from one of these tests had to be discarded due to errors in biomass analyses. The first batch test was conducted at a time when there was significant nitrification occurring in the Deep Column, while the remaining two tests were performed after cessation of nitrification. The data from the test with nitrification was kept separate from those without nitrification. The data from the remaining two batch tests were pooled for reduction and analysis.

The methodology used for the batch tests was to prepare a set of four rectangular plexiglass reactors with a high length-to-width ratio. Varying amounts of mixed liquor from the Deep Column were added to provide different F/M ratios, feed was added as a concentrate, and the volume was set at 4.0 liters by addition of dechlorinated tap water. Samples were taken for the determination of biomass and substrate concentrations at time zero and at the end of the 24-hour reaction period. A reactor with an intermediate F/M was analyzed hourly to provide the additional data necessary for determination of the removal rate and maximum growth rate.

All analytical determinations were done according to Standard Methods (1986). Oxygen uptake determinations were made of the mixed liquor at intervals throughout the reaction period using a YSI (Yellow Springs Instruments) BOD probe and recording meter (model 55). The batch bioreactors were aerated with humidified air to supply oxygen and to completely mix the reactor contents. Temperature during the reaction period was between 20 and 23°C. The pH of the reactor contents was from 8.5 to 8.9. The reaction time for the batch tests was 24 hours.

2.8.2.1 Batch Test with Nitrification

The initial batch test was conducted on October 5-6, 1988 (Day 121-122). At the time of this test the Deep Column was operating at an F/M of 0.29 per day, an HRT of about 1 day, and an estimated SRT of 39 days. The batch reactors were set up according to Table 10 and the tests were conducted as described above. After the 24-hour incubation period the samples were analyzed and the data reduced and analyzed. The batch reactor biomass and substrate concentrations and the calculated F/M ratios for the 4 batch reactors are shown in Table 11.

TABLE 10
BATCH REACTOR TEST 1 START-UP COMPOSITION

Component (l).	1	2	3	4
Mixed Liquor	3.5	3.0	2.0	1.0
Feed (10X)	0.3	0.3	0.3	0.3
Dilution Water	0.2	0.7	1.7	2.7
TOTAL VOLUME	4.0	4.0	4.0	4.0

TABLE 11
BATCH REACTOR TEST 1 BIOMASS AND SUBSTRATE CONCENTRATIONS

#	F/M ^a	MLVSSo ^b	MLVSSe	CODo	CODe	TOCo	TOCe	NH ₃ o	NH ₃ e
1	0.32	2371	2520	764	102	223	25	90	2
2	0.37	2033	2110	761	91	222	23	89	1
3	0.56	1355	1520	756	87	218	17	88	2
4	1.11	678	851	751	106	215	23	87	39

^a F/M = food to microorganism ratio (CODo/MLVSSo).

^b o = initial, e = final.

The oxygen uptake rates for each batch reactor were plotted over time and are shown in Figures 31 through 34. The area under each curve was determined by fitting a curve to the data using GRAPHER and integrating. The resulting value is the total oxygen used during the batch period of incubation and is known as the Or. The Or and other reduced data from this batch test are shown in Table 12.

Kinetic coefficients were determined with the data from Tables 11 and 12 using the methods discussed below. These kinetic coefficients can be used for design and comparison purposes.

The maintenance plot determines the biomass yield coefficient, Y_g, and the endogenous decay coefficient, K_d. The equation for this is shown in linear form as Equation 17 (Reynolds 1982)

$$\frac{dx}{X} = Y_g \frac{dS}{X} - K_d \quad (17)$$

Figure 31. Plot of the oxygen uptake rate through the 24-h reaction period for the batch kinetic reactor operated at an F/M of 0.32.

Figure 32. Plot of the oxygen uptake rate through the 24-h reaction period for the batch kinetic reactor operated at an F/M of 0.37.

Figure 33. Plot of the oxygen uptake rate through the 24-h reaction period for the batch kinetic reactor operated at an F/M of 0.56.

Figure 34. Plot of the oxygen uptake rate through the 24-h reaction period for the batch kinetic reactor operated at an F/M of 1.11.

TABLE 12
REDUCED DATA FROM BATCH KINETIC TEST 1

#	Mean MLVSS	dx ^a	dTOC	dCOD	dNH ₃	Or
1	2446	149	199	662	87.8	912
2	2071	78	198	670	88.3	978
3	1438	165	202	669	86.3	692
4	764	174	192	645	48.3	454

^a d = delta, or change in X or substrate concentration.

Where dx is the change in MLVSS, X is the mean MLVSS, and dS is the change in substrate (TOC, COD or NH₃) concentration. When Equation 17 is plotted, the slope is Y_g and the y intercept is K_d. The maintenance plots for these batch tests are shown in Figures 35 through 37.

The oxygen coefficients, Y' and K_e', were determined via plotting of Equation 18 (Reynolds 1982), where Or is the oxygen utilized, Y' is the oxygen coefficient, and K_e' is the endogenous oxygen coefficient. When Equation 18 is plotted in a linear form, the slope is Y' and the y intercept is K_e'. The oxygen coefficient plots for this batch test are shown in Figures 38 through 40.

$$\frac{Or}{X} = Y' \frac{S}{X} + K_e' \quad (18)$$

The kinetic coefficients calculated from the batch data are shown in Table 13. The values obtained for K_d and Y_g are in the range often obtained for other types of wastewaters (Benefield and Randall 1980). The higher oxygen requirement, Y', based on TOC, versus that obtained based on COD is expected, since TOC is expressed as carbon and COD as oxygen. The reverse is true for biomass yield, Y_g, where the value is greater for COD than for TOC. The coefficients Y_g, K_d, and Y', based on ammonia, are all much higher than for either COD or TOC. These values are probably skewed high due to the fact that the nitrifying bacteria undoubtedly make up a very small fraction of the biomass in the reactors. Additionally, the kinetic values for TOC and COD are likely skewed somewhat due to the fact that nitrification affects oxygen usage and biomass production.

Figure 35. Maintenance plot for the determination of Y_g , the biomass yield coefficient, and K_d , the endogenous decay coefficient, based on COD. The linear correlation coefficient, R^2 , for this plot, based on a least squares linear regression, is 0.958.

Figure 36. Maintenance plot for the determination of Y_g , the biomass yield coefficient, and k_d , the endogenous decay coefficient, based on TOC. The linear correlation coefficient, R^2 , for this plot, based on a least squares linear regressions, is 0.961.

Figure 37. Maintenance plot for the determination of Y_g , the biomass yield coefficient, and K_d , the endogenous decay coefficient, based on NH_3 . The linear correlation coefficient, R^2 , for this plot, based on a least squares linear regression, is 0.704.

Figure 38. Oxygen plot for the determination of Y' , the oxygen coefficient, and K_e' , the endogenous oxygen coefficient, based on COD. The linear correlation coefficient, R^2 , for this plot, based on least squares linear regression, is 0.860.

Figure 39. Oxygen plot for the determination of Y' , the oxygen coefficient, and Ke' , the endogenous oxygen coefficient, based on TOC. The linear correlation coefficient, R^2 , for this plot, based on least squares linear regression, is 0.856.

Figure 40. Oxygen plot for the determination of Y' , the oxygen coefficient, and Ke' , the endogenous oxygen coefficient, based on NH_3 . The linear correlation coefficient, R^2 , for this plot, based on least squares linear regression, is 0.736.

TABLE 13

KINETIC COEFFICIENTS FROM BATCH TEST 1 USING A NITRIFYING SLUDGE

Coefficient	Basis			Units
	TOC	COD	NH ₃	
Y _g	0.319	1.077	5.350	mg MLVSS/mg S ^a
K _d	0.041	0.043	0.159	1/day
Y'	1.089	0.326	5.864	mg O ₂ /mg S
K _e '	0.326	0.324	0.184	mg O ₂ /mg MLVSS-day

^a S = substrate (TOC, COD or NH₃).

Observed COD and TOC removals in the batch tests ranged from 86 to 88% and 86 to 92%, respectively. Observed ammonia removals ranged from 55 to 98%. Ammonia removal determinations are complicated by the fact that thiocyanate is present in the feed at a concentration of 100 mg/l. Ammonia is a degradation product of thiocyanate. Thus, the actual ammonia removals were probably even higher than those reported.

Although nitrification was not a goal of this research program, it was gratifying to find that it could be sustained at the 1-day HRT in the Deep Column. However, nitrification was lost in the Deep Column when the loading was increased to provide HRTs of less than 1 day.

In summary, this initial batch test has shown the range of values that can be expected for kinetics of substrate removal and biomass production with the use of a nitrifying sludge.

2.8.2.2 Batch Test without Nitrification

Two batch kinetic tests were conducted with non-nitrifying sludge obtained from the Deep Column reactor on Day 289 and Day 315. The operating history of these sludges is shown in Table 14. The batch reactors were set up in a manner similar to that outlined in Section 2.2.2.1, except that feed strength was varied to provide a broader range of F/Ms. The F/Ms obtained, as well as data on the biomass and substrate concentrations from these tests are shown in Table 15. The data in Table 15 show that, as desired, a broader range of F/M was covered by the batch tests.

The plots of oxygen uptake rates measured throughout the incubation period for the six reactors used are shown in Figures 41 through 46. GRAPHER was used to fit curves to these data and the resulting equations of the curves were integrated to provide the area under the curve, O_r, which is the oxygen utilized during the incubation period. Values of O_r thus obtained are shown in Table 16 along with other reduced data from these batch tests.

TABLE 14
OPERATING HISTORY OF THE BIOMASS USED FOR NON-NITRIFYING BATCH KINETIC TESTS

Parameter	Day of Operation	
	289	315
F/M (1/day)	0.19	0.35
MLVSS (mg/l)	3400	4650
SRT (days)	9	6
HRT (hours)	10	3.6

TABLE 15
BIOMASS AND SUBSTRATE CONCENTRATIONS FROM THE
NON-NITRIFYING BATCH KINETIC TESTS

#	F/M ^a	MLVSS _o ^b	MLVSS _e	COD _o	COD _e	TOC _o	TOC _e	NH _{3o}	NH _{3e}
1	0.336	5200	5010	1749	174	440	46	552	272
2	0.460	3650	3760	1680	154	419	37	458	230
3	0.672	2400	2650	1612	121	398	34	363	105
4	0.863	3237	3520	2915	146	697	49	335	305
5	0.986	1570	1550	1549	68	378	24	276	200
6	1.240	2312	2488	2915	373	697	96	335	264

^a F/M = food-to-microorganism ratio (COD_o/MLVSS_o).

^b o = initial, e = final.

Figure 41. Plot of the oxygen uptake rate through the 24-h reaction period for the batch kinetic reactor operated at an F/M of 0.336.

Figure 42. Plot of the oxygen uptake rate through the 24-h reaction period for the batch kinetic reactor operated at an F/M of 0.460.

Figure 43. Plot of the oxygen uptake rate through the 24-h reaction period for the batch kinetic reactor operated at an F/M of 0.672.

Figure 44. Plot of the oxygen uptake rate through the 24-h reaction period for the batch kinetic reactor operated at an F/M of 0.863.

Figure 45. Plot of the oxygen uptake rate through the 24-h reaction period for the batch kinetic reactor operated at an F/M of 0.986.

Figure 46. Plot of the oxygen uptake rate through the 24-h reaction period for the batch kinetic reactor operated at an F/M of 1.240.

TABLE 16
REDUCED DATA FROM THE BATCH KINETIC TESTS

#	Mean MLVSS	dx^a	dCOD	dNH ₃	Or
1	5105	-190	1575	280	1882
2	3705	110	1526	227	1604
3	2525	250	1491	258	1208
4	3378	283	2769	30	4724
5	1630	120	1481	76	865
6	2353	83	2542	71	2222

^a d = delta, or change in x or substrate.

The biomass yield coefficient, Y_g , and the endogenous decay coefficient, K_d , were obtained with the use of Equation 17, as described above. The maintenance plots thus obtained for COD and TOC are shown in Figures 47 and 48, respectively.

The data points on Figures 47 and 48 show a marked non-linearity at F/M values above 0.67 per day. This is not too surprising since typical F/M values are in the range of 0.2 to 0.4 for conventional systems, but may be up to 0.4 to 1.5 for some high-rate processes (Metcalf and Eddy 1979). However, these high F/Ms are generally found in the food processing industries, where the organic components are non-toxic. In gasification wastewaters, many components may be toxic including ammonia, phenol, cresols, cyanide, thiocyanate and others (Slack 1979 and Valiknac and Neufeld 1978). Thus, with this synthetic wastewater, and similar gasification wastewaters, F/Ms of 0.67 should be maximums.

The oxygen coefficients, Y' and Ke' , were calculated as described above using Equation 18. The oxygen plots for COD and TOC are shown in Figures 49 and 50. The oxygen plots show good linearity for all data, and were not affected by high F/Ms.

One batch reactor, operated with an initial F/M of 0.67, was used for the determination of the reaction rate constant, K , and the growth kinetics. The decrease in COD concentration with incubation time for this reactor is shown in Figure 51. The decrease is linear with a correlation coefficient, R^2 , of 0.948 and a rate of decrease in COD of 74.8 mg/l-hr. The increase in biomass concentration with incubation time in this batch reactor is shown in Figure 52. This plot is linear from the incubation time of 4 hours to 9 hours, with an R^2 value of 0.974 and a rate of increase in biomass of 1027 mg/l-hr of MLVSS.

Figure 47. Maintenance plot for the determination of Y_g , the biomass yield coefficient, and K_d , the endogenous decay coefficient, based on COD. The linear correlation coefficient, R^2 , for this plot, based on a least squares linear regression, is 0.980.

Figure 48. Maintenance plot for the determination of Y_g , the biomass yield coefficient, and K_d , the endogenous decay coefficient, based on TOC. The linear correlation coefficient, R^2 , for this plot, based on a least squares linear regression, is 0.985.

Figure 49. Oxygen plot for the determination of Y' , the oxygen coefficient, and K_e' , the endogenous oxygen coefficient, based on COD. The linear correlation coefficient, R^2 , for this plot, based on least squares linear regression, is 0.918.

Figure 50. Oxygen plot for the determination of Y' , the oxygen coefficient, and K_e' , the endogenous oxygen coefficient, based on TOC. The linear correlation coefficient, R^2 , for this plot, based on least squares linear regression, is 0.925.

Figure 51. Decrease in COD concentration with incubation time for the batch reactor operating at an F/M of 0.67 per day.

Figure 52. Increase in biomass concentration (as MLVSS) with incubation time for the batch reactor operating at an F/M of 0.67 per day.

The pseudo first-order reaction rate constant, K , was determined by the plot shown in Figure 53 (Reynolds 1980). This figure reveals a biphasic plot of K rates with a transition period between two linear areas between 10000 and 24000 mg MLVSS-hr. The initial, higher removal rate was 0.0700 ± 0.0023 l/g MLVSS-hr (R^2 of 0.998), which occurred at substrate concentrations of 1600 to 300 mg/l as COD. The lower linear rate was 0.0022 ± 0.0004 l/g MLVSS-hr (R^2 of 0.969) and occurred during substrate concentrations of 180 to 150 mg/l as COD. The average rate was 0.0143 l/g MLVSS-hr.

The biphasic nature of COD removal is due to the heterogeneous nature of the feed. Some components of the feed are more easily degraded, or simply preferentially used, over others. The phenomena observed with respect to COD is similar to diauxy (also known as catabolite repression), which has long been known in microbiology. Diauxy, in strict terms, refers to the complete consumption of one substrate before beginning consumption of a second (Stanier et al. 1976). This probably did not occur in this case since the synwater contains 5 separate compounds that can be oxidized for energy production.

The biphasic kinetics for COD removal of this waste complicates design of commercial units since it is not known which rates can be applied to which components of the waste stream. However, since it is known that there exists an order of preference decreasing from fatty acids>phenol>thiocyanate>cyanide (Gallagher and Mayer 1985), it can be assumed that thiocyanate was the rate-limiting component of the COD. In addition, cresols are known to be inhibitory, especially the ortho isomer that was in the synwater (Hrudey and Fedorak 1988). Figure 53 shows a transition zone between 300 to 180 mg/l COD. The COD equivalent of thiocyanate in the synwater was 176 mg/l, while for o-cresol the COD equivalent present was 220 mg/l. Thus, although it is likely that thiocyanate had the major effect, it is not possible to discount o-cresol as an additional rate-limiting organic component of the wastewater.

The reaction rate coefficient was also determined by the method of Eckenfelder (Adams et al. 1981). Equation 19, as shown below was used to analyze the data from the batch test with the F/M of 0.67:

$$\frac{S_0 - S_e}{X_t} = K_1 S_e \quad (19)$$

where S_0 is the initial substrate concentration, S_e is the substrate concentration at time t , X is the biomass concentration at time t , and t is the elapsed incubation time. The equation is shown plotted in Figure 54. This plot looks very much like the mirror image of Figure 53, and reveals biphasic kinetics. In this case the highest rate for K_1 is 0.0153 ± 0.0016 per day (R^2 0.988).

The maximum specific growth rate, U_{max} , and the Michaelis-Menten half-saturation constant, K_m , were calculated via the use of Equation 20:

$$\frac{1}{U} = \frac{K_m}{U_{max}} \left(\frac{1}{S} \right) + \frac{1}{U_{max}} \quad (20)$$

where U is the specific growth rate and S is the substrate concentration in the reactor (Irvine 1980). In order to obtain representative kinetic data for an evaluation of Equation 20, U was plotted against the COD concentration at

Figure 53. Plot used for determination of K , the reaction rate constant, for the batch reactor operated at an F/M of 0.67 per day. This plot reveals biphasic kinetics of removal.

Figure 54. Eckenfelder plot for determination of the reaction rate constant for the batch reactor operating at an F/M of 0.67 per day.

the various sampling times throughout the incubation period. The results of this are shown in Figure 55. The non biodegradable fraction of the COD was determined from the intercept of the curve with the x-axis. COD values for Equation 20 were then corrected by this value. The batch data are shown plotted according to Equation 20 in Figure 56. In this figure, the y intercept is $1/U_{max}$, and the slope is K_m/U_{max} . The least squares linear correlation coefficient, R^2 , for this plot is 0.882.

The means and standard deviations for the removal of COD, TOC and ammonia for the final two combined batch tests were $91.9 \pm 2.9\%$, $90.8 \pm 2.4\%$, and $38 \pm 21\%$, respectively. Some ammonia removal did occur during these batch tests even though little or no nitrification was occurring in the Deep Column at the time the biomass was sampled. The bulk of the observed ammonia removal is likely attributable to air stripping. Vigorous aeration, as was employed, at the pH range used (8.5 to 8.9) significant quantities of ammonia should be stripable.

Table 17 shows the kinetic values obtained from the analysis discussed above. No values were computed for ammonia oxidation since the analysis of the data revealed non linearity ($R^2 < 0.5$). All kinetic values obtained, with the exception of those for K, are within usual ranges reported by other investigators for petroleum, coking or other industrial wastewaters (Reynolds 1982, Metcalf and Eddy 1979, Grady and Lim 1980). Even the highest K values determined in Figure 53 are about an order of magnitude lower than other values found in the literature. The Eckenfelder K_1 was also biphasic, but has different units from K. The highest observed K_1 was in the usual range found by other investigators. Perhaps a more typical K would have been found at a batch F/M of about 0.3 per day.

Some differences are noted when comparing kinetic values obtained from the nitrifying sludge to those from a non-nitrifying sludge (Tables 13 and 17). The major difference lies in the values reported for Y_g and K_d . These differences, although large, can probably be attributed to the active nitrification in the initial batch test. The production of biomass via nitrification could result in low estimates for endogenous decay and high estimates of biomass yield, as were found.

2.9 Microbial Ecology

An understanding of the ecological relationships among the microbes and the operating environment of a biological system is essential to predicting the performance of the system. Preliminary microbial evaluations were performed by the following: 1) isolating the principal species from the Deep Column reactor, 2) characterizing them according to standard biochemical/physical characteristics, 3) determining relative growth rates of some of these isolates and 4) comparing the enzyme compositions of these isolates and the mixture of microbes from the reactor via electrophoretic techniques.

Figure 55. Plot of the specific growth rate against the COD concentration for the batch kinetic test with an F/M of 0.67 per day. The point where the curve intercepts the x axis is the non biodegradable fraction of COD.

Figure 56. Plot for the determination of the maximum specific substrate utilization rate, U_{max} , and the Michaelis-Menten half-saturation constant, K_m . The slope is K_m/U_{max} , and the y intercept is $1/U_{max}$.

TABLE 17
KINETIC COEFFICIENTS FROM BATCH TESTING USING A NON-NITRIFYING SLUDGE

Coefficient	Basis		Units
	COD	TOC	
Y _g	0.47	2.01	mg MLVSS/mg S ^a
K _d	0.17	0.19	1/day
Y'	0.31	0.31	mg O ₂ /mg S
K _e '	0.25	1.08	mg O ₂ /mg MLVSS-day
K	0.070 ^b	--	l/g MLVSS-hr
K _l	0.0153 ^b	--	1/day
U _{max}	0.213	--	1/hour
K _m	230	--	mg/l S

^a S = substrate (COD or TOC).

^b Highest observed value of the biphasic kinetics.

2.9.1 Allozymes

2.9.1.1 Introduction

Conventional techniques that have been applied to the problem of species comparisons at the microbial level include immunochemical and dilution plating. Immunochemical methods are very sensitive, but require expensive and time consuming chemical development. Dilution plating methods assume that the numbers of the various species found after plating are a true representation of the in situ species composition and species rank. However, some species, which may represent a very small percent of the total active population of microbes, will be capable of very high growth rates in the plating media. Plating media is typically very rich, often containing as much as 1% glucose and a protein digest. While in the microbial environment, including many biological reactors, the microbes are often surviving under conditions of a very severe carbon limitation.

In order to evaluate the magnitude of the role played by microbes in the Deep Column reactor, principal isolates were tested for allozyme profiles and compared to the mixed microbial consortia in the reactor via the technique of enzyme electrophoresis. Allozymes are different forms of the same particular enzyme. For example, a very important enzyme in all living organisms is adenylate kinase (AK). This enzyme phosphorylates adenosine monophosphate molecules to the level of the diphosphate (ADP). Phosphorylated adenylates are key carriers of energy. This enzyme and others, has a certain amount of variability in its structure due to the natural rate of mutagenesis. This

variability in enzymes is often preserved at various levels in the biota, as low as individual populations in a species or subspecies. These differences have been used to construct phylogenetic trees on the origins and relatedness of species and populations (Selander et al. 1986). Differences in allo- (or iso-) enzymes as small as a single amino acid residue can be detected via differences in electrophoretic mobility (electromorphs).

Enzyme electrophoresis requires plating of the microbes, but the proportion of the isolates in the population, or species rank, is inferred from the enzyme patterns. Enzyme electrophoresis has been used by a number of investigators in genetics and systematics research in both bacteria and higher animals, but, to date, it has not been applied to microbial ecology (Selander et al. 1986, Pinero et al. 1988).

2.9.1.2 Materials and Methods

The source of bacterial strains was the Deep Column biological reactor that had been operated for a period of 10 months on a synthetic wastewater consisting of phenol, o-cresol, acetate, formate, ammonium thiocyanate, ammonium hydroxide and sodium hydroxide. The pH of the synthetic wastewater was 7.0 and the chemical oxygen demand was 1000 mg/L. A fresh sample from this reactor was homogenized for 60 s in a Waring blender to break up the bacterial floc into individual cells. The homogenate was then serially diluted and spread in triplicate onto a plating media consisting of 3 g trypticase soy broth (BBL), 15 g agar (Difco), and 200 ml of synthetic wastewater diluted to 1. The plates were incubated at 30°C for 3 days. The total number of colonies was determined on the basis of the dilution, which resulted in between 30 and 300 colonies per plate. Morphotypes were selected from these plates on the basis of colony size, shape, color, and consistency. The morphotypes were picked to trypticase soy agar (BBL) slants for further characterization.

Motility, indole production and nitrite reduction was determined using MI media (BBL) with added agar (2%) to make it semisolid. Indole was tested for with freshly prepared Kovac's reagent and nitrite reduction was tested for using the sulfanilic acid and N-(1-Naphthyl)-ethylenediaminedihydrochloride method (Smibert and Krieg 1981). Gram stains were performed when the cultures were in the exponential growth phase (18 hrs) and cell size, morphology and gram reaction were noted. Cells for lysates were prepared by inoculating 150 ml of trypticase soy broth (BBL) in a 250-ml Erlenmeyer flask with the isolates. The cultures were incubated with shaking (1100 rpm gyratory) at room temperature for about 48 h. After incubation the cultures were cooled on ice, pelleted by centrifugation at 10,000 x g for 10 minutes at 4°C. The pellets were re-suspended with 2-3 ml of ice-cold Tris-EDTA-NADP buffer (10mM-1mM-0.5mM, pH 6.8). The cells were sonicated with a Branson model S75 sonicator at 6.5-7 amps for 30-40 s using a microtip and ice bath cooling. The sonicated suspension was clarified by centrifugation at 28,000 x g for 20 minutes. The resulting lysate was collected and stored frozen (-70°C) until needed.

Horizontal slab starch gels were prepared and operated essentially as described by Selander et al. (1986). Gels were prepared by mixing 48 g of starch (Connaught Laboratories) with 420 mls of the appropriate gel buffer. Gel and electrode buffers used are shown in Table 18. The starch-buffer mixture was boiled, degassed and poured into a 450-ml, 9- by 120- by 210-mm

TABLE 18
BUFFER SYSTEMS FOR ELECTROPHORESIS OF BACTERIAL ENZYMES

System	Electrode buffer	Gel buffer
A	Tris-Citrate pH 8.0 83.2 g/L Tris 33.09 g/L citric acid	Tris-Citrate pH 8.0 (electrode buffer diluted 1:29)
B	Tris-Citrate pH 6.3 27.0 g/L Tris 18.07 g/L citric acid	Tris-Citrate pH 6.7 0.97 g/L Tris 0.63 g/L citric acid
C	Borate pH 8.2 18.5 g/L boric acid 2.4 g/L NaOH	Tris-Citrate pH 8.7 9.21 g/L Tris 1.05 g/L citric acid

plexiglass gel mold. The solidified gel was cooled to 4°C prior to loading. Gels were used within 12 hours of preparation. Slits were cut into the center of the gels for insertion of lysate-impregnated wicks. Wicks were cut from Whatman #3 filter paper (3 by 9 mm) were dipped into freshly thawed lysate, blotted and inserted into the slit on the gel. Loaded gels were electrophoresed for appropriate time periods ranging from 4 to 5 hours at 75 mA at 4°C to prevent overheating of the gel and subsequent enzyme damage.

After electrophoresis the gels were sliced and stained according to protocols described by Selander et al. (1986). Since only 11 samples were being evaluated, and 26 slots were available on each gel, two sets of samples were run per gel. Each gel was sliced horizontally 3 times, resulting in a total of 6 slices per gel. Staining solutions were incubated with the gel slices until good band visualization was obtained or for a maximum of 18 h. Electromorphs or allozymes were scored by designating the bands with lower case letters from the anode to the cathode.

2.9.1.3 Results

Table 19 shows the various enzyme and buffer system combinations that were used. The majority of the enzymes tested are in central metabolic pathways that are present in nearly all living organisms. Thus, the absence of a reaction for an enzyme in a particular isolate is probably a function of the following: 1) inadequate buffer system, 2) failure of the staining technique, 3) inappropriate electrophoresis conditions, which may not separate the enzyme and keep it in the used portion of the gel, or 4) inadequate enzyme concentration (below the level of detection under the conditions used).

TABLE 19
BUFFER SYSTEMS AND ENZYME STAINS USED

Buffer System	Enzymes
A	ADH, AK, EST, FUM, GDH, G6P, IDH, IDH, LDH, ME, PEP, PGI
B	ADH, FUM, IDH, MDH, PGI, SOD,
C	ADH, FUM, G6P, LDH, PEP, SOD,

ADH = alcohol dehydrogenase	IDH = isocitrate dehydrogenase
AK = adenylate kinase	LDH = lactate dehydrogenase
EST = esterase	ME = malic enzyme
FUM = fumerase	PEP = dipeptidase
GDH = glutamate dehydrogenase	PGI = phosphoglucoisomerase.
G6P = glucose-6-phosphate dehydrogenase	

Table 20 shows a listing of microbiological characters for the various isolates. These data show that each isolate is different, although not necessarily at the species level. Thus, a comparison of allozymes should be valid for the purposes intended. Tables 2. and 22 show the allozyme profiles obtained for the isolates and the consortia from which they were isolated. Quite a few of the enzymes did not visualize under the conditions used. Buffer system A produced the best results, with respect to the numbers of enzymes visualized.

2.9.1.4 Discussion

Although the data do show the presence of electromorphs or purported allozymes for many of the tested enzymes, the undetection of the enzyme(s) among either individual isolates or the consortia precludes the intended use of the data. Actual allozymes may not even be present, as post-translational modification of the enzyme may result in electromorphs from otherwise identical gene products. The consortia undoubtedly contained a number of microbes that were not isolated and compared. For example, the consortia contained nitrifying bacteria, which, because of their autotrophy and slow growth rate, are exceedingly difficult to isolate and grow. Other similar microbes may be a part of the consortia and prevent utilization of this technique as planned.

2.9.2 Growth Rate Comparisons

2.9.2.1 Introduction

Growth kinetics were evaluated on some of the microbial isolates to establish the relative roles of these microbes in the reactor. Idealized growth kinetics exhibit five generally distinct phases of growth. In the initial phase, occurring between inoculation and the onset of exponential growth, the microbes are preparing for growth by synthesizing the required enzymes and building block molecules. The length of the initial or lag phase

TABLE 20
MICROBIOLOGICAL CHARACTERS OF THE ISOLATES

Isolate	Colony Size (mm)	Colony Color	Cell Size (u)	Nitrite Reduction	Indole Production
1	3	W	3.3 x 0.7	+	-
2	2	C	0.5 x <0.5	-	-
3	1	W	1.0 x 0.4	-	-
4	3	W	2.0 x 0.6	+	-
5	4	W	2.0 x 0.7	+	-
6	2	G	2.0 x 0.2	+	+
7	0.4	W	1.0 x 0.5	+	-
8	2	W	2.0 x 0.8	+	-
9	1.5	Y	1.2 x 0.5	-	-
10	1.3	W	2.7 x 0.5	-	+/-

W = white
C = cream
G = gold
Y = yellow
+/- = weakly positive

TABLE 21
ALLOZYME PROFILES FOR THE BACTERIAL ISOLATES USING BUFFER SYSTEM A

Isolate	ADH	AK	EST	FUM	GDH	IDH	ME	MDH	PEP	PGI
1	b	-	abc	-	-	b	-	a	b	bce
2	-	c	-	-	b	-	-	-	-	-
3	-	-	-	a	-	-	-	-	b	-
4	b	b	-	-	-	a	-	a	b	c
5	a	ab	-	-	b	c	-	-	d	d
6	-	-	-	-	b	-	-	-	-	-
7	-	-	-	-	a	d	-	a	af	-
8	b	c	-	a	-	d	a	b	c	c
9	-	-	-	-	b	-	-	-	-	-
10	-	-	-	-	-	-	-	-	-	-
consortia	-	-	-	a	-	-	a	a	abce	abde

TABLE 22
ALLOZYME PROFILES FOR THE BACTERIAL ISOLATES USING BUFFER SYSTEMS B AND C

Isolate	Buffer System B	Buffer System C
	----- IDH	----- ADH
1	-	-
2	b	-
3	-	-
4	-	-
5	a	-
6	-	a
7	-	-
8	-	-
9	a	-
10	-	-
consortia	-	-

is dependent on several factors including: 1) the size of the inoculum, 2) the capability of the microbes to degrade the available substrate, 3) temperature, 4) the presence of inhibitory components, and 5) mixing and supply of nutrients. Following lag phase there is a small transition period after which exponential growth begins. During exponential growth the biomass concentration changes very rapidly with doubling times dependent on the microbe and abiotic factors as described for the lag phase. Doubling times may range from as low as 20 minutes for *Escherichia coli* to many hours for slow growing microbes.

As substrate or other nutrients become limiting, or as inhibitory components accumulate (often by-products of metabolism), growth slows. The stationary phase is essentially a resting stage during which growth and death are roughly equal. Microbes in this stage of growth are utilizing internal stores of energy and/or degrading excess cellular components. Sometimes during growth with mixed substrates, additional growth surges are noted during stationary phase, which delay the onset of death. This phenomenon has been termed diauxy and is attributed to the fact that when faced with multiple substrates, a microbe will not necessarily degrade all of them simultaneously, but will usually degrade them sequentially in order of easiest to most difficult to degrade. Diauxy explains why some carbon sources break through a reactor before others when a reactor is heavily loaded with mixed substrates. Similarly, under sudden stress, rather than observing a proportional decrease in removal of all available substrates, the more difficult to degrade are found. This can have profound consequences when the more difficult to degrade components are highly regulated compounds.

Following the stationary phase another short transition period is usually found, followed by a period of exponential death. In some cases a short growth spurt is observed during the death phase, as some microbes are capable of growth on components released during death of other microbes. It is important

to understand that when describing the growth kinetics of microbial systems, the data represent an average value. At any one time microbes can be found that are in all phases of growth (asynchronous growth).

Many bioreactors used for wastewater treatment, especially activated sludge systems, are operated in the mid- to late-stationary phase. This is a consequence of the desirability of process stability and of the limiting amounts of carbon available. Plug flow reactors, however, generally operate closer to the exponential phase.

2.9.2.2 Materials and Methods

Growth kinetics of the isolates were analyzed by inoculating a liquid media consisting of 12.5% of full-strength synthetic feed. One-tenth of a ml of a 24-hour culture of each isolate, grown in trypticase soy broth (BBL), which was assumed to be in the exponential phase of growth, was inoculated into 150 mls of media in a 250-ml nephelometric flask. The inoculated flasks were incubated at room temperature with gyratory shaking at 100 rpm. Periodic measurements of absorbance were made by inserting the special arm of the nephelometric flask into a spectrophotometer set at 660 nm. Measurement of absorbance at low culture densities (<1.1) is a direct measure of biomass for microbes that are: 1) non-filamentous, 2) not highly colored, and 3) do not result in profound changes in morphology (Koch 1981). Thus, the absorbance readings may be used for a comparison of relative changes in biomass over time (growth kinetics).

2.9.2.3 Results and Discussion

The total bacterial count performed for the isolation of the bacteria from the Deep Column resulted in an estimate of 1.5×10^8 colony-forming units (CFU)/ml. The assumption is that each CFU represents a single viable bacterium. However, in a poorly mixed sample a CFU may represent two or a small cluster (microcolony) of bacteria.

Table 23 shows the length of the lag period, the growth rate, as absorbance units/hr during exponential phase, the R^2 value for the least squares linear estimate of growth during the exponential phase, and the growth pattern observed. Figures 57 through 62 show the growth data for the isolates. Isolates 6 and 9 were lost after the initial characterization and allozyme analysis. Isolates 8 and 10 were not subjected to growth rate analysis due to time constraints.

The isolates for which growth kinetics were analyzed showed three patterns: 1) a short lag period followed by rapid growth, 2) a long lag period followed by rapid growth, and 3) a long lag period followed by very slow growth. These patterns can be interpreted as follows: 1) the isolate was well adapted to the substrate (probably most important in reactor zones with high concentrations (feed end)); 2) the isolate was somewhat inhibited by the test substrate concentrations (probably most important at somewhat lower substrate concentrations than used with Isolate 1); and 3) the isolate was inhibited by the test substrate concentrations and probably lacking an essential nutrient. Microbes displaying Pattern #3 probably are important at the effluent end of the reactor. Moreover, these microbes probably rely on other microbes to supply substrates they can use (metabolic by-products) or trace nutrients such as vitamins or iron-transport proteins (siderophores).

TABLE 23

RELATIVE LAG PERIODS AND GROWTH RATES FOR ISOLATES FROM
THE DEEP COLUMN REACTOR UNDER BATCH CONDITIONS

Isolate	Lag Period (hours)	Growth Rate (A_{660}/hr)	R^2	Growth Pattern
1	13	0.0080	0.974	2
2	7	0.0132	0.999	1
3	10	0.0006	0.763	3
4	8	0.0070	0.977	1
5	6	0.0055	0.945	1
7	10	0.0007	0.846	3

Figure 57. Batch growth curve for Isolate 1 from the Deep Column reactor.

Figure 58. Batch growth curve for Isolate 2 from the Deep Column reactor.

Figure 59. Batch growth curve for Isolate 3 from the Deep Column reactor.

Figure 60. Batch growth curve for Isolate 4 from the Deep Column reactor.

Figure 61. Batch growth curve for Isolate 5 from the Deep Column reactor.

Figure 62. Batch growth curve for Isolate 7 from the Deep Column reactor.

2.9.3 Summary of Microbial Ecology Investigations

The allozyme data failed to provide the desired information. Apparently the technique lacks the sensitivity to pick up all of the various allozymes present in individual and mixed cultures. Moreover, the method requires isolation of component species of the consortia, which can prove difficult. Growth rate data, on the other hand, may provide a better understanding of the roles of the microbes in the consortia.

It would prove interesting and would probably provide a better understanding of the roles of the microbes to perform a more detailed analysis of their roles in the bioreactor. Included among the desired analyses should be determination of the growth kinetics of individual isolates at various strengths of feed, growth kinetics of the isolates mixed together, and analysis of contaminant-specific removal kinetics. An alternate technique to allozyme profiles that should provide direct evidence of species proportions in the bioreactor is desired. One method that may fulfill this need is the use of DNA probes. This method would still require isolation and growth of the individual components, but it is much more sensitive, and with the use of multiple probes, it can be very specific.

An alternate method is the use of immunochemical methods. This method also requires that the species be isolated and specific antibodies against them be made. These antibodies are then tagged with fluorescent labels. The tagged antibodies can then be reacted with an aliquot of reactor liquor and multiple species composition can be viewed under a fluorescent microscope. All of these techniques are time-consuming, expensive, and beyond the scope of this research.

2.10 Conclusions

Reliable estimates of reaction rate constants have not been obtained as a result of difficulties with obtaining substrate and biomass differences with reactor length in continuous operation. Rates obtained via batch methods are relatively low and biphasic, indicating inhibition and/or diauxy. Implications for biphasic kinetics on actual operations are not known. Despite the disappointing results with rate constants, performance of the unit was excellent. The unit was very stable, required very little maintenance and gave consistent removals. At moderately high HRTs (about 1 day) reasonable quantities of nitrification could be sustained.

The performance obtained at the 2.16-hour HRT, the lowest attained, revealed a nonsteady-state MLVSS of 5000 to 5500 mg/l and COD removals of 90 to 96% with an inhibitory wastewater. This is excellent performance in any treatment system.

Overall, the concept of a plug flow, pure oxygen system has been tested on the pilot scale, preliminary kinetic evaluations have been obtained, and performance at HRTs of from 2.6 days to 2.16 hours has been demonstrated. This concept appears to be viable for applications that have oxygen available. Systems could, with reduced efficiency, be operated with air instead of oxygen. Pilot-scale comparisons with air should be conducted to demonstrate performance.

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APPENDIX A
COMPUTER PROGRAMS FOR KINETIC ANALYSIS

Several computer programs have been written for the analysis of kinetic data obtained during the continuous operation of the Deep Column reactor. The objectives in writing these programs were two-fold: first, to simplify the analysis of the data, and secondly, to provide a means of evaluating the effects of changes in process variables quickly and easily. The programs have been written in Basic and are described below along with the assumptions and equations associated with them.

Program 1, shown below, calculates the reaction rate constant, K, for the Deep Column reactor. This program uses a modification of Equation A-1, shown below (Benfield and Randall 1980):

PROGRAM 1

```

10  REM THIS PROGRAM CALCULATES THE REACTION RATE CONSTANT FOR THE
20  REM PURE OXYGEN PLUG FLOW DEEP COLUMN REACTOR
30  REM K = REACTION RATE CONSTANT
40  REM T = HYDRAULIC RETENTION TIME
50  REM D = DIFFUSIVITY CONSTANT
60  REM C1 = INFLUENT CONCENTRATION
70  REM C2 = EFFLUENT CONCENTRATION
80  REM A = SQR(1 + 4*K*T*D)
90  PRINT "ENTER THE HYDRAULIC RETENTION TIME IN HOURS";
100 INPUT T
110 PRINT "ENTER THE DIFFUSIVITY CONSTANT";
120 INPUT D
130 PRINT "ENTER THE INFLUENT CONCENTRATION IN MILLIGRAMS/LITER";
140 INPUT C1
150 PRINT "ENTER THE EFFLUENT CONCENTRATION IN MILLIGRAMS/LITER";
160 INPUT C2
170 PRINT "ENTER THE TOTAL LENGTH TRAVELED IN THE COLUMN IN METERS";
180 INPUT LT
190 PRINT "ENTER THE LENGTH OVER WHICH K IS TO BE CALCULATED IN METERS";
200 INPUT LI
210 B = LT/LI
220 C4 = (C1-C2)/B
230 FOR C3 = C2 TO C1 STEP C4
240 X = EXP (1/2*D))*4*C3/C1
250 A = 1
260 I = 1
270 DEF FNF(A) = EXP(A/(2*D))*(A+1/A+2)-X
280 DEF FNG(A) = EXP(A/(2*D))*(2*D*(A^2)+2*(A^2)+3*A-2*D)/(2*D*(A^2))
290 DEF FNH(A) = EXP (A/2*D))*(A^4+2*(A^3)*D+3*(A^3)-2*A*D-A+4*D)/(2*(A^3)*D)
300 N = 25
310 WHILE(I<=N)
320     A1 = A - FNF(A)*FNG(A)/(FNG(A)^2-FNF(A)*FNH(A))
330     REM IF NOT(ABS(A1-A)<TOL)THEN
340     I = I + 1
350     A = A1
360 WEND
370 K = (A^2-1)/(4*T/B*D)
380 PRINT "THE REACTION RATE CONSTANT IS ";K;" MILLIGRAMS/(LITER*HOUR)
390 NEXT C3
400 END

```

$$\frac{S_o}{S_e} = \frac{4 a e^{(1/2)d}}{(1 + a)^2 e^{a/2d} - (1 - a)^2 e^{-a/2d}} \quad (A-1)$$

where

$$a = .1 + 4Ktd \quad \text{and} \quad d = \frac{D}{v l} = \frac{Dt}{l^2}$$

and d is the diffusivity constant or dispersion number, which has values from 0 to infinity; D is the axial dispersion coefficient (area/time); l is the reactor length; and v is the fluid velocity.

If the dispersion number is small (less than 2.0), the second term of the denominator of Equation A-1 becomes very small and this equation may be modified as an approximation, as shown in Equation A-2.

$$\frac{S_o}{S_e} = \frac{4 a e^{(1-a)/2d}}{(1 + a)^2} \quad (A-2)$$

Since the dispersion number for the Deep Column reactor has been determined to be 0.0217, Equation A-2 was assumed to be valid for estimating the K. Equation A-2 is solved for in Program 1 using Newton's fast method.

Program 2, shown below, calculates the growth yield, Yg, and the endogenous decay coefficient for the Deep Column reactor. This program requires two sets of removal and biomass data to be obtained during steady state at different solids retention times (inverse of the growth rate). The equation used to solve for Yg and Kd is shown as Equation A-3.

$$\frac{1}{\theta c} = -K_d + Y_g \frac{(S_o - S_e)}{X_o} \quad (A-3)$$

where θc is the solids retention time ($1/\theta c$ = growth rate), X is the biomass concentration (MLVSS), θ is the hydraulic retention time, Kd is the endogenous decay coefficient and Yg is the biomass yield coefficient.

When $1/\theta c$ is plotted as a function of $(S_o - S_e)/X_o$, the result is a straight line with a slope of Yg and a y intercept of -Kd (Grady and Lim 1980).

PROGRAM #2

```

10  REM THIS PROGRAM CALCULATES THE TOTAL GROWTH YIELD AND MICROBIAL DECAY
20  REM COEFFICIENT FOR A PLUG FLOW DEEP COLUMN REACTOR WHEN DATA IS KNOWN
30  REM FOR TWO DIFFERENT STEADY STATE CONDITIONS
40  REM U = SPECIFIC GROWTH RATE
50  REM SA = SLUDGE AGE
60  REM S1 = INFLUENT SUBSTRATE CONCENTRATION
70  REM S2 = EFFLUENT SUBSTRATE CONCENTRATION
80  REM Y = GROWTH YIELD

```



```

90  REM X = BIOMASS CONCENTRATION
100 REM Q = SPECIFIC RATE OF SUBSTRATE REMOVAL
110 REM F = INFLUENT FLOW RATE
120 REM V = VOLUME OF REACTOR
130 REM T = HYDRAULIC RETENTION TIME
140 PRINT "THIS PROGRAM CALCULATES THE TOTAL GROWTH YIELD AND MICROBIAL"
150 PRINT "DECAY COEFFICIENT FOR A PLUG FLOW DEEP COLUMN REACTOR WHEN DATA"
160 PRINT "IS KNOWN FOR TWO DIFFERENT STEADY STATE CONDITIONS."
170 PRINT
180 PRINT "ENTER THE FOLLOWING VALUES FOR THE FIRST SET OF DATA"
190 PRINT
200 PRINT "ENTER THE INFLUENT SUBSTRATE CONCENTRATION IN MG/LITER";
210 INPUT S1
220 PRINT "ENTER THE EFFLUENT SUBSTRATE CONCENTRATION IN MG/LITER";
230 INPUT S2
240 PRINT "ENTER THE HYDRAULIC RETENTION TIME IN HOURS";
250 INPUT T
260 PRINT "ENTER THE BIOMASS CONCENTRATION IN MILLIGRAMS/LITER";
270 INPUT X
280 PRINT "ENTER THE SLUDGE AGE IN HOURS";
290 INPUT SA
300 REM PRINT "ENTER THE VOLUME OF THE REACTOR IN LITERS";
310 REM INPUT V
320 REM PRINT "ENTER THE INFLUENT FLOW RATE IN LITERS/HOURS";
330 REM INPUT F
340 REM T = V/F
350 REM Q = F*(S1-S2)/(V*X)
360 REM Q = (S1-S2)/(X*T)
370 REM U = 1/SA
380 Q1 = (S1-S2)/(X*T)
390 U1 = 1/SA
400 PRINT
410 PRINT "ENTER THE FOLLOWING VALUES FOR THE SECOND SET OF DATA"
420 PRINT
430 PRINT "ENTER THE INFLUENT SUBSTRATE CONCENTRATION IN MG/LITER";
440 INPUT S1
450 PRINT "ENTER THE EFFLUENT SUBSTRATE CONCENTRATION IN MG/LITER";
460 INPUT S2
470 PRINT "ENTER THE HYDRAULIC RETENTION TIME IN HOURS";
480 INPUT T
490 PRINT "ENTER THE BIOMASS CONCENTRATION IN MILLIGRAMS/LITER";
500 INPUT X
510 PRINT "ENTER THE SLUDGE AGE IN HOURS";
520 INPUT SA
530 REM PRINT "ENTER THE VOLUME OF THE REACTOR IN LITERS";
540 REM INPUT V
550 REM PRINT "ENTER THE INFLUENT FLOW RATE IN LITERS/HOUR";
560 REM INPUT F
570 REM T = V/F
580 REM Q = F*(S1-S2)/(V*X)
590 REM Q = (S1-S2)/(X*T)
600 REM U = 1/SA
610 Q2 = (S1-S2)/(X*T)
620 U2 = 1/SA

```

```

630 PRINT
640 M = (Q2-Q1)/(U2-U1)
650 IF U2 > U1 GOTO 670
660 M = (Q1-Q2)/(U1-U2)
670 YT = 1/M
680 PRINT "THE TOTAL GROWTH YIELD FOR THE REACTOR IS ";YT
690 KD = Q1 - M*U1
700 PRINT
710 PRINT "THE MICROBIAL DECAY COEFFICIENT IS ";KD;" PER HOUR"
720 END

```

Program 3, shown below, is used to calculate the maximum specific growth rate (U_{max}), and the saturation constant (K_m), where K_m is the substrate concentration when U_{max} is one-half.

$$\frac{1}{(S_o - S_e)/\phi X} = \frac{K_m}{U_{max}} \frac{1}{Q S_o / X V} + \frac{1}{U_{max}} \quad (A-4)$$

In Equation A-4, F is the flow rate of feed and V is the reactor volume. $Q S_o / X V$ is equal to the F/M ratio for the reactor. When $1/(S_o - S_e)/\phi X$ is plotted against $1/Q S_o / X V$, the result is a straight line with a slope of K_m/U_{max} and a y intercept of $1/U_{max}$ (Kincannon and Stover 1984).

PROGRAM #3

```

10 REM THIS PROGRAM CALCULATES THE MAXIMUM SPECIFIC GROWTH RATE FOR A
20 REM PLUG FLOW DEEP COLUMN REACTOR WHEN DATA IS KNOWN FOR TWO DIFFERENT
30 REM STEADY STATE CONDITIONS
40 REM U = SPECIFIC GROWTH RATE
50 REM UM = MAXIMUM SPECIFIC GROWTH RATE
60 REM SA = SLUDGE AGE
70 REM S1 = INFLUENT SUBSTRATE CONCENTRATION
80 REM S2 = EFFLUENT SUBSTRATE CONCENTRATION
90 REM V = VOLUME OF REACTOR
100 REM F = INFLUENT FLOW RATE
110 REM T = HYDRAULIC RETENTION TIME
120 REM X = BIOMASS CONCENTRATION
130 REM KS = SATURATION CONSTANT
140 PRINT "THIS PROGRAM CALCULATES THE MAXIMUM SPECIFIC GROWTH RATE FOR A"
150 PRINT "PLUG FLOW DEEP COLUMN REACTOR WHEN DATA IS KNOWN FOR TWO"
160 PRINT "DIFFERENT STEADY STATE CONDITIONS."
170 PRINT
180 PRINT "ENTER THE FOLLOWING VALUES FOR THE FIRST SET OF DATA"
190 PRINT
200 PRINT "ENTER THE INFLUENT SUBSTRATE CONCENTRATION IN MG/LITER";
210 INPUT S1
220 PRINT "ENTER THE SLUDGE AGE IN HOURS"
230 INPUT SA
240 PRINT "ENTER THE VOLUME OF THE REACTOR IN LITERS";
250 INPUT V
260 PRINT "ENTER THE INFLUENT FLOW RATE IN LITERS/HOURS";

```

```

270 INPUT F
280 PRINT "ENTER THE BIOMASS CONCENTRATION IN MG/LITER";
290 INPUT X
300 REM T = V/F
310 REM PRINT "ENTER THE HYDRAULIC RETENTION TIME IN HOURS";
320 REM INPUT T
330 PRINT
340 U1 = 1/SA
350 A1 = (F*S1)/(X*V)
360 X1 = 1/A1
370 Y1 = SA
380 PRINT "ENTER THE FOLLOWING VALUES FOR THE SECOND SET OF DATA"
390 PRINT
400 PRINT "ENTER THE INFLUENT SUBSTRATE CONCENTRATION IN MG/LITER";
410 INPUT S1
420 PRINT "ENTER THE SLUDGE AGE IN HOURS";
430 INPUT SA
440 PRINT "ENTER THE VOLUME OF THE REACTOR IN LITERS";
450 INPUT V
460 PRINT "ENTER THE INFLUENT FLOW RATE IN LITERS/HOUR";
470 INPUT F
480 PRINT "ENTER THE BIOMASS CONCENTRATION IN MG/LITER";
490 INPUT X
500 REM T = V/F
510 REM PRINT "ENTER THE HYDRAULIC RETENTION TIME IN HOURS";
520 REM INPUT T
530 PRINT
540 U2 = 1/SA
550 A2 = (F*S1)/(X*V)
560 X2 = 1/A2
570 Y2 = SA
580 M = (Y2-Y1)/(X2-X1)
590 IF X2 > X1 GOTO 610
600 M = (Y1-Y2)/(X1-X2)
610 B = Y1 - M*X1
620 UM = 1/B
630 PRINT "THE MAXIMUM SPECIFIC GROWTH RATE IS ";UM;" PER HOUR"
640 KS = UM*M
650 PRINT "THE SUBSTRATE LOADING AT WHICH THE RATE OF SUBSTRATE UTILIZATION"
660 PRINT "IS ONE-HALF THE MAXIMUM RATE IS ";KS;" MG/LITER"
670 END

```

1. Program/Project Identification No. 21-MC10637	2. Program/Project Title ADVANCED WASTEWATER TREATMENT	3. Reporting Period 4/1/88 through 6/30/89
4. Name and Address University of North Dakota Energy and Mineral Research Center P.O. Box 8213, University Station, Grand Forks, ND 58202		5. Program/Project Start Date 4/1/86
		6. Completion Date 6/30/92

[illegible]

12	Remarks
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13. Signature of Recipient and Date John E. Gallagher 10/13/89	14. Signature of DOE Reviewing Representative and Date
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U.S. DEPARTMENT OF ENERGY
FEDERAL ASSISTANCE MANAGEMENT SUMMARY REPORT

1. Program/Project Identification No. DE-FC21-86MC10637	2. Program/Project Title Advanced Wastewater Treatment	3. Reporting Period 4/1/88 through 6/30/89
4. Name and Address Energy and Mineral Research Center Box 8213, University Station Grand Forks, ND 58202		5. Program/Project Start Date 4/1/86
		6. Completion Date 6/30/92

Milestone ID. No.	Description	Planned Completion Date	Actual Completion Date	Comments
A.7	Preliminary Process Design and Economic Assessment	5/88	5/88	
A.8	Final Report	5/88	5/88	
B.5	Operation with Synthetic	3/89	4/89	
B.6	Preliminary Economic Assessment	5/89		
B.7	Final Report	6/89		
C.4	Final Report	7/88	7/88	

END

**DATE
FILMED**

9 / 11 / 92