1 OF 4

Low-Rank Coal Research

**Quarterly Report
January - March 1990**

August 1990

Work Performed Under Contract No.: DE-FC21-86MC10637

**For
U.S. Department of Energy
Office of Fossil Energy
Morgantown Energy Technology Center
Morgantown, West Virginia**

**By
University of North Dakota
Energy and Environmental Research Center
Grand Forks, North Dakota**

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Morgantown Energy Technology Center
P.O. Box 880
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August 1990

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2.0 CONTROL TECHNOLOGY AND COAL PREPARATION RESEARCH

2.1 Flue Gas Cleanup

FLUE GAS CLEANUP

Quarterly Technical Progress Report
for the Period January - March 1990

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FLUE GAS CLEANUP

1.0 INTRODUCTION

The objective of the Department of Energy (DOE) Flue Gas Cleanup Program, under the direction of the Pittsburgh Energy Technology Center (PETC), is to promote the widespread use of coal. This is to be accomplished by providing the technology necessary for utilization of coal in an environmentally and economically acceptable manner. The program addresses the reduction of acid rain precursor emissions as well as developing technologies with the potential to meet more stringent emissions control requirements for SO_2 , NO_x , and particulate matter.

Activities within the Energy & Environmental Research Center's (EERC's) Cooperative Agreement Flue Gas Cleanup Project address the advanced NO_x control and fine particulate control areas of the DOE Flue Gas Cleanup Program. Specific activities involve the development of a catalytic fabric filter for NO_x and particulate control and methods to measure the cohesive strength and reentrainment potential of fly ashes relative to fine particle emissions from fabric filters.

2.0 GOALS AND OBJECTIVES

The overall objective of the catalytic fabric filter effort is the development of 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. The specific goals of the program are to develop a catalytic fabric that will provide:

- 90% NO_x removal with <25 ppm ammonia slip.
- A particulate removal efficiency of >99.5%.
- A bag/catalyst life of >1 year.
- A 20% cost savings over conventional baghouse and SCR control technology.
- Compatibility with SO_2 removal systems.
- A nonhazardous waste material.

The general objective of the fine particulate control effort is to develop methods to help characterize, control, and model fine particulate emissions from a fabric filter. Characterization efforts include the development of methods to measure the cohesive strength and reentrainment potential of fly ashes. Control and modeling efforts involve relating these parameters to the level of fine particle emissions from fabric filters. Specific goals for the next year include the following:

- Evaluate existing methods and select or develop reliable methods to measure the cohesive strength of fly ash.

- Correlate measured cohesive strength with other ash properties such as particle size, particle shape, surface area, porosity, and ash chemistry.
- Measure reentrainment potential of ash from the surface of a fly ash filter cake or bulk fly ash and relate it to the measured cohesive strength.

Specific project activities to be completed during the fourth year of the Cooperative Agreement include the following:

- Perform project planning activities and develop a detailed statement of work for the fourth year of the Cooperative Agreement (July 1, 1989, through June 30, 1990).
- Perform bench-scale catalytic fabric screening tests using actual flue gas from pulverized coal combustion.
- Initiate planning for catalytic filter bag evaluation and parametric tests.
- Review methods to measure the cohesive strength of bulk fly ash and evaluate selected methods by generating cohesive strength data for both conditioned and nonconditioned fly ash, comparing the data with other measurable fly ash properties.
- Construct a bench-scale fly ash reentrainment device to perform bench-scale tests quantifying reentrainment behavior for both conditioned and nonconditioned fly ash.

Specific project activities during the third quarter of the fourth year of the Cooperative Agreement included the following:

- Complete Task B, including the evaluation of the effects of coal type on catalyst-coated fabrics.
- Complete analysis of catalyst-coated fabric samples used for Task B testing. Specifically, determine the vanadium concentration and monosorb BET surface area for each fabric sample.
- Initiate tests using the fly ash reentrainment system.

3.0 ACCOMPLISHMENTS

3.1 Task B -- Fabric Screening Tests

3.1.1 Facilities and Procedures

To minimize the amount of construction necessary prior to testing, the 0.8-ft² fabric filter holder and oven used in Task A were used as part of the slipstream system in Task B. The slipstream sample system was designed and constructed such that a portion of the flue gas produced from a 550,000-Btu/hr pc-fired combustor (PTC) was drawn through a filter sample at the required

air-to-cloth ratio and measured using a calibrated orifice. After the filter, the flow was split three ways. One stream was sent to a sample conditioner and flue gas analyzers, a second stream was used to measure ammonia/SO₃, and the balance of the flue gas was sent to a gas pump and dry gas meter to control the total system flow. A schematic of the slipstream sample system is shown in Figure 1.

Pressure drop across the filter was measured continuously. Periodically, it was necessary to clean the filter during some of the tests. To do this, the gas flow was reversed through the filter sample, causing the dust cake to be disturbed. Although the dust was not actually removed from the filter, this approach was sufficient to keep the pressure drop at a manageable level.

The ammonia flow rate to the combustion system was determined by first measuring the total flue gas flow rate with a calibrated orifice and/or Annubar flow measuring device. Then the amount of ammonia needed was calculated, based on the initial NO_x baseline value. The inlet ammonia flow rate was controlled using a mass flow meter with an automatic controller.

Ammonia was injected into the center of the 3.625-inch diameter flue gas duct through a nozzle that consisted of a 1/4-inch stainless steel closed end tube with six 0.028-inch diameter holes around the circumference of its tip. This injection configuration along with a flue gas Reynolds number of about 29,000 provided adequate mixing of the ammonia and the flue gas prior to drawing a flue gas sample through the slipstream sample system.

To provide on-line NO_x analyses, instrumentation included two Thermo Electron Model 10 Chemiluminescent NO_x Analyzers with molybdenum converters. The approach used to determine the amount of NO_x was to monitor the NO_x after the slipstream sample system (prior to starting the ammonia injection) to establish a baseline reading. At the end of the test, the ammonia was shut off to again establish the baseline readings. An NO_x analyzer at the combustor exit was used to record fluctuations in the total NO_x concentration entering the slipstream sample system.

Other on-line gas analysis instrumentation included two Beckman Model 755 O₂ analyzers, two Dupont Model 400 SO₂ analyzers, a Beckman Model 865 CO₂ analyzer, and a Beckman Industrial Model 880 CO analyzer. The flue gas was continually sampled both prior to and following the slipstream sample system. Heat-traced line was used prior to the sample conditioners to prevent water condensation in the sample lines. All gas monitoring instrumentation were routinely calibrated with certified span gases.

Data, including gas concentrations, system temperatures, and pressures, were automatically logged by use of a Kaye data logger and circle charts. Also, backup data were routinely recorded in a log book by the operators.

Ammonia and SO₃ were measured using wet chemistry methods. Ammonia was extracted from the flue gas stream using a pump and then bubbled through dilute sulfuric acid where the ammonia was absorbed. The dissolved ammonia content was then measured using a specific ion electrode, after bringing the pH of the solution to 11 with sodium hydroxide. The total volume of flue gas sampled was measured using a dry gas meter.

Figure 1. Schematic of slipstream sample system.

SO_3 was measured using the selective condensation procedure where the flue gas is passed through a condenser at a temperature maintained between 140° and 190°F . In this range the SO_3 (sulfuric acid) is condensed while all other flue gas constituents remain in the gas phase. The condensate is then rinsed from the condenser and the SO_3 concentration determined by titration.

3.1.2 Results and Discussion

Four coals were selected for use during Task B experiments to determine the effects of coal type on the catalyst-coated fabric performance (NO_x removal efficiency and ammonia slip). These included a medium sulfur washed Illinois #6 bituminous, a high sulfur Pyro Kentucky bituminous, a Jacobs Ranch subbituminous, and a South Hallsville, Texas, lignite. The ultimate and proximate analyses for each of the coals are presented in Table 1. The washed Illinois #6 bituminous coal was the baseline coal used for the fabric screening tests reported in the October through December 1989 Quarterly Technical Progress Report.

Following the fabric screening tests, two fabrics, fabrics #2 and #13, were selected to be tested using the remaining three coals. For the first 6 hours of each test the air-to-cloth ratio was held constant at 3 ft/min. However, near the end of each test, the air-to-cloth ratio was adjusted to 2 ft/min and to 4 ft/min, respectively, for 1 hour. The ammonia/ NO_x molar ratio was 0.9 for all the tests. Table 2 summarizes the test results while firing each of the four coals for fabrics #2 and #13. The data is also represented graphically in Figures 2 through 7.

TABLE 1
ANALYSES OF COALS USED IN TASK B
(On an As-Received Basis)

	<u>Washed Illinois #6</u>	<u>Kentucky Pyro</u>	<u>Wyodak Jacobs Ranch</u>	<u>South Hallsville</u>
Coal Type	Bituminous	Bituminous	Subbituminous	TX Lignite
<u>Proximate Analysis, wt%</u>				
Moisture	13.7	5.9	23.1	36.8
Volatile Matter	32.8	31.7	33.0	23.6
Fixed Carbon	43.2	48.1	38.5	29.8
Ash	10.3	13.3	5.5	9.6
<u>Ultimate Analysis, wt%</u>				
Hydrogen	5.8	5.5	6.8	6.6
Carbon	61.0	65.6	52.5	39.8
Nitrogen	1.0	1.3	0.7	0.5
Sulfur	2.7	4.6	0.3	1.3
Oxygen (Diff.)	19.2	9.7	34.2	42.2
Ash	10.3	13.3	5.5	9.6
Heating Value (Btu/lb)	10,819	11,857	9,129	6,719

Ammonia slip measurements and SO₃ concentrations were made for each test. In addition, for the Pyro Kentucky bituminous coal, the concentration of HCl was measured due to high levels of chlorine in the coal (0.2%). As a baseline, an HCl measurement was also made using South Hallsville, which has very low chlorine content. The ammonia slip was higher than would be expected for several of the tests. Therefore, it is likely the ammonia/NO_x molar ratio was not as constant as would have been desired. There was some instability in the combustion process which resulted in NO_x readings that were ± 50 ppm, and it was not always possible to adjust the ammonia flow rate to correct for this change.

To get a more accurate indication of the SO₃ concentration in the flue gas, the ammonia was turned off during the time when the SO₃ measurements were made. During this time, the NO_x removal efficiency went to zero, as is shown in Figures 2 through 5. Although the ammonia was not on, the SO₃ concentrations were still extremely low (<2 ppm) for all the tests. This result was somewhat unexpected, especially for the high sulfur coal (3800 ppm SO₂ in the flue gas) Pyro Kentucky Bituminous. A more detailed evaluation of SO₃ measurement techniques is needed.

TABLE 2
RESULTS FROM TASK B -- EFFECTS OF COAL TYPE

Fabric Number	A/C Ratio (ft/min)	NH ₃ /NO _x Molar Ratio	NO _x Inlet (ppm)	NO _x Outlet (ppm)	NO _x Removal Efficiency (%)	Ammonia Slip (ppm)	SO ₃ Conc. (ppm)	HCl Conc. (ppm)	Particulate Removal Efficiency (%)
Washed, Illinois, #6 Bituminous									
2	2	0.9	540	58	89.3	5	2	---	99.8
2	3	0.9	535	81	84.9	7	2		
2	4	0.9	590	112	81.0	22	124		
13	2	1.1	673	34	94.9	64	4	---	99.4
13	3	1.1	686	64	90.7	58	2		
13	4	1.1	688	126	81.7	88	169		
Jacobs Ranch, Wyoming, Subbituminous									
2	2	0.9	785	59	92.5	86	<1	---	99.9
2	3	0.9	760	75	90.1				
2	4	0.9	800	90	88.8				
13	2	0.9	645	80	87.6	99	<1	---	99.9
13	3	0.9	680	105	84.6				
13	4	0.9	675	195	71.1				
South Hallsville, Texas, Lignite									
2	3	0.9	900	175	80.6	121	1	17	----
13	2	0.9	820	110	86.6	75	1	<1	99.8
13	3	0.9	810	145	82.7				
13	4	0.9	825	195	76.4				
Pyro Kentucky Bituminous									
2	2	0.9	970	93	90.4	10	1	---	99.7
2	3	0.9	930	130	86.0				
2	4	0.9	925	178	80.8				
13	3	0.9	810	170	79.0	30	1	142	96.6

Figure 2. NO_x removal efficiency as a function of time, fabric, and air-to-cloth ratio for a washed Illinois #6 bituminous coal.

Figure 3. NO_x removal efficiency as a function of time, fabric, and air-to-cloth ratio for a Jacobs Ranch subbituminous coal.

Figure 4. NO_x removal efficiency as a function of time, fabric, and air-to-cloth ratio for a South Hallsville, Texas, lignite.

Figure 5. NO_x removal efficiency as a function of time, fabric, and air-to-cloth ratio for a pyro Kentucky bituminous coal.

Figure 6. Comparison of the catalytic performance using four different coals for fabric #2.

Figure 7. Comparison of the catalytic performance using four different coals for fabric #13.

As was expected, the HCl concentration in the flue gas during the tests using Pyro Kentucky bituminous coal was high, 142 ppm. The calculated value for a coal with a chlorine content of 0.2% burned in the EERC PTC is 149 ppm. In addition, two HCl measurements were made during the tests burning the South Hallsville, Texas, lignite, which has essentially zero chlorine content. The first test using fabric #2 verified this, as the measured concentration was <1 ppm. However, the HCl concentration in the flue gas for the second South Hallsville test using fabric #13 was 17 ppm. This test was completed following a Pyro Kentucky test, and therefore the higher HCl value may have been a result of residual HCl absorbed on fly ash adhering to the combustor wall or flue gas duct.

As is shown in Figure 6, it appears that NO_x removal efficiency with fabric #2 was similar (85% to 90%) for three of the four coals fired in the pilot-scale combustor. The exception was observed when firing the South Hallsville, Texas, lignite. Although an obvious explanation for this result (80% NO_x removal efficiency and 121 ppm ammonia slip) is not apparent, EERC believes that the filtration characteristics of the South Hallsville fly ash may have contributed to the observed result. Specifically, South Hallsville, Texas, lignite is known to produce an ash difficult to collect in a fabric filter (1). A large number of pinholes was present in the dust cake at the conclusion of the test. Pinholes may result in localized areas of very high air-to-cloth ratios which, depending on the number and size of the pinholes, can limit contact between the flue gas and the catalyst, resulting in decreased NO_x removal efficiency.

For fabric #13 (shown in Figure 7) the results using South Hallsville, Texas, lignite were more successful as excessive pinholing did not occur. However, the NO_x removal efficiency was somewhat lower, about 83% compared to 86% and 90% for the Jacobs Ranch and Illinois #6 coals, respectively, again indicating that some coals appear to have an effect on catalyst-coated fabric performance. The results using the Pyro Kentucky bituminous coal with fabric #13 are suspect due to an upset in the pilot-scale combustion system. Excessive slagging resulted in an unstable flame in the burner, causing an early shutdown of the test.

Figures 2 through 5 compare the NO_x removal efficiency as a function of time for fabrics #2 and #13 while firing the four different coals. With the possible exception of the South Hallsville, Texas, lignite (Figure 4), the NO_x removal efficiency was greater for fabric #2 than for fabric #13.

Surface area and vanadium concentrations were determined for each of the fabrics tested. The surface area was measured using a BET monosorb surface area analyzer. The vanadium concentration on the fabric was determined by first weighing a small amount of the catalyst-coated fabric, and then dissolving it in a solution of ultrapure hydrofluoric acid followed by a solution of ultrapure aqua regia. The liquid was then diluted to 100 mL with deionized water and analyzed for vanadium using atomic absorption techniques.

Table 3 presents the surface area and vanadium concentration data for each of the fabrics tested. Both were measured prior to exposure to the flue

gas and after completion of the reactivity tests. In all cases, exposure of the fabric samples to flue gas resulted in a substantial decrease in surface area. Although the vanadium concentration on the fabric did tend to show a decrease after exposure to flue gas, for several of the fabrics (#2, #5, #14), the change was essentially zero. Figure 8 shows surface area as a function of vanadium concentration for both the exposed and unexposed fabrics. The two plots are anchored at the theoretical surface area calculated for a blank fabric. Both the graph and table tend to support the conclusion that a large percentage of the catalyst pore structure was located at or near the surface. During use, some of the catalyst sluffs off at the surface, resulting in a greater percentage decrease in surface area.

BET surface area data for the fabric samples exposed to flue gas are plotted as a function of ammonia slip in Figure 9. The figure includes data from Task A, as presented in the previous annual report (2). Task B data only included the fabrics that were tested at an ammonia/ NO_x molar ratio of 0.9 and at an air-to-cloth ratio of 2 ft/min, so that comparisons can be made to Task A results. Although there is some data scatter, the conclusions that were made previously appear to be valid. Fabric samples having a surface area of 6 to 9 m^2/g resulted in low ammonia slip (<10 ppm). Surface area values between 4 and 6 m^2/g resulted in moderate ammonia slip (10 to 50 ppm). Below 4 m^2/g , the ammonia slip values increased exponentially.

Although other factors such as weave texturization may also be important, Figure 10 shows that the concentration of catalyst on the fabric and the available surface area are directly proportional to NO_x removal efficiency. It is unclear as to why the surface area was so low for fabric #7 in relationship to the NO_x removal efficiency, as this was not the case when vanadium concentration was plotted as a function of NO_x removal efficiency.

Table 3 shows that two different samples of fabrics #2 and #13 were used in Task B. The first fabric samples were used to complete the fabric screening tests while firing the Illinois #6 coal and tests with the Jacobs Ranch subbituminous coal. However, after completing the two tests with the Jacobs Ranch coal, the fabrics were no longer usable due to excessive fraying. It was then necessary to obtain new fabric samples from Owens-Corning Fiberglas. There was a measurable difference in catalyst concentration between the first and second fabric samples. However, after the fabrics had been exposed to flue gas, the surface areas were similar. The issue of quality control, with respect to the coating process, has not been specifically addressed in any of the work completed by EERC. A joint review of the recent data by EERC and Owens-Corning Fiberglas would be appropriate, with respect to coating process and quality control issues.

3.2 Task E - Fine Particulate Characterization

Work was completed this past quarter in three areas in support of Task E. Extensive testing was completed with the Cohetester instrument, which provides a direct measurement of the tensile strength of a bulk powder such as fly ash. Testing was also completed with a Powder Characteristics Tester to determine aerated and bulk porosities for some fly ash samples, and initial

TABLE 3

VANADIUM CONCENTRATION AND BET SURFACE AREA
FOR EACH OF THE CATALYST-COATED FABRICS TESTED^{a,b,c}

Fabric No.	Vanadium Concentration			BET Surface Area		
	Unexposed (mg/g)	Exposed (mg/g)	Change (%)	Unexposed (m ² /g)	Exposed (m ² /g)	Change (%)
Blank	0.03	---	---	0.56	---	---
2	9.1	9.0	1.1	9.50	6.19	34.8
2	8.4	8.3	1.2	10.68	5.11	52.2
3	4.7	3.7	21.3	3.31	1.54	53.5
4	4.7	4.2	10.6	4.28	2.02	52.8
5	5.5	5.4	1.8	5.79	3.74	35.4
7	7.6	6.3	17.1	6.62	2.74	58.6
13	6.8	6.1	10.3	5.76	4.04	29.9
13	8.4	8.0	4.8	6.52	4.00	38.7
14	3.4	3.6	-5.9	3.09	1.90	38.5
15	7.7	5.7	26.0	6.24	3.79	39.3

^aUnexposed and exposed refer to exposure to flue gas.

^bVanadium concentration is expressed as mg₂ vanadium per g of coated fabric.

^cFabric BET surface area is expressed as m² per g of coated fabric.

Figure 8. Vanadium concentration of both the exposed and unexposed catalytic fabrics as a function of surface area.

Figure 9. Surface area as a function of ammonia slip for both Task A and Task B results.

Figure 10. NO_x removal efficiency as a function of Vanadium concentration and surface area.

tests were completed with the recently constructed reentrainment device to measure K_2 for several dusts. Some of these results were presented in a paper entitled "Enhancing Baghouse Performance with Conditioning Agents: Basis, Developments, and Economics" by S.J. Miller and D.L. Laudal, at the Eighth EPA/EPRI Symposium on the Transfer and Utilization of Particulate Control Technology, which was held March 20-23, 1990, in San Diego, CA.

A schematic of the Cohetester is shown in Figure 11. The Cohetester measures the horizontal tensile force of the powder bed formed in the split cell consisting of 2 semicircles. There is no contact and thus no friction between the cell components during the testing sequence. An ash sample is placed in a 5-cm diameter cell split into two halves. One half of the cell is stationary, and the other half is suspended such that the cell can be pulled apart with minimal force when no powder is in the cell. When the powder bed is pulled, it is extended in the same direction as the tensile force. The Cohetester measures this displacement of the bed as well as the tensile force simultaneously, and the fracture curve is plotted on an X-Y recorder. Multiple tests at different compaction forces provide information to plot cohesive tensile strength as a function of porosity for a given ash. An example of the fracture curves is shown in Figure 12.

Cohetester tests were completed on previously collected fly ash samples, including those from tests in which ammonia and SO_3 were used as conditioning agents upstream of a baghouse and from tests without conditioning. Analysis of samples with the Cohetester should help to provide a better understanding of, and an explanation for, the reduced particulate emissions and baghouse pressure drop that occurred with conditioning. Three composite samples of baghouse hopper ash were previously collected during each 500-hour baseline and conditioning test with Monticello coal (one composite sample per week). Cohetester results with these six samples are shown in Figure 13. From these results we can conclude that conditioning significantly increased the cohesive tensile strength for a given porosity. The range in porosities was determined by the range in compaction force, which was the same for both conditioning and baseline tests. The maximum compaction force allowable with the Cohetester resulted in a porosity of 39% for the baseline samples and 53% for the conditioned tests. Similarly, the minimum compaction force resulted in a porosity of only 51% for the baseline samples, compared to 67% for the conditioned samples. These results showed that another effect of conditioning was to greatly reduce the packing tendency of the ash.

Cohetester results for conditioned and baseline ash samples from Pittsburgh No. 8 coal are shown in Figure 14. Again, the conditioned sample had a much greater tensile strength at the same porosity, and the baseline sample has a much greater tendency to pack. While the difference between conditioned and baseline samples was obvious, there was also a difference in the cohesive curves when the Pittsburgh No. 8 and Monticello samples were compared. At the maximum compaction force, the tensile strength for the Pittsburgh No. 8 was much lower. This comparison was more easily seen in Figure 15 where both sets of data are shown in addition to Cohetester results with a Beulah fly ash. An exponential curve is fit to each data set in Figure 15. As porosity approaches 100%, the tensile strength should approach zero. Interestingly, the conditioned Monticello and Pittsburgh No. 8 data form the same approximate exponential curve, indicating that, at the same porosity,

Figure 11. Schematic of the Cohetester.

Figure 13. Cohesive tensile strength as a function of ash porosity for Monticello ash samples as measured by the Cohetester method.

Figure 12. Example of fracture curves produced with the Cohetester showing tensile strength as a function of displacement for several levels of compaction.

Figure 14. Cohesive tensile strength as a function of ash porosity for Pittsburgh No. 8 ash samples as measured by the Cohetester method.

Figure 15. Cohesive tensile strength as a function of ash porosity for Pittsburgh No. 8, Monticello, and Beulah ash samples as measured by the Cohetester method. Exponential curves are fit to each data set.

they have the same tensile strength. However, the compaction force required to attain the same porosity value is different--the Monticello sample having a greater tendency to compact. Previously measured particle-size distributions for the Monticello and Pittsburgh ashes did not indicate any significant differences in particle sizes. Therefore, the explanation for the differences in behavior between the Monticello and Pittsburgh ashes is not clear. Other possible influences include the amount of surface moisture on the particle morphology. The Beulah ash sample (BU275) data closely followed the conditioned Monticello ash, in terms of covering the same porosity range and forming the same approximate exponential curve as the conditioned samples. The Beulah ash had not been conditioned, but in previous work had shown excellent collectibility characteristics. No conditioning experiments have been done with the Beulah ash, but an interesting question is whether conditioned Beulah ash would form a tensile strength-porosity curve to the right of the baseline curve.

Porosity characteristics of the baseline and conditioned ashes were also measured with a powder characteristics tester that performs several different mechanical measurements of bulk powder, such as fly ash (3). Two of the more useful measurements appear to be the aerated and packed density which, along with particle density, provide aerated and packed porosity. The aerated porosity is obtained by sifting an ash sample through a vibrating 60-mesh screen into a 100-cc cup, so that dust overflows the cup edge. The excess dust is scraped off with a knife edge and the weight of the known volume of dust is measured to determine the bulk density. The packed density is determined by adding an extension to the cup and filling the extension with additional sifted ash. The cup with the extension is then placed in a mechanism that raises the cup about 1/2 inch and lets the cup fall against a stop. This is done once per second for a period of 3 minutes. The cup extension is then removed and the excess dust scraped off as before. There is no external compaction force on the dust layer. Compaction is caused by the natural settling that occurs as the dust is shocked. Results of these tests are shown in Table 4 for the baseline and conditioned samples. Three or four repeat tests were completed on each of the three baseline and conditioned baghouse ash samples. Standard deviations shown in Table 4 include all baseline results grouped together and all conditioned results grouped together. Although there is slightly more data variation for the conditioned samples compared to the baseline samples, the effect of conditioning on the aerated and packed densities is very clear. These data again demonstrate that the baseline ash has a high tendency to compact and that conditioning imparts to the ash a resistance to packing. It would appear that dust cake porosity might be predicted by these measurements, but enough data are not available to correlate with actual dust cake porosity. In addition, actual dust cake porosity may depend on other factors such as face velocity, fabric type, and cleaning method. Nevertheless, the aerated and packed porosity measurements would appear to be useful methods in helping to predict baghouse pressure drop. However, further experimentation is needed to determine the effect of relative humidity on the absolute values of both packed and aerated porosities.

K_2 was measured for each of the three composite baghouse hopper ash samples for the baseline and conditioning tests. To determine K_2 , a 150 g sample of ash was placed in the reentrainment cell, a cylinder with a porous bottom, and the pressure drop across the ash layer was measured at constant

TABLE 4
AERATED AND PACKED POROSITY a,b

Ash type	Aerated porosity (%)	σ	n	Packed porosity (%)	σ	n
Monticello baseline	62.6	0.6	9	40.1	0.8	9
Monticello conditioned	75.8	1.5	10	55.0	1.2	11

a σ = standard deviation

b n = number of tests

air flow rate through the dust for several levels of dust compaction. The porosity of the ash layer was calculated by measuring particle density by helium pycnometry and by measuring the dust layer thickness and cylinder diameter. Results of the K_2 measurements are shown in Figure 16, along with the Carman-Kozeny and Bush models that define K_2 in terms of porosity and particle size. The Carman-Kozeny relationship is derived from a theoretical capillary model and, assuming spherical particles, takes the form (4):

$$K_2 = 36 k \mu (1 - \epsilon) / \epsilon^3 P_p D^2 \quad \text{Eq. 1}$$

where

K_2 = specific dust cake resistance coefficient (sec/ft); note:
 K_2 can be converted to inches of water-ft-min/lb by multiplying by
a factor of 311.6

k = Carman-Kozeny constant (~ 5) (dimensionless)
 μ = gas viscosity (lb-sec/ft²)
 ϵ = porosity (dimensionless, void volume fraction)
 P_p = particle density (lb/ft³)
 D^p = particle diameter (ft)

Bush et al. and Cushing et al. (5,6) have reported an empirical relationship between K_2 and porosity for coal fly ash:

$$K_2 = (4 \mu / D^2 P_p) [(1 - \epsilon)/\epsilon] [7.5 + 9.1(1 - \epsilon) - 35.8(1 - \epsilon)^2 + 560(1 - \epsilon)^3] \quad \text{Eq. 2}$$

Figure 16. Specific dust cake resistance coefficient, K_2 , as a function of ash porosity with Carman-Kozeny and SoRI/Bush models fit to data.

where the D term is referred to as the drag equivalent diameter. In the Carman-Kozeny equation, D refers to the actual physical diameter for monosized spheres. For fly ash with a broad particle-size distribution, the mass median diameter generally cannot be used for D for either equation. The value of the characteristic diameter is dependent on the particle-size distribution, specific surface area, and particle shape. These equations show that K_2 is most sensitive to particle size (or the characteristic particle-size term) and porosity. Any attempt, then, to alter K_2 should focus on these properties, and any explanation of a change in K_2 must include particle size and porosity. A curve for each of the models was fit to the measured K_2 and porosity values for both the baseline and conditioned data. It appears the baseline data follow both models closely, while the data from the conditioned test seem to more closely fit the Carman-Kozeny relationship. Both the baseline and conditioned results represent data from three separate samples. For a single sample, the K_2 measurements should define a smooth curve with minimal data scatter, as was the case for the individual samples. All data from the three baseline samples fit a nice curve with little variability. While the three conditioned samples showed more variability, their composite data still defined a distinct curve separate from the baseline data. The reason why the baseline and conditioned data formed separate curves is not clear. If the particle size distributions and the specific surface areas are unchanged, it is expected that the two data sets would define the same K_2 curve. Plausible explanations are that the particle-size distribution for the conditioned samples was somewhat smaller than the particle-size distribution for the baseline samples, or the conditioned samples had an increased specific surface area. Previous data have not clearly indicated any shift in the fly

ash particle-size distribution as a result of conditioning (7). Coulter Counter data did show the volumetric median diameter of one of the conditioned samples to be 11 μm compared to 13 μm for the baseline samples, but extensive data were not taken, and specific surface area measurements have not yet been completed.

The explanation why the baseline data in Figure 16 were over a porosity range of 43% to 60% (void fraction of 0.43 to 0.60), while the conditioned data covered a range of 58% to 75% is that the baseline ash had a much greater tendency to compact. Procedures were the same for all tests in that the same approximate compaction force was used to obtain the low porosity measurements, and no external compaction force was used to obtain the maximum porosity measurements. Ash porosity as a function of compaction force appears to be an important property of the dust which is also evident from other measurements.

Several important observations are obtained from the K_2 data and models in Figure 16. First, both the data and models demonstrated that a small increase in porosity can significantly reduce K_2 . At constant dust cake weight and face velocity, this would correspond to a proportional decrease in baghouse pressure drop. Second, conditioning caused a distinct difference in the measured porosity range. These curves by themselves do not define the porosity of the baghouse dust cake, but it would appear to be a safe assumption that dust cake porosity for the baseline and conditioning tests would be somewhere between the respective minimum and maximum porosity values shown. The actual K_2 values of the dust cake during operation can be determined from dust loading and pressure drop data. The 500-hour tests were started with new bags, and the first 4 hours were conducted without bag cleaning. After the initial 4 hours, the tube sheet pressure drop was 10.5 inches of water for the baseline test and 2.15 inches of water for the conditioned test, which corresponds to a K_2 of 17 inches of water-ft-min/lb for the baseline test and 3.5 for the conditioned test. Looking at Figure 16, this implies that the dust cake porosity was about 47% for the baseline test and 71% for the conditioned test. K_2 can also be approximated by the increase in pressure drop between bag cleanings. From the 500-hour tests, pressure drop increased about 6.5 inches (from about 3 to 9.5 inches) between the 2-hour bag cleaning intervals for the baseline test, compared to about 1.4 inches (from about 0.8 to 2.2 inches) for the conditioning test. These data result in somewhat higher K_2 values of 21 for the baseline test corresponding to a dust cake porosity of 45% and 4.5 for the conditioned test corresponding to a dust cake porosity of 68%.

From the bench-scale and baghouse K_2 data, we concluded that the actual dust cake porosity for the baseline test was in the range of 45% to 47% and for the conditioned test in the range of 68% to 71%. Looking at the tensile strength values for these porosity ranges, an interesting result was observed. The corresponding tensile strength for the baseline tests was in the range of 0.7 to 1.0 g_f/cm^2 compared to 0.4 to 0.6 g_f/cm^2 for the conditioned tests. While there was some data scatter in this porosity range for the baseline tests and extrapolation of the conditioned data was necessary to obtain the tensile strength value for the highest porosity, the results indicated that the actual tensile strength of the dust cake decreased with conditioning, rather than increased. This result was not predictable because previous measurements of ash pellet strength (2) and effective angle of internal friction (7) showed that conditioning caused an increase in the

cohesive strength of the ash. However, this result was highly desirable because it would appear that bag cleanability would be directly related to the actual dust cake tensile strength. A reduction in dust cake tensile strength should facilitate bag cleaning. These results should be considered preliminary and need to be verified with other tests. The Cohetester tensile strength measurement, however, appears to be a good method to evaluate fly ash for fabric filter performance and possibly predict bag cleanability.

To summarize the effect of conditioning on baghouse pressure drop, several measurements showed a significant increase in ash porosity, which directly translates to increased dust cake porosity and reduced baghouse pressure drop. The conditioning has a double effect in that it increases porosity, which allows operation at a lower pressure drop. The lower pressure drop, in turn, reduces the compaction pressure on the dust layer, allowing a high porosity to be maintained. The reverse is true for the baseline ash or any ash that has a high tendency to compact. The tendency to compact causes high pressure drop, which results in a greater compaction force, leading to even lower porosity and higher pressure drop. Therefore, a treatment, such as ammonia and SO₃ conditioning that reduces the compaction tendency of the ash, can be effective in reducing baghouse pressure drop.

3.3 Project Budget and Milestones

The federal assistance Management Summary Report is presented as Tables 5 and 6. The report presents the budget information and milestone information through March 1990. In the previous quarterly reports for the current project year, a project budget of \$200,000 was identified. Table 5 presents a project budget of \$248,000. The \$48,000 increase represents funds carried over from the previous project year. This carryover was planned and approved early in the current project year. The scope of work for the current project year was prepared assuming the \$48,000 carryover would be available; therefore, no change in the current scope of work is planned at this time. Project milestones are on schedule at this time.

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2.2 Waste Management

WASTE MANAGEMENT

**Quarterly Technical Progress Report
for the Period January 1 through March 31, 1990**

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WASTE MANAGEMENT

1.0 GOALS AND OBJECTIVES

The objective of the Waste Management project is to characterize waste materials and by-products from advanced coal utilization processes, evaluate potential uses for these materials, and identify potential adverse environmental impacts associated with their use and/or disposal. Research is also being done to develop innovative waste management techniques for conventional and advanced coal utilization processes to comply with existing and/or future environmental regulations.

The activities of the Waste Management project include the following tasks:

- Task 1. Activated Carbon Evaluation
Purpose - to evaluate the use of coal gasification char as activated carbon.
- Task 2. Waste Characterization
Purpose - to characterize solid wastes from advanced coal utilization processes being developed at the Energy and Environmental Research Center (EERC).
- Task 3. Coal Utilization Waste Conditioning Study
Purpose - to evaluate conditioning procedures for advanced coal utilization wastes.
- Task 4. Bituminous Coal Fly Ash Data Collection and Evaluation
Purpose - to collect and evaluate data concerning the chemical and mineral compositions and physical properties of bituminous coal fly ash.

2.0 ACCOMPLISHMENTS

The following are the accomplishments of the Waste Management project for this reporting period:

2.1 Activated Carbon Evaluation

Limited testing of commercial activated carbons was performed during this period. A mild gasification lignite char was selected for further evaluation of activated carbon characteristics. Testing of the mild gasification chars will commence when they are made available.

2.2 Waste Characterization

Limited trace element characterization of the four bed materials submitted for this task was completed during this quarter. The trace element characterization included method development for an appropriate dissolution technique. Several initial dissolution techniques resulted in incomplete sample dissolution. The undissolved residues from these techniques were

submitted for scanning electron microscopy microprobe analysis. Results of this technique indicated the residues contained only calcium. The remaining trace element characterization will be completed on sample solutions generated from the original dissolution techniques.

Leachates generated from the EPA-EP toxicity leaching tests, toxicity characteristics leaching procedure (TCLP) and the synthetic groundwater leaching procedure (SGLP) short-term leaching tests were analyzed for trace constituents identified in the previous quarterly report. Leachates from the long-term leaching (LTL) tests were also analyzed for the same trace constituents. An additional set of long-term leaching experiments were initiated. Originally this set was planned as a four-week experiment. Results from the one-week LTL prompted re-evaluation of the second LTL experiments, and it was decided to extend the leaching time to three months.

2.3 Coal Utilization Waste Conditioning Study

During this reporting period, leaching tests were performed on advanced coal utilization wastes to study the effect of conditioning moisture on trace element leaching. The wastes studied included a composite cyclone ash and a baghouse fly ash from the Shawnee AFBC unit, an ESP fly ash from the Black Dog AFBC unit, and a Class C fly ash from a conventional cyclone-fired boiler.

Leaching test data from the Black Dog, TVA, and Riverside ashes, which had been conditioned with different moisture levels, were evaluated to determine the effect of conditioning moisture on trace element leaching. The test data indicated that selenium, chromium, barium, and molybdenum were the principally measured trace elements present in the ash leachates at environmentally significant concentrations. To illustrate the test results, plots were developed showing leachate trace element concentrations as a function of conditioning moisture levels. The plots showed that in several cases, a functional relationship appeared to exist between concentrations of some trace elements in the leachates and the moisture level used to condition the ash prior to compacting and curing.

2.4 Bituminous Coal Fly Ash Data Collection and Evaluation

During this quarter, groups having agreed to participate by providing the requested information and/or ash samples were sent an informational packet to facilitate their participation. A copy of the information request is included as Appendix A. The Edison Electric Institute Power Directory Data Base was received and reviewed for additional contacts for participation in the Coal Ash Data Base. The existing updated version of the Western Fly Ash Data Base was reviewed, and additional fields for inclusion of other data pertinent to bituminous coal ash were created.

Initial contacts continued throughout the quarter by mail and telephone to identify additional participants.

3.0 PROJECT RESULTS

3.1 Activated Carbon Evaluation

3.1.1 Introduction

No changes.

3.1.2 Research Scope

The objective of this research task has been modified due to changes in the scope of mild gasification. Testing will continue on the evaluation of chars from the mild gasification process and will be directed specifically toward characterization and evaluation of chars from the mild gasification of lignite.

3.1.3 Activated Carbon Evaluation Results

The hardness number is a measure of the resistance of a granular carbon to the effects of handling and carbon attrition. The GAC hardness number has no relation to the hardness scale used for plastics, metals, or minerals. It is used as a measurable characteristic of a carbon for comparison to other activated carbons.

Hardness numbers were calculated for Calgon F-300 and F-400 and for Hydrodarco 3000 and 4000 granular activated carbons that were subjected to the action of steel balls on a Ro-Tap machine (1). Table 1 summarizes results of hardness number determinations. The maximum hardness number is 100. "H" represents the hardness number, and "H₂" is a check on the accuracy of the test. Results obtained during hardness evaluations were all within 2% of the calculated values.

3.2 Waste Characterization

3.2.1 Introduction

Wastes from advanced coal utilization processes being developed at UNDEERC are characterized for the selection of appropriate waste management techniques and to identify any significant or unusual problems associated with the advanced process wastes. The characterization protocol determines the chemical and mineralogical composition, physical properties, and leaching behavior of the waste materials. The information obtained from the characterization studies can be used to assess the environmental impacts, handling properties, and utilization potential of the advanced process wastes.

3.2.2 Research Scope

The wastes to be characterized in this task will be obtained from ongoing coal utilization research at UNDEERC. Wastes considered for this task may include materials from the low-temperature coal gasifier and the circulating fluidized-bed combustor (CFBC). Emphasis for the waste characterization task for the current year is on limestone bed materials from the Hydrogen Production project.

TABLE 1

HARDNESS NUMBER DETERMINATIONS OF COMMERCIAL ACTIVATED CARBONS

	(A) Weight of Sample Loaded onto Hardness Pan (g)	(B) Weight of Sample Retained on Test Sieve (g)	(C) Weight of Sample Collected on Catch Pan (g)	$H = (B/A)100$	$H_2 = (1-C/A)100$
Calgon F-300	50.0	36.61	12.87	73.2	74.3
Calgon F-400	50.0	40.16	9.18	80.3	81.6
Hydrosorb 3000	50.0	32.78	16.52	65.6	67.0
Hydrosorb 4000	50.0	28.09	21.37	56.2	57.3

3.2.3 Waste Characterization Results

The physical properties, major chemical constituents, and the proton induced x-ray emission (PIXE) screening study results have been included in previous quarterly reports. Results from the initial limited trace element characterization are listed in Table 2. Temperatures and steam/carbon ratios are listed as identifiers for each bed material. All of these bed materials are limestone. For each of these four trials, Wyodak coal was used, and a reducing atmosphere was maintained.

Leaching results from the EPA-EP toxicity, TCLP, SGLP, and the one-week LTL experiments performed during the previous quarter are included as Appendix B.

3.3 Ash Conditioning Study3.3.1 Introduction

Coal combustion wastes are usually conditioned prior to disposal by adding water. Conditioning helps to control dusting, increase the cohesiveness of the waste, and facilitate compacting at the disposal site. Previous research conducted at EERC has shown that, for self-hardening fly ashes, conditioning also initiates chemical reactions which increase the unconfined compressive strength of the compacted ash and reduce its hydraulic conductivity (1). These results suggest that appropriate conditioning of self-hardening ashes may affect their long-term environmental impact to a much greater extent than previously thought.

Wastes from advanced coal utilization processes, such as atmospheric fluidized-bed combustion (AFBC) and coal gasification, often display some

TABLE 2
TRACE CONSTITUENTS OF HYDROGEN PRODUCTION BED MATERIALS

	6-W380L	10R-W180L	12R-W275L	14-W170L
Temperature (Ave. °C)	801.70	806.36	749.95	698.59
Steam/Carbon (Ave.)	3.41	1.28	2.35	1.57
(concentrations are µg/g)				
Barium	32	86	58	55
Boron	360	360	559	219
Chromium	7.2	26	8.6	11
Lead	0.7	1.7	2.3	1.2
Manganese	280	312	91	137
Titanium	62	384	91	137

degree of self-hardening behavior, particularly if they contain spent, calcium-based sorbents. Hardening occurs because free lime in the spent sorbent reacts with pozzolanic components of the ash to form interparticle bridges.

Since the amounts of waste produced from advanced coal utilization processes will increase as the advanced processes replace conventional processes, a research project is being conducted to optimize the conditioning process for advanced process wastes to reduce their long-term environmental impacts. The objective of the project is to determine the relation between conditioning moisture and the compacted dry density, unconfined compressive strength, permeability coefficient, and amounts of trace metals leached from several representative advanced process wastes. Additionally, a self-hardening fly ash from a conventional coal combustion process has been included in this study to determine whether conventional and advanced process wastes react to the conditioning process in a similar manner.

3.3.2 Materials and Methods

The advanced process wastes being studied include a composite cyclone ash and a baghouse fly ash from the Shawnee AFBC unit, an ESP fly ash from the Black Dog AFBC unit, and a spent bed material ash from the KRW fluidized-bed gasifier. All three wastes were produced from processes that used limestone addition to the bed for sulfur capture.

The AFBC units are both commercial scale plants. The Black Dog Plant is owned by Northern States Power Company; it has a 125-MW generating capacity and burns western subbituminous coal. The Shawnee Plant is owned by the Tennessee Valley Authority; it has a 160-MW generating capacity and burns bituminous coal. The KRW gasifier is a pilot-scale unit. It is being developed for integrated gasification combined cycle (IGCC) applications. The spent bed material being used for this study was obtained from a gasification run that used Pittsburgh #2 bituminous coal.

In addition to the three advanced process wastes, a self-hardening fly ash from a conventional cyclone-fired boiler burning a western subbituminous coal was included in this study. The fly ash was produced at the Riverside Plant owned by Northern States Power Company. This ash was included because it exhibits similar behavior in many respects to the AFBC ashes. If it is found that the behaviors of the Riverside fly ash and the advanced process wastes are fundamentally related, this will indicate that many techniques already developed for conditioning of conventional self-hardening fly ash can be successfully applied to some advanced process wastes.

The research plan for this project consists of an initial characterization task to establish baseline elemental composition, mineral composition, and physical property data for the coal combustion wastes. Moisture-density tests will be done to determine optimum moistures for maximum compacted dry densities. Unconfined compressive strength tests, permeability tests, and leaching tests will be done to determine how these important disposal-related properties vary as a function of the conditioning moisture level and how they relate to the optimum moisture (for maximum compacted density).

The moisture-density tests were performed by: (1) mixing each waste material with different amounts of water using a paddle type mixer, (2) allowing the mixtures to stand for 35 minutes and then remixing the material by hand, (3) preparing duplicate 1/30 ft³ cylinders from each mix using standard Proctor compaction, and (4) measuring the dry density and moisture content of each cylinder.

The mixtures were allowed to stand for 35 minutes before compacting to allow them to hydrate and cool somewhat. Since it would take at least 35 minutes at a commercial plant to haul the conditioned waste to the disposal site and place it, this time interval was thought to be fairly representative of in-field disposal conditions.

The waste cylinders prepared for the moisture-density tests were cured for 28 days at 70°F and then tested for unconfined compressive strength and permeability coefficient. The unconfined compressive strength was measured by loading a cylinder to failure in a testing machine and calculating the unit stress. The permeability coefficient was measured by wrapping a cylinder in a rubber membrane, confining the specimen in a triaxial cell, and measuring the rate at which water flowed through the specimen using a pressure head of approximately 5 psi.

Finally, leaching tests were performed on the conditioned ashes. For these tests, fragments from the compressive strength tests were crushed and passed through a no. 16 sieve. Trace elements were then extracted from the sieved material using a generic leaching test developed at EERC (i.e., the

synthetic groundwater leaching procedure). Each leachate was analyzed for arsenic, barium, cadmium, chromium, lead, mercury, selenium, silver, boron, and molybdenum concentrations. The data thus generated was evaluated to determine whether a functional relationship existed between the moisture level used to condition the ash and the amounts of trace elements leached.

3.3.3 Experimental Results

The results of the leaching tests performed on the Black Dog, TVA, and Riverside ashes conditioned with different moisture levels are contained in Tables 3, 4, and 5 respectively. The tables also contain physical property test results for each ash. The leaching test results for selenium, barium, chromium, and molybdenum are plotted as a function of conditioning moisture content in Figures 1, 2, 3, and 4 respectively.

Based on the plots of the leaching data, several different types of functional relationships appear to exist between the leachate trace element concentrations and the conditioning moisture levels. In some cases, the added moisture and curing of the compacted ash specimens produced lower leachate trace element concentrations, while in a few cases, the added moisture actually produced higher trace element concentrations. In those cases where the leachate trace element concentrations were found to decrease when conditioning moisture was added, the data indicated that either the concentrations decreased continually as the moisture level increased or they reached some minimum value at an intermediate moisture addition level.

The results of the leaching studies generally suggest that moisture conditioning, compacting, and curing the ashes from both advanced and conventional coal utilization processes can affect their leaching behavior.

3.4 Bituminous Coal Fly Ash Data Collection and Evaluation

3.4.1 Introduction

The objectives of the coal fly ash research during the first year will be to identify and evaluate bituminous coal fly ash data. The effort for the second and third years of the project will be to collect and characterize samples of bituminous coal fly ash according to characterization protocols developed under the Western Fly Ash Research, Development, and Data Center and to expand the existing data base on western coal fly ashes to include information on bituminous coal fly ashes gained through this task.

3.4.2 Research Scope

Chemical, mineralogical, and physical characterization information on bituminous coal fly ashes from varying sources will be obtained and added to an existing coal fly ash data base currently containing information on over 500 western coal fly ashes. The information will be collected from voluntary participants who generate or market bituminous coal fly ash or other research groups having access to this type of information. If sources of information being sought are inadequate, the information will be supplemented by characterization of submitted samples at the EERC Coal By-Products Laboratory and the NDSU Chemistry Department.

The addition of this information to the current Western Fly Ash Data Base will facilitate basic understanding of the character of bituminous coal fly ash and the variability of the material. This information will be valuable in current and future coal ash research.

3.4.3 Bituminous Coal Fly Ash Data Collection and Evaluation Results

Pertinent information on coal fly ash identification, source, and characterization that is not included in the current coal fly ash data base has been identified for the Bituminous Coal Fly Ash Data Base. The data collection effort is ongoing.

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TABLE 3
LEACHING TEST RESULTS FOR THE CONDITIONED BLACK DOG AFBC ASH

	Specimen No.					
	1	2	3	4	5	6
Conditioning Moisture Addition Level (% Dry Wt.)	0	28.1	31.9	36.0	41.9	44.1
Compacted Dry Density (lbs/cu.ft.)	NA	70.5	71.6	73.0	69.0	68.0
Unconfined Compressive Strength (PSI)	NA	177	234	330	366	229
Permeability Coefficient (cm/sec)	NA	1.7E-4	1.4E-6	2.9E-6	1.4E-6	1.2E-6
Leachate Arsenic Conc. (µg/l)	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0
Leachate Barium Conc. (mg/l)	<0.02	0.28	0.26	0.23	0.23	0.25
Leachate Cadmium Conc. (mg/l)	<0.02	0.03	<0.02	<0.02	<0.02	<0.02
Leachate Chromium Conc. (mg/L)	<0.02	0.17	<0.02	0.08	0.08	0.13
Leachate Lead Conc. (µg/l)	<10	<10	<10	<10	<10	<10
Leachate Mercury Conc. (µg/L)	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
Leachate Selenium Conc. (µg/l)	6.8	<2.0	2.0	<2.0	<2.0	<2.0
Leachate Silver Conc. (µg/L)	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Leachate Boron Conc. (mg/l)	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Leachate Molybdenum Conc. (mg/l)	0.39	0.37	0.42	0.49	0.4	0.39

NA - Not Applicable

TABLE 4
LEACHING TEST RESULTS FOR THE CONDITIONED TVA DOG AFBC ASH

	Specimen No.					
	1	2	3	4	5	6
Conditioning Moisture Addition Level (% Dry Wt.)	0	17.0	26.4	29.8	34.6	39.2
Compacted Dry Density (lbs/cu.ft.)	NA	73.9	76.2	76.9	76.2	72.3
Unconfined Compressive Strength (PSI)	NA	213	328	366	320	227
Permeability Coefficient (cm/sec)	NA	1.1E-4	3.8E-5	1.8E-5	3.9E-6	2.0E-5
Leachate Arsenic Conc. (µg/L)	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0
Leachate Barium Conc. (mg/L)	0.2	0.22	0.22	0.20	0.20	0.20
Leachate Cadmium Conc. (mg/L)	<0.02	0.03	0.03	<0.02	<0.02	<0.02
Leachate Chromium Conc. (mg/L)	0.14	<0.02	0.12	0.08	0.08	0.12
Leachate Lead Conc. (µg/L)	<10	<10	<10	<10	<10	<10
Leachate Mercury Conc. (µg/L)	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
Leachate Selenium Conc. (µg/L)	8.5	3.8	4.5	2.9	2.9	2.5
Leachate Silver Conc. (µg/L)	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Leachate Boron Conc. (mg/L)	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Leachate Molybdenum Conc. (mg/L)	0.17	0.14	0.24	0.11	0.11	0.20

NA - Not Applicable

TABLE 5
LEACHING TEST RESULTS FOR THE CONDITIONED RIVERSIDE FLY ASH

	Specimen No.					
	1	2	3	4	5	6
Conditioning Moisture Addition Level (% Dry Wt.)	0	4.1	5.1	8.9	10.6	12.6
Compacted Dry Density (lbs/cu.ft.)	NA	94.1	88.5	86.2	87.1	82.6
Unconfined Compressive Strength (PSI)	NA	231	334	405	401	387
Permeability Coefficient (cm/sec)	NA	2.7E-5	ND	1.7E-5	3.8E-5	9.4E-5
Leachate Arsenic Conc. (µg/L)	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0
Leachate Barium Conc. (mg/L)	0.91	0.73	0.37	0.46	0.28	0.08
Leachate Cadmium Conc. (mg/L)	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Leachate Chromium Conc. (mg/L)	0.31	0.20	0.28	0.27	0.30	0.33
Leachate Lead Conc. (µg/L)	<10	<10	<10	<10	<10	<10
Leachate Mercury Conc. (µg/L)	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
Leachate Selenium Conc. (µg/L)	55.0	55.0	49.0	50.0	48.0	64.0
Leachate Silver Conc. (µg/L)	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Leachate Boron Conc. (mg/L)	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Leachate Molybdenum Conc. (mg/L)	0.79	0.49	0.60	0.52	0.49	0.46

NA - Not Applicable
ND - Data Not Available

Figure 1. Leachate selenium concentration vs. conditioning moisture level for the Riverside, Black Dog, and TVA ashes.

Figure 2. Leachate barium concentration vs. conditioning moisture level for the Riverside and Black Dog ashes. TVA graph showed negligible data.

Figure 3. Leachate chromium concentration vs. conditioning moisture level for the Riverside, Black Dog, and TVA ashes.

Figure 4. Leachate molybdenum concentration vs. conditioning moisture level for the Riverside, Black Dog, and TVA ashes.

APPENDIX A

APPENDIX A

INFORMATION FOR INCLUSION IN THE BITUMINOUS COAL ASH DATA BASE

Requested by University of North Dakota Energy and Environmental Research Center for a research project funded through the U.S. Department of Energy. Your voluntary participation is appreciated.

Source Information (This information will be coded in the data base to ensure anonymity of participants.)

1. Name of power company
2. Name of plant
3. Location of plant
4. Coal source
5. Boiler type
6. Boiler manufacturer
7. Source of ash (if handled by party other than the power company)
8. Collection method
9. Other information the participant finds pertinent and that is essential to identification or characterization of the ash

Chemical Composition (ASTM C618) or Other Analyses (e.g., XRD, ICAP, etc.)

1. Silicon dioxide (wt% SiO_2)
2. Aluminum oxide (wt% Al_2O_3)
3. Iron oxide (wt% Fe_2O_3)
4. Sulfur trioxide (wt% SO_3)
5. Calcium oxide (wt% CaO)
6. Magnesium oxide (wt% MgO)
7. Moisture content (wt% at 105°C)
8. Loss on ignition (wt% LOI at 750°C)
9. Available alkali (wt% Na_2O)
10. Sodium oxide (wt% Na_2O)
11. Potassium oxide (wt% K_2O)
12. Other major, minor, or trace elements such as As, Se, Ti, etc.
13. Leaching results on the ash such as EPA-EP tox, TCLP, ASTM, or other leaching tests

Physical Test Results (ASTM C618)

1. Fineness (% retained on 325-mesh sieve)
2. Pozzolanic Activity Index with Portland cement (% ratio to control at 28 days)
3. Pozzolanic Activity Index with lime (psi, at 7 days)
4. Water requirement (% of control)
5. Soundness/autoclave expansion (%)
6. Specific gravity
7. Other parameters (slag viscosity, melting point, etc.)

Mineralogical Data

1. Mineralogical phases
2. Quantitative phase analysis
3. Other spectral information such as infrared or laser raman

APPENDIX B

ANALYTICAL RESULTS ON TASK 2 BED MATERIAL LEACHATES

	TCLP LEACHING			
	<u>6-W380L</u>	<u>10R-W180L</u>	<u>12R-W275L</u>	<u>14-W170L</u>
Aluminum	0.48	0.59	0.70	0.72
Arsenic	<5.0	<5.0	<5.0	<5.0
Boron	0.56	1.12	0.13	0.10
Cadmium	<0.02	<0.02	<0.02	<0.02
Calcium	2690	2630	2470	2290
Chromium	<0.1	<0.02	<0.1	<0.1
Copper	<0.2	<0.2	<0.2	<0.2
Iron	1.0	1.0	0.98	0.98
Lead	<0.5	<0.5	<0.5	<0.5
Magnesium	<0.1	<0.1	<0.1	<0.1
Manganese	<0.02	<0.02	<0.02	<0.02
Mercury	<3.0	<3.0	<3.0	<3.0
Molybdenum	<0.1	<0.1	<0.1	<0.1
Nickel	<0.1	<0.1	<0.1	<0.1
Phosphorous	<0.5	<0.5	<0.5	<0.5
Potassium	0.9	0.7	1.1	1.4
Selenium	<5.0	<5.0	<5.0	<5.0
Silicon	1.7	1.8	1.9	1.9
Silver	<0.2	<0.2	<0.2	<0.2
Sodium	3.0	6.3	2.4	7.0
Strontium	14.0	15.0	3.2	3.3
Titanium	<0.2	<0.2	<0.2	<0.2
Zinc	<0.1	<0.1	<0.1	<0.1
Zirconium	<0.1	<0.1	<0.1	<0.1

ANALYTICAL RESULTS ON TASK 2 BED MATERIAL LEACHATES

	EP-TOX LEACHING			
	<u>6-W380L</u>	<u>10R-W180L</u>	<u>12R-W275L</u>	<u>14-W17CL</u>
Aluminum	0.54	0.68	0.63	1.7
Arsenic	<5.0	<5.0	<5.0	<5.0
Boron	0.50	0.92	0.24	0.07
Cadmium	<0.02	<0.02	<0.02	<0.02
Calcium	2690	2650	2600	2360
Chromium	<0.1	<0.1	<0.1	<0.1
Copper	<0.2	<0.2	<0.2	<0.2
Iron	1.0	1.0	1.0	0.93
Lead	<0.5	<0.5	<0.5	<0.5
Magnesium	<0.1	<0.1	<0.1	<0.1
Manganese	<0.02	<0.02	<0.02	<0.02
Mercury	<3.0	<3.0	<3.0	<3.0
Molybdenum	<0.1	<0.1	<0.1	<0.1
Nickel	<0.1	<0.1	<0.1	<0.1
Phosphorous	<0.5	<0.5	<0.5	<0.5
Potassium	1.0	0.7	0.9	1.6
Selenium	<5.0	<5.0	<5.0	<5.0
Silicon	1.7	1.7	2.1	2.3
Silver	<0.2	<0.2	<0.2	<0.2
Sodium	2.6	5.4	2.1	6.6
Strontium	14	15	3.2	3.3
Titanium	<0.2	<0.2	<0.2	<0.2
Zinc	<0.1	<0.1	<0.1	<0.1
Zirconium	<0.1	<0.1	<0.1	<0.1

ANALYTICAL RESULTS ON TASK 2 BED MATERIAL LEACHATES

	SGLP 18 HR			
	<u>6-W380L</u>	<u>10R-W180L</u>	<u>12R-W275L</u>	<u>14-W170L</u>
Aluminum	0.26	0.35	0.30	0.32
Arsenic	<5.0	<5.0	<5.0	<5.0
Boron	0.46	0.98	0.17	0.45
Cadmium	<0.02	<0.02	<0.02	<0.02
Calcium	950	955	945	960
Chromium	<0.1	<0.02	<0.1	<0.1
Copper	<0.2	<0.2	<0.2	<0.2
Iron	0.44	0.44	0.45	0.45
Lead	<0.5	<0.5	<0.5	<0.5
Magnesium	<0.1	<0.1	<0.1	<0.1
Manganese	<0.02	<0.02	<0.02	<0.02
Mercury	<3.0	<3.0	<3.0	<3.0
Molybdenum	<0.1	<0.1	<0.1	<0.1
Nickel	<0.1	<0.1	<0.1	<0.1
Phosphorous	<0.5	<0.5	<0.5	<0.5
Potassium	1.0	0.7	1.7	5.6
Selenium	<5.0	<5.0	<5.0	<5.0
Silicon	0.99	0.98	1.0	1.0
Silver	<0.2	<0.2	<0.2	<0.2
Sodium	2.4	5.7	1.7	5.6
Strontium	14.0	15.0	1.3	1.5
Titanium	<0.2	<0.2	<0.2	<0.2
Zinc	<0.1	<0.1	<0.1	<0.1
Zirconium	<0.1	<0.1	<0.1	<0.1

ANALYTICAL RESULTS ON TASK 2 BED MATERIAL LEACHATES

	LTL 1 WK			
	<u>6-W380L</u>	<u>10R-W180L</u>	<u>12R-W275L</u>	<u>14-W170L</u>
Aluminum	0.38	0.43	0.39	0.40
Arsenic	<5.0	<5.0	<5.0	<5.0
Boron	<0.5	<0.5	<0.5	<0.5
Cadmium	<0.02	<0.02	<0.02	<0.02
Calcium	950	915	940	940
Chromium	<0.1	<0.1	<0.1	<0.1
Copper	<0.2	<0.2	<0.2	<0.2
Iron	0.46	0.43	0.42	0.45
Lead	<0.5	<0.5	<0.5	<0.5
Magnesium	<0.1	<0.1	<0.1	<0.1
Manganese	<0.02	<0.02	<0.02	<0.02
Molybdenum	<0.1	<0.1	<0.1	<0.1
Nickel	<0.1	<0.1	<0.1	<0.1
Phosphorous	<0.5	<0.5	<0.5	<0.5
Potassium	1.6	1.6	2.3	4.5
Selenium	<5.0	<5.0	<5.0	<5.0
Silicon	0.99	0.94	0.97	1.0
Silver	<0.2	<0.2	<0.2	<0.2
Sodium	3.0	7.6	2.4	8.6
Strontium	17.0	19.0	2.4	2.3
Titanium	<0.2	<0.2	<0.2	<0.2
Zinc	<0.1	<0.1	<0.1	<0.1
Zirconium	<0.1	<0.1	<0.1	<0.1

2.3 Regional Energy Policy Program for the Northern Great Plains

**REGIONAL ENERGY POLICY PROGRAM
FOR THE NORTHERN GREAT PLAINS**

**Quarterly Technical Progress Report for the Period
January - March 1990**

by

**University of North Dakota
Energy and Environmental Research Center
Box 8213, University Station
Grand Forks, ND 58202**

Contracting Officer's Technical Representative: John Byam

for

**U.S. Department of Energy
Morgantown Energy Technology Center
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1.0 INTRODUCTION

The United States is the world's leading consumer of energy. The production and consumption of energy varies over the country as a function of climate, the availability of natural resources, economics, and culture. The northern Great Plains region (Montana, Wyoming, North Dakota, and South Dakota), an area characterized by many similarities in climate, culture, and physiography:

- Accounts for over 10 percent of domestic hydrocarbon production, a major share of low-rank, low-sulfur coal production, a significant steam-generated electrical capability, and a significant portion of domestic uranium production.
- Contains significant oil shale, geothermal, nuclear, and conventional fossil fuel resources.
- Contains significant research capability, particularly with regard to coal-conversion, and oil shale technologies and the environmental effects of fossil fuel production, conversion, and utilization.
- Is a net exporter of energy and fossil fuel materials.
- Is a significant consumer of fuel and fossil fuel by-products in the agricultural sector.
- Receives significant revenues and economic support from fossil fuel exploration, production, conversion, and transportation industries, as well as from ancillary industries.

2.0 PROGRAM OBJECTIVES

Energy-related activities are significant in the economy at the regional, state, and local levels. Fluctuations in energy markets can have marked effects on government revenues and programs as well as on the economy. Since the end of the Second World War, the northern Great Plains has experienced economic "booms" related to oil and gas, coal, oil shale, hydroelectric power, and uranium. Since the early 1970s, the energy market has had to deal with the increase in environmental awareness and the growth and diversification of energy sources and suppliers on a global scale. For example, prospects for the continued growth of the region's coal sector depend to a significant degree on the the nature of federal actions with respect to air quality and waste management. Currently, an attempt is being made during the development of a National Energy Strategy (NES) to take into account the mix of environmental, fiscal, social, research, economic, national security, and resource issues that form the energy picture of the nation. Ensuring the optimal production and utilization of the region's energy resources, within the framework of the developing NES, could be enhanced by responses and initiatives both at the state and regional levels. Once the basic framework of the strategy is in place, periodic review of the policy with respect to the region would be augmented by ready access to pertinent data for the region. To this end, the objectives of the Regional Energy Policy Program for the

northern Great Plains as originally proposed were to:

- Gather, develop, and disseminate information necessary for well-founded energy initiatives in the region.
- Promote and assist in the integration and coordination of the energy-planning efforts of individual states in the region.
- Foster communication between the public and private sector concerning energy-planning needs in the region.
- Achieve objectives and carry out activities in a manner consistent with the National Energy Strategy.

The mission of the Energy Policy Program for the northern Great Plains can best be achieved through an information clearinghouse/data center. We are proceeding in this direction with the development of the "Energy Policy Information Center (EPIC) for the northern Great Plains".

3.0 YEAR 1 GOALS/ACTIVITIES

Year 1 efforts of the Regional Energy Policy Program for the northern Great Plains were designed to initiate the development of an up-to-date listing of energy resources, production, and consumption in the region, as well as a computer-based system to facilitate the efficient identification, collection, and manipulation of energy-related information.

TASK A. Development of an Information Management System

The initial efforts of the program will focus on the identification, acquisition, and organization of pertinent energy information and the development of a computer-based system to manage this information.

TASK B. Compilation of an Annotated Bibliography

The review of information in Task A will form the basis for initiation of an annotated bibliography.

TASK C. Compilation of an Energy Resource Data Base

The review of information acquired in Task A will form the basis for initiation of an energy resource data base.

TASK D. Annual Report

4.0 ACCOMPLISHMENTS

During the first and second quarters (the last half of August 1989 until December 31, 1989) activities included: 1) acquiring computer hardware (a.1), 2) identifying and characterizing pertinent data bases and information sources (a.2), and 3) initiating a literature search (a.3, b.1, b.2). During the third quarter, efforts focused on:

- 1) The continuation of work on Tasks A & B.

Task A. Development of an Information Management System

During this period, the identification and assessment of energy-related data bases for the region (subtask a.2) continued.

Task B. Completion of an Annotated Bibliography

During this period, the acquisition and review of relevant documents (subtask b.2), begun in the second quarter, continued. In the second quarter, a preliminary review of computer data bases indicated that over one thousand citations were available for the northern Great Plains. Following a preliminary review over 200 of these references were ordered. In addition, a significant number of references, not listed in the computer data bases, have been noted and are being ordered. Bibliographic information for these documents is being entered in a standardized computer-based Q&A software package format (subtask b.1). Reviews are progressing as time allows.

- 2) Tracking the developing National Energy Strategy (NES) through discussions with personnel in the Department of Energy Office of Policy, Planning, and Analysis. These activities included: 1) obtaining and reviewing a preliminary draft of the NES, and 2) attendance at a hearing regarding the role of regulation in the energy sector.
- 3) Initiation of work on Task C: Compilation of an Energy Resource Data Base.
- 4) Initiation of work on Regional Energy Sector Profiles designed to eventually contain information on occurrence, production, consumption, marketing, environmental issues, regulations, and revenue for each energy source in the region.

5.0 TRIPS/PRESENTATIONS

Trips and presentations during the third quarter included:

Washington, D.C., January 21-24 -- Visited the Office of Policy and Planning, discussions with personnel concerning the status of the NES, obtained and reviewed a draft of the NES and portions of the testimony, and attended a NES hearing on the role of regulation in the energy sector.

6.0 FUTURE ACTIVITIES

Activities in the fourth quarter will include:

- 1) Continuation of work on Tasks A, B, and C and related activities.
- 2) Continued tracking of NES developments, including the acquisition and review of the Interim Report on the NES available April 1 as well as the "White Papers" on specific topics which will be available shortly thereafter.
- 3) Continued contact with energy officials and representatives of the private sector concerning regional policy issues.
- 4) Initiate the compilation of historical information on federal and regional energy-related initiatives.

3.0 ADVANCED RESEARCH AND TECHNOLOGY DEVELOPMENT

3.1 Turbine Combustion Phenomena

TURBINE COMBUSTION PHENOMENA

**Quarterly Technical Progress Report
for the Period January - March 1990**

by

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**U.S. Department of Energy
Office of Fossil Energy
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TURBINE COMBUSTION PHENOMENA

1.0 INTRODUCTION

Under DOE sponsorship coal/water slurry fuels have been investigated as fuels for gas turbine engines for several years, but the major technical problems still inhibiting commercialization are deposits on the pressure and suction sides of the turbine blades, reducing the gas flow area and the turbine efficiency; acceptable coal burnout, given the short residence time inherent with gas turbine engines; corrosion of turbine blades by condensed alkali sulfates; erosion of turbine blades and other components by ash particles entrained in the products of combustion; and control of NO_x , SO_2 , and particulate emissions. The release of certain mineral matter species found in both raw and beneficiated coals can lead to ash deposition on surfaces, regardless of the ash content of the fuel. This deposition can lead to corrosion and metal loss of critical turbine components and, ultimately, to derating, unavailability, or catastrophic failure of the power generation system. Alkali metals and sulfur, existing as impurities in coal, have been identified as key components in the initiation of deposition and the onset of corrosion.

Up to the last four years, low-rank coals (LRCs) were not considered as potential fuels for gas turbine engines 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 over 35 wt.%, due to the high moisture levels in LRCs. 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 a solids loading up to 50% and a heating value over 6000 Btu per pound of slurry. Subbituminous coals also respond very well to hydrothermal treatment and produce higher quality slurries. Availability of a slurry with a high enough fuel value to sustain combustion makes it possible to take advantage of the 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 nonagglomerating tendency relative to bituminous slurries, reducing the importance of atomization to very fine droplet sizes.

2.0 GOALS AND OBJECTIVES

The overall objective of this research is to continue to expand the data base on the effects of low-rank coals' unique properties on its combustion behavior in pressurized combustion systems such as gas turbine engines. Research will be directed toward understanding the properties of LRC fuels which affect ignition and burn times, combustion efficiency, vaporization and deposition of inorganics, and the erosion of critical gas turbine components. Special emphasis will be placed on an investigation of LRC high-shear rheology

and its effect on atomization and combustion behavior, an evaluation of LRCs' nonagglomerating properties using laser-based diffraction techniques (Insitac PCSV), an investigation of particulate hot-gas cleanup techniques, and inorganic transformations/alkali vaporization using a pressurized drop-tube furnace.

2.1 Years Four Through Six Project Objectives

A. Revise Technology and Market Assessment.

This literature review will enable UNDEERC personnel to assess the current status of coal-fired gas turbine research to determine what recent advances have been made by other researchers. This effort will build upon the technology and market assessment made at the start of this program.

B. Characterization of LRCs' Atomization Properties.

The objective of this task is to investigate the effects of coal type, particle-size distribution, solids loading, additive package, and shear rate on LRC slurry rheology. High-shear rheology will be measured using a capillary extrusion viscometer modified to perform rheological tests at shear rates up to 200,000 1/sec. This task will also examine the pressurized atomization characteristics of these LRC fuels with a Malvern 2600 particle-size analyzer and still photography in a pressurized spray chamber under construction at UNDEERC. The combustion behavior of these same fuels will be evaluated under similar air-to-fuel and pressure ratios in the gas turbine simulator. This task would also look at different atomizer types in a effort to minimize spray droplet size distributions for a given rheology and atomizing air-to-fuel ratio.

C. Evaluation of LRC Fuel Agglomeration.

The objective of this task is to evaluate the agglomerating or nonagglomerating tendencies of LRC fuels by providing optical access for an Insitac PCSV particle-size analyzer at various residence times along the axis of a pressurized drop-tube furnace under construction at UNDEERC. Thus product of combustion (POC) particle-size distributions as a function of residence time, the starting particle-size distribution, and droplet size can be measured to determine if the smaller particle-size distributions found in the LRC fly ash are the result of a gradual burnout of slurry droplet agglomerates or the result of agglomerate disintegration into its original particle-size distribution due to the high thermal friability of LRC fuels.

D. Investigation of Particulate Hot-Gas Cleanup Systems.

The objective of this task is to evaluate potential hot-gas particulate cleanup techniques as to their relative probability of success and to test the best two or three systems in the turbine simulator. This task would include a technology assessment building upon a previous literature search performed on hot-gas cleanup techniques. These techniques

could include, but would not be limited to, ceramic cross flow filters and filter candles, nested fiber filters, cyclones, HTHP ESPs. Potential also exists for investigating an alkali vapor cleanup device (i.e., sorbent-packed beds, etc.).

E. Ash Transformation and Alkali Vaporization Studies.

The objective of this task is to investigate the ash transformations experienced by the mineral matter in beneficiated low-rank coal fuels. Very little research to date has investigated the effects of pressure and coal beneficiation on the reaction pathways taken by the mineral matter present in LRC fuels. These transformations should be dependent on the cleaning techniques used and the level of cleaning achievable on the various coal types. Mineral matter transformations of beneficiated LRC under turbine operating conditions will be investigated in a pressurized drop-tube furnace under construction at UNDEERC. This drop-tube furnace will be capable of combusting both slurry droplets and coal particles. The effects of residence time, temperature, pressure, atmosphere, and gas/fuel flow rates can be varied to examine their effects on ash transformations and carbon burnout. The drop tube will also provide carbon burnout as a true function of residence time, given the laminar gas flow. The effects of deposition probe shape and temperature and approaching gas velocity on the measured deposition rates can also be investigated. Optical ports into the drop tube will enable quantities of alkali vapor/aerosols in the gas streams to be measured using in situ methods. Another advantage of the pressurized drop-tube furnace is the small quantities of fuel (up to 1.5 lbs/hr) needed to conduct extensive deposition and burnout testing as compared to the turbine simulator (approximately 150 lbs/hr).

F. Investigation of Slagging Combustor Design.

Should concurrent beneficiation of LRC studies at UNDEERC indicate that acceptable ash levels and composition not be achievable, a vertically fired combustion zone would be built to replace the horizontally fired rich combustion zone on the current turbine simulator. This modification would enable the combustor to operate in a slagging combustor mode versus the current nonslagging combustor mode. Work on this task would be dependent on the results of the work in progress and would be subject to DOE approval.

2.2 Fourth Year Goals and Objectives

Task A - Revise Technology and Market Assessment.

This task involves updating the previous literature assessment made at the beginning of the program.

Task B - Characterization of LRCs' Atomization Properties.

This task involves the investigation of LRCs' fuel atomization and viscosity properties using a capillary viscometer and a pressurized spray

chamber with a Malvern particle-size analyzer and still photography to determine spray droplet sizes. In addition, this task will conduct a parametric investigation of different atomizers for atomization effectiveness. This includes the commercially available Delavan and Parker-Hannifan atomizers, along with the UNDEERC developed B-II nozzle. This task will also evaluate atomizer combustion performance under the same operating conditions in the turbine simulator combustion rig.

Task C - Evaluation of LRC Fuel Agglomeration

This task consists of using laser-based diagnostics (i.e., Insitex PCSV) and particulate sampling to determine if LRC slurry droplets are friable enough to break into their original particle sizes as hypothesized or remain as agglomerates which must burn out.

Task D - Investigation of Particulate Hot-Gas Cleanup Systems.

This task involves evaluating potential hot-gas particulate cleanup techniques for use in direct coal-fired gas turbines to test the two best techniques in combustion tests on the turbine simulator. These techniques could include, but would not be limited to, ceramic cross flow filters and filter candles, nested fiber filters, cyclones, HTHP ESPs, etc.

Task E - Ash Transformation and Alkali Vaporization Studies.

Technical work in this task for Year 4 consists of finishing construction on the PDTF and subsequent combustion tests using selected beneficiated coals to determine the effects of residence time, gas composition, temperature, and pressure on carbon burnout and ash deposition.

Task F - Investigation of Slagging Combustor Design.

No technical work in this task will be performed in Year 4. If coal ash properties dictate, construction of a first-stage slagging combustor would begin late in Year 5.

3.0 BACKGROUND

3.1 One Million-Btu/hr Gas Turbine Combustor

To meet the objectives of the program, a pressurized combustion vessel was built to allow the operating parameters of a direct-fired gas turbine combustor to be simulated. 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 would have a significant effect on the measured combustion performance. Based on computer modeling, a rich-lean, two-stage nonslagging 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 on the gas turbine combustor and its turbomachinery.

A short description of the gas turbine simulator is given here; a more detailed description is given elsewhere (1,2,3). Figure 1 is a schematic of the 1-MM Btu/hr gas turbine combustor, showing its internal design. Figure 2 is a photograph of the 1-MM Btu/hr gas turbine combustor. The head section of the turbine has an interchangeable, horizontal, flat-bladed air swirler for controlling the primary air-fuel spray and developing a recirculation zone in the rich combustion zone. A Delavan Swirl-Air nozzle with a 50° spray angle is currently used as the atomizer. The pressurized combustion vessel itself is comprised of several short sections of refractory-lined stainless steel pipe. These sections are water-jacketed to provide cooling of the external pressure vessel wall. This modular design allows the length of the combustion zones to be varied. The removal of some of these modules allows the effect of residence time to be investigated under similar flow conditions.

The quench zone of the turbine simulator was designed to promote rapid mixing of the secondary air with the POC exiting the rich combustion zone, thus minimizing the occurrence of localized "hot spots" and the formation of thermal NO_x. 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 a lean zone exit temperature of 2000°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). Four air-cooled probes with various contact angles were machined from thick-walled high-temperature alloy tubing and were installed to simulate the leading edge of turbine blades. Additional cooling air was added after the first two probes to cool the exit gas stream up to 200°F, such that gas temperature as well as metal temperature can be investigated for their effects on deposition/erosion/corrosion (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 before passing them 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. 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.

3.2 Scanning Electron Microscope Techniques

Computer-controlled scanning electron microscopy (CCSEM) is used to characterize minerals in unaltered coal samples and inorganic phases in combustion products such as char or fly ash. 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 heart of the CCSEM analysis system is a recently installed annular backscattered electron detector (BES). The BES system is used because the coefficient of

Figure 1. Schematic of 1-MM Btu/hr gas turbine simulator.

Figure 2. Photograph of 1-MM Btu/hr gas turbine simulator.

backscatter (the fraction of the incoming beam that is backscattered) 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 coal minerals can be easily discerned from the coal 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 matrix and the 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 rotated diameters about the center of the particle are measured, and the particle 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 LotusTM transportable file for data reduction and manipulation. The CCSEM data provides quantitative information concerning not only the mineral types which are present, but their size and shape characteristics as well. Since the same analysis can be performed on the initial coal and resultant fly ash or char, direct comparisons can be made and inorganic transformations inferred.

In order to quantitatively determine the distribution of phases in fly ashes, deposits, and slags, the scanning electron microscopy point count technique (SEMP) was developed. 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 for data base analysis. The software is used to calculate molar and weight ratios for each point. Using these ratios, the points which have compositions of known phases (common to ashes and coal minerals) are identified and counted. The software then finds the relative percents of all the identified points as well as the percent number of unknown phases. The unknown phases are those for which there is no known phase corresponding to the chemical composition. In addition, the average chemical composition of all the points in the sample is calculated. Previous work at UNDEERC has shown that the SEMPC average composition corresponds very well to the bulk chemical analysis (4). The quantitative ability of the SEMPC allows for detailed comparisons to be made between different samples.

4.0 ACCOMPLISHMENTS

4.1 Detailed Design of a High-Temperature, High-Pressure Cyclone

A high-temperature, high-pressure (HTHP) cyclone was selected as the first stage in a particulate hot-gas cleanup device. The design goal was to remove 95% of 5-micron particulate. The cyclone was also designed to fit inline with the current turbine simulator located at the UNDEERC. Design conditions were selected to match those experienced in the turbine simulator at its 1-MM Btu/hr firing rate. These conditions resulted in a gas flow rate of approximately 400 scfm entering the cyclone at 2000°F and 160 psig. Cyclone dimensions were selected using the dimensions reported by Perry (5) and Stairmand (6). Table 1 shows the calculated collection efficiency and pressure drop of the HTHP cyclone at different diameters. Using the methodology reported by Lapple (7), a cyclone diameter of 5 inches was calculated to

TABLE 1

HIGH-PRESSURE, HIGH-TEMPERATURE CYCLONE DESIGN RESULTS AT 400 SCFM,
175 PSIA, AND 2000°F

Cyclone Diameter (in.)	50% Cut Size (μm)	Collection Efficiency (@ 5 μm)	Differential Pressure (in H_2O)
5.5	2.51	0.80	46.7
5.0	2.17	0.84	68.3
4.5	1.86	0.88	104.1
4.0	1.56	0.91	166.8
3.5	1.27	0.94	284.5

provide a collection efficiency of approximately 85% for 5-micron particles and to have a pressure drop less than 2.5 psi.

Figure 3 is a drawing showing the design of the high-temperature, high-pressure (HTHP) cyclone which will be inserted in the turbine simulator combustion system located at the UNDEERC. This cyclone will be fabricated from 8-inch schedule 40 pipe which is welded to form an off-center tee. This pipe will be water-jacketed to keep the metal wall temperatures low. As shown in Figure 3, the cyclone dimensions will be cast in refractory inside the tee. This cyclone will replace the last section of the lean combustion zone shown in Figure 1. Openings have been included in the vessel walls for measuring the inlet and outlet combustion gas temperatures and pressures. In addition, openings have also been included for taking upstream particulate samples, while an existing port will allow downstream particulate samples to be collected for measuring the cyclone efficiency. A second opening was added for a water-jacketed and sealed boroscope viewing system which is currently being ordered. This boroscope will allow the flame quality and stability to be monitored during combustion tests.

4.2 Pressurized Spray Chamber

Due to emphasis on completing the pressurized drop-tube furnace and a busy construction schedule for the operations group with large pilot plant-scale projects in circulating fluid-bed combustion and mild gasification, atomization testing has been postponed until more operator time becomes available.

4.3 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 is 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.

Figure 3. Design of HTHP cyclone for testing in 1-MBtu/hr gas turbine simulator.

The pressurized drop-tube furnace (PDF) is capable of operating under the following conditions:

Temperature: ambient to 1500°C
 Pressure: ambient to 20 atm.
 Oxygen: 0 - 20 mole%
 Gas flow: 0 to 400 slpm at 20 atm.
 Residence time: 0 to 0.50 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 which will allow the design goals to be met. A drawing of the PDTF facility is given in Figure 4. The entire PDTF is constructed of standard 24" and 6" flanged pipe sections. The large pressure vessel contains the furnace sections of the PDTF as shown in Figure 5. Figure 6 is a photograph of the PDTF after assembly for shakedown testing. The walls of the vessel are water-cooled to dissipate the heat from the furnaces. There is a preheater and two furnace sections located above the optical sight ports and one furnace below 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 feedthrough terminals in the bottom blind flange of the pressure vessel.

Above the large pressure vessel shown is the injector section containing the injector assembly. The injector is a one-inch diameter water-cooled probe sheathed in high-temperature insulation. Figure 7 is a photograph showing the translating mechanism used 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 zero and 0.5 seconds. Small viewports in the pipe crosses at the bottom and top of the injector section allow visual inspection of the probe and the 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. Both assemblies are interchangeable to allow for feeding powdered or slurry fuels and for collecting deposition or fly ash samples.

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. Figure 7 also shows the sample feeder pressure vessel located next to the sample injector translating mechanism. The design allows the actual sample feeder to be constructed of lightweight material, since it does not have to withstand more than slight pressure differentials. A small sight port allows inspection of the feeder operation, and the removal of a blind flange gives access to the vessel for filling or adjustment of the feeder. The lightweight feeder can then hang from a load cell in the pressure vessel to provide 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 mole% at flow rates up to 400 liters/minute. The furnace pressure is controlled by a letdown control valve at the exit of the furnace.

Figure 4. Pressurized drop-tube furnace process schematic.

Figure 5. Furnace assembly in PDTF vessel.

Figure 6. Photograph of PDTF pressure vessel.

Figure 7. Photograph of PDFF translating mechanisms.

This quarter the furnace sections were mounted and wired in the 24-inch pressure vessel, and the optical insulation and all other insulation were installed. All the pressure vessel sections were reassembled and torqued to their proper setting. All thermocouple, pressure transducer, and mass flow controller wiring was completed. The water-cooled injection and sampling probes were fabricated, and the portions which would be inserted in the hot furnace were covered with insulation. These probes and their translating mechanisms were installed on the PDTF. The translating mechanisms were tested and calibrated to determine the actual location of the probes in the furnace at any given position of the translating mechanism. All cooling water, nitrogen, oxygen, and air lines were plumbed in to the appropriate ports and flowmeters. A coal feeder was fabricated and installed in the separate six-inch cross. Figure 8 is a schematic of the coal feeder used in the PDTF.

The complete system was given a final pressure check at 250 psig. The furnace elements were baked out at 1200°C, according to insulation bakeout procedures. The PDTF furnaces and controllers functioned properly, and the cooling water was found to keep the external air gap around the furnace and the injection and deposition probes at reasonable temperatures. A shakedown test was performed to test the complete PDTF system. During this shakedown testing, several problems were encountered. One problem was that the load cell for monitoring the coal feed rate was too small; thus, the coal feeder used most of the load cell range before any coal was loaded into the feeder. In addition, problems were encountered when feeding coal, due to the PDTF gas flowmeters being sized too small, thus limiting the gas velocity used to pneumatically convey the coal particles into the PDTF. Further examination indicated that the coal was plugging close to the tip of the injection probe. It was also observed that the deposition substrate temperature was too low, due to the substrate being mounted right on the end of the water-cooled deposition probe. A thermal barrier, such as ceramic insulation, will have to be inserted between the probe and the substrate in order to achieve higher metal temperatures. During this testing, the heating elements for the bottom furnace burned out, leading to extremely low gas temperatures being measured in the optical access area. The PDTF will have to be partially disassembled and the furnace repaired before any meaningful testing can be accomplished.

4.4 SEM Analytical Results

CCSEM analyses were performed on the original CWF tested in the 1-MM Btu/hr gas turbine simulator in order to establish a baseline for comparison with deposits generated at 1100°C from these fuels in the PDTF facility. The Otisca CWF is a Taggart seam, Virginia bituminous coal bought commercially from Otisca, Ind. (Syracuse, NY). The Kemmerer and Beulah-Zap fuels were prepared at UNDEERC. The Kemmerer fuel was acid-cleaned only, while the Beulah-Zap fuel was both physically and chemically cleaned, and both were then hydrothermally treated and micronized. Tables 2 and 3 show the proximate and ultimate analyses, ash fusion temperatures, particle-size and x-ray fluorescence analyses previously reported on these fuels.

Figure 8. Schematic of coal feeder for pressurized drop-tube furnace.

TABLE 2

PROXIMATE AND ULTIMATE ANALYSES OF LRC FUELS TESTED IN TURBINE PROGRAM

<u>Sample:</u>	<u>Otisca</u>	<u>Kemmerer</u>	<u>Beulah-Zap</u>
PDU Test No.	N/A	38	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 diff.)	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 (°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	15.9
Top Size (99%<) (microns)	15.2	34.9	59.6

TABLE 3

X-RAY FLUORESCENCE ANALYSIS OF LRC FUELS TESTED IN TURBINE PROGRAM

<u>High-Temperature Ash Results (% of ash, SO₃-free)</u>	<u>Otisca Fuel</u>	<u>Kemmerer Fuel</u>	<u>Beulah-Zap Fuel</u>
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

Tables 4, 5, and 6 show the CCSEM analysis performed on these same fuels. The first seven columns are all in weight percent on a mineral basis in a certain size distribution, while the last column is the total weight percent on a coal basis, regardless of size. The analysis for the Otisca CWF shows that there were no minerals above 10 microns and only 16 wt.% of mineral particles were over 4.6 microns. In addition, two compounds (aluminosilicate and pyrite) comprise 60 wt.% of the minerals. The identified mineral phases account for approximately half of the ash level reported in the proximate analysis. For the Kemmerer CWF, quartz, aluminosilicate, and pyrite are the major mineral types. About 38 wt.% of all the minerals are greater than 10 microns. It is interesting to note that quartz comprises approximately 57.5 wt.% of the minerals, and aluminosilicate constitutes another 24 wt.% of the minerals. Approximately 83 wt.% of the ash in the coal is in the mineral form, which is consistent with this fuel being acid-cleaned only.

The major minerals identified in the Beulah CWF are quartz and pyrite; however, the iron oxide level is higher than would be expected for the Beulah fuel and is probably the result of some of the magnetite used in the heavy media separation remaining with the fuel. Approximately 43 wt.% of the minerals in the Beulah fuel are greater than 10 microns. The high level of unknowns is also unusual and merits further examination. Only 9 wt.% of the ash in the Beulah fuel was identified as minerals in the CCSEM analysis. From

TABLE 4
SUMMARY OF CCSEM RESULTS FOR OTISCA FUEL

	Weight Percent Mineral Basis Particle-Size Distribution (μm)						Total wt. %	
	<2.2	2.2-4.6	4.6-10	10-22	22-46	>46	Total	Coal Basis
QUARTZ	3.5	3.1	1.0	0.0	0.0	0.0	7.6	0.03
IRON OXIDE	0.7	1.1	2.6	0.0	0.0	0.0	4.4	0.02
ALUMINOSILICATE	14.6	15.7	7.0	0.0	0.0	0.0	37.3	0.16
CA AL-SILICATE	0.1	0.0	0.0	0.0	0.0	0.0	0.1	0.00
FE AL-SILICATE	3.8	1.6	0.0	0.0	0.0	0.0	5.3	0.02
K AL-SILICATE	3.2	4.3	4.4	0.0	0.0	0.0	11.9	0.05
PYRITE	16.4	5.1	1.0	0.0	0.0	0.0	22.5	0.10
GYP SUM	0.8	1.7	0.0	0.0	0.0	0.0	2.4	0.01
BARITE	0.1	0.0	0.0	0.0	0.0	0.0	0.1	0.00
CA SILICATE	0.0	0.2	0.0	0.0	0.0	0.0	0.2	0.00
GYP/AL SILICATE	0.1	0.0	0.0	0.0	0.0	0.0	0.1	0.00
ALUMINA	0.1	0.4	0.0	0.0	0.0	0.0	0.5	0.00
CALCITE	0.0	0.4	0.0	0.0	0.0	0.0	0.4	0.00
RUTILE	0.5	0.3	0.0	0.0	0.0	0.0	0.8	0.00
PYRRHOTITE/SULFA	1.0	0.0	0.0	0.0	0.0	0.0	1.0	0.00
SI-RICH	0.5	0.4	0.0	0.0	0.0	0.0	0.9	0.00
UNKNOWN	3.2	1.4	0.0	0.0	0.0	0.0	4.6	0.02
TOTAL	48.5	35.5	16.0	0.0	0.0	0.0	100.0	0.43

TABLE 5
SUMMARY OF CCSEM RESULTS FOR MICRONIZED KEMMERER

	Weight Percent Mineral Basis Particle-Size Distribution (μm)						Total wt. %	
	<2.2	2.2-4.6	4.6-10	10-22	22-46	>46	Total	Coal Basis
QUARTZ	7.5	8.8	8.6	13.3	19.4	0.0	57.7	1.09
IRON OXIDE	0.8	0.6	1.0	0.0	0.0	0.0	2.4	0.05
ALUMINOSILICATE	7.3	5.0	8.5	3.6	0.0	0.0	24.4	0.46
CA AL-SILICATE	0.2	0.3	0.0	0.0	0.0	0.0	0.5	0.01
FE AL-SILICATE	0.1	0.1	0.0	0.0	0.0	0.0	0.2	0.01
K AL-SILICATE	1.0	0.7	0.0	0.0	0.0	0.0	1.7	0.03
PYRITE	3.3	1.8	0.0	0.0	0.0	0.0	5.1	0.10
BARITE	0.1	0.2	0.0	0.0	0.0	0.0	0.3	0.01
CA SILICATE	0.1	0.0	0.0	0.0	0.0	0.0	0.1	0.00
CA ALUMINATE	0.1	0.1	0.3	0.0	0.0	0.0	0.6	0.01
RUTILE	0.2	0.6	0.0	0.0	0.0	0.0	0.8	0.02
DOLOMITE	0.0	0.0	0.7	0.0	0.0	0.0	0.8	0.02
PYRRHOTITE/SULFA	0.1	0.0	0.0	0.0	0.0	0.0	0.1	0.00
CA-RICH	0.1	0.0	0.0	0.0	0.0	0.0	0.1	0.00
SI-RICH	0.1	0.1	0.0	0.0	0.0	0.0	0.2	0.00
UNKNOWN	1.2	1.7	0.0	2.1	0.0	0.0	5.0	0.10
TOTAL	22.3	20.1	19.2	19.0	19.4	0.0	100.0	1.89

TABLE 6
SUMMARY OF CCSEM RESULTS FOR BEULAH FUEL

	Weight Percent Mineral Basis Particle-Size Distribution (μm)						Total wt. %	
	<2.2	2.2-4.6	4.6-10	10-22	22-46	>46	Total	Coal Basis
QUARTZ	16.8	6.2	0.9	1.5	2.8	4.6	32.8	0.08
IRON OXIDE	1.3	2.7	0.0	0.0	0.0	0.0	4.1	0.01
ALUMINOSILICATE	1.8	1.6	0.0	2.2	0.0	0.0	5.6	0.01
CA AL-SILICATE	0.2	0.1	0.0	0.0	0.0	0.0	0.3	0.00
FE AL-SILICATE	0.1	0.1	0.0	0.0	0.0	0.0	0.2	0.00
K AL-SILICATE	0.2	1.0	0.0	0.8	0.0	0.0	2.0	0.01
PYRITE	10.3	3.1	2.8	0.0	0.0	0.0	16.1	0.04
GYPSUM	0.2	0.5	0.4	0.3	0.0	0.0	1.3	0.00
CA SILICATE	0.1	0.6	0.0	0.0	0.0	0.0	0.7	0.00
GYP/AL SILICATE	0.0	0.0	0.0	1.6	2.1	0.0	3.8	0.01
CA ALUMINATE	0.1	0.0	0.0	0.0	0.0	0.0	0.1	0.00
RUTILE	0.2	0.4	0.0	0.0	0.0	0.0	0.6	0.00
PYRRHOTITE/SULFA	0.1	0.0	0.0	0.0	0.0	0.0	0.1	0.00
CA-RICH	0.0	0.1	0.0	0.0	0.0	0.0	0.1	0.00
SI-RICH	0.3	0.1	0.0	0.3	0.0	0.0	0.7	0.00
UNKNOWN	2.4	1.4	0.9	6.5	20.3	0.0	31.5	0.08
TOTAL	34.1	17.9	5.0	13.2	25.3	4.6	100.0	0.24

CCSEM analysis, most of the 2.56% ash in the Beulah was either organically bound or less than 1 μm in average diameter, the lower detection limit of CCSEM. The Beulah organically bound fraction has much larger quantities of Fe_2O_3 and CaO than the other coals, and only a fraction of these components are accounted for by discrete minerals. The Fe_2O_3 and CaO may act as fluxing agents, effectively lowering the ash fusion temperature in an aluminosilicate system. This would help induce slag and deposit formation at the 2000°F temperatures present in the gas turbine simulator. Ash fusion temperatures were much lower for the Beulah-Zap as compared to the other test coals. Chemical fractionation analysis may need to be done on the Beulah coal to determine the portion of inorganic constituents that remain organically bound.

The importance of the CCSEM results as an interpretative tool is more evident when combined with the ash content and composition of the fuels. It can be argued that a larger particle-size distribution of minerals in coal can significantly increase subsequent fly ash particle impaction rates on turbine blades, which in turn increases the potential for deposit development. Larger quantities of minerals were noted in the >10 μm range for the Beulah (43%) and the Kemmerer (38%) fuel, as compared to the Otisca (0%) fuel on a mineral basis, which is consistent with the deposition seen in the turbine simulator.

5.0 FUTURE PLANS

Future plans include finishing the construction of the HTHP cyclone vessel, conducting a hydrostatic pressure test of the vessel, and casting the cyclone in refractory. The HTHP cyclone will be installed in the 1-MM Btu/hr gas turbine combustor and shakedown testing initiated. Spray tests in the pressurized spray chamber using previously tested CWF will be performed. Shakedown testing of the PDTF using the fuels previously tested in the gas turbine simulator will be accomplished. Future plans also include tests to look at what effects various levels of coal cleaning and different types of additives for increasing the ash melting temperatures have on the measured deposition rates and composition. A slurry feed system for the PDTF will be constructed, so fuel agglomeration tests can be completed.

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3.2 Combustion Inorganic Transformation

COMBUSTION INORGANIC TRANSFORMATIONS

**Sixteenth Quarterly Technical Progress Report
for the Period January through March 1990**

by

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COMBUSTION INORGANIC TRANSFORMATIONS

EXECUTIVE SUMMARY

Task 1: Improvements to the CCSEM Methodology

Coal samples were prepared for computer-controlled scanning electron microscopy (CCSEM) testing and repeatability testing was begun. Preliminary results of CCSEM precision testing using Beulah coal are reported. The precision of the CCSEM technique is not nearly at the level we desire. Comparison of EERC and PSI CCSEM results for Beulah coal show some discrepancies, especially with the clay minerals and total mineral content. Based on the data it appears we need to analyze more larger-sized minerals in a typical CCSEM run to improve counting statistics.

Discussions with several other groups performing similar analyses were held in preparation for the eventual round robin of the coal standards. Arrangements were made for the purchase and installation of a new automated digital electron microscope/microprobe system (ADEM). The ADEM will provide us with increased automation, new capabilities, and help to alleviate the present sample backlog. The CCSEM image analysis interface was completed, allowing for simultaneous digital image collection during CCSEM analysis.

Task 2: Mineral and Ash Characterization

Fourteen deposits were analyzed for Physical Sciences Incorporated Technology Company (PSIT) for phase assemblage determinations using scanning electron microscopy point-count (SEMP). The deposits were generated from the following coals: San Miguel, Beulah, Kentucky #11, Illinois #6, Kentucky #9, Eagle Butte, and Upper Freeport.

Task 3: Laboratory-Scale Combustion Testing

Combustion testing of Kentucky #9 and San Miguel coals in the drop-tube furnace was nearly completed. Fly ash was generated at three temperatures for three different size fractions of both coals and collected using both the multicyclone and the impactor. Bulk fly ash samples were also collected on a filter for the unsized and 53-74 μ m coal feeds. Short residence time chars were generated for the Kentucky #9. All of the samples were submitted for analysis, using either CCSEM or SEMPC.

Particle-size distributions of discrete mineral or amorphous phases in intermediates produced in the drop-tube furnace (DTF) for two coals were examined. Time resolved particle-size distributions (PSDs) of phases show that Beulah and Upper Freeport phases coalesce with time. The Upper Freeport shows an initial increase in the amounts of particles in the lower-size ranges due to fragmentation of minerals or the formation of smaller inorganic ash droplets from submicron minerals or inorganics. The transformation of selected inorganic components through time was also noted. Sodium and calcium organically associated in the Beulah react readily with smaller-sized kaolinitic clays and to a much lesser degree with quartz. Pyrite appears to

undergo fragmentation during combustion in the Beulah and Upper Freeport with a resulting increase in iron oxide.

1.0 GOALS AND OBJECTIVES

The overall objective of this project is the development of a unified picture of the physical and chemical changes that occur in coal inorganic matter during combustion. The research focuses on three main tasks. The first task will involve developing the computer-controlled scanning electron methodology to determine the distribution of mineral grains in pulverized coals. The second task will involve determining the inorganic components in coal and coal ash-derived components for coals and ashes generated in the PETC mineral matter programs at EERC and Physical Sciences, Inc., Technology Company (PSIT). The third task will study the physical and chemical changes of inorganic phases during combustion in laboratory-scale combustion equipment.

The ultimate goal of the project is to develop a means to predict the state (vapor, liquid, or solid), composition, and size of the inorganic material at any point in a combustion system, given the coal composition and combustion conditions. The first task focuses on developing a method to effectively determine the size, composition, and juxtaposition of mineral grains in pulverized coals. In addition, chemical fractionation is used to determine the abundance of organically associated inorganic constituents in the lower rank subbituminous and bituminous coals. Proper determination of the inorganic components in coal is an essential requirement in understanding and ultimately predicting the transformations of inorganic components during coal combustion. The second task involves characterizing coals, chars, and ashes. Coals will be examined by CCSEM and chemical fractionation to determine the association, size, composition, and juxtaposition of the inorganic components in coals.

Chars and ashes produced in Task 3 will be examined to determine their bulk composition, surface composition, phase distribution, and morphology. This will be accomplished primarily by utilizing surface science equipment, scanning electron microscopy/electron microprobe analysis, x-ray fluorescence, and x-ray diffraction. The objective of this task is to follow the transformation of inorganic constituents at various degrees of coal particle burnout to produce the fly ash. The third task involves using the drop-tube furnace system to produce chars at various degrees of burnout and ultimately a carbon-free fly ash. In addition, precisely formulated model mineral/coal mixtures are being produced and combusted to examine in detail some of the transformations that occur. In conjunction with these three tasks is an ongoing effort to evaluate all data produced, with respect to reproducibility, including coal characterization data, char and fly ash formation studies with the drop-tube furnace, and ash characterization data. A means of predicting the fate of inorganic constituents during combustion cannot be adequately developed without consistent, quantitative data. During the past three years, this project has focused on developing consistent and quantitative techniques to produce and analyze the inorganic components in coals, chars, and fly ash. Data is currently available on five coals, and two more will be examined this year. A modeling effort will be initiated this year to predict the size and

composition of ash particles based on coal composition and combustion conditions. This effort will be coordinated with the work presently being conducted at EERC on viscosity modeling (1) and thermochemical equilibrium modeling (2).

Task 1: Improvements to the CCSEM Methodology

The specific objectives of the CCSEM improvements task during this quarter were to:

- 1) Evaluate the precision of the CCSEM technique using coal samples.
- 2) Make arrangements for a limited round robin of tested coal samples with other labs.
- 3) Complete interface of CCSEM computer with image analysis computer to allow for digital image collection.

Task 2: Mineral and Ash Characterization

The specific objective of the mineral and ash characterization task during this quarter was to characterize fourteen deposits for PSIT using SEMPC.

Task 3: Laboratory-Scale Combustion Testing

The specific objectives of the laboratory-scale combustion testing task during this quarter were to:

- 1) Produce intermediates for Kentucky #9 and San Miguel coal in the drop-tube furnace by combusting three size fractions at 1300, 1400, and 1500°C.
- 2) Produce intermediates for Kentucky #9 and San Miguel bulk coal samples in the drop-tube furnace and collect on a bulk filter.
- 3) Produce short residence time chars for the Kentucky #9 coal in the drop-tube furnace at 1500°C for the 53-74 μm coal fraction.
- 4) Analyze the evolution of fly ash particle-size and composition using CCSEM data of time-resolved intermediates of various test coals.

2.0 TASK 1: IMPROVEMENTS TO THE CCSEM METHODOLOGY

2.1 Introduction

The objective of Task 1 is to provide precise characterization of the mineral matter in coals. Current methods of coal minerals characterization do not provide the level of detail needed to predict the interactions that take place during combustion. Mineral characteristics that affect mineral behavior during combustion include: 1) chemical composition, 2) size, 3) association of minerals with coal matrix, 4) mineralogical associations, and 5) mineral

shape. Presently, coal minerals are being characterized using a computer-controlled scanning electron microscopy/microprobe method (CCSEM). CCSEM analysis gives mineral compositions and sizes. Task 1 seeks to enhance the present methodology to include other significant mineral characteristics, such as the mineral associations, mineral shapes or morphology, and the relationships of the minerals to the coal matrix.

The task 1 project plan will use CCSEM together with an automated image acquisition and characterization program (AIA) to provide the data needed. Initial efforts are focused on testing the accuracy and precision of the present CCSEM methodology and on installing and developing the image analysis system.

2.2 Description of System

The SEM/microprobe system at the EERC consists of a JEOL 35U scanning electron microscope/microprobe, a GW electronics backscatter electron detector, an ultrathin window energy-dispersive x-ray detector, a wavelength dispersive x-ray detector, digital beam control, a Tracor-Northern 5600 x-ray microanalyzer control system, a Tracor-Northern 8500 image analyzer, and stage automation. The Tracor-Northern 5600 is interfaced with a MicroVax II and personal computer system for advanced data manipulation.

The key components of the SEM system that make it possible to image, size, and analyze inorganic particles include the backscatter electron detector, digital beam control, and the ultrathin window energy dispersive x-ray detector. The Tracor-Northern 5600 image analysis system allows for the automated acquisition and beam control, with data storage accomplished using the MicroVax II or a PC. The Tracor-Northern 8500 image analysis system allows for the automated acquisition, storage, and processing of images from the SEM. Figure 1 shows a schematic of the system hardware including the newly acquired image analysis components installed during this reporting period.

The CCSEM analysis uses backscattered electron imaging (BEI) and energy-dispersive spectra (EDS) detection to analyze minerals. Since the mineral or ash particles appear brighter in BEI relative to the lower atomic number background of the matrix, a distinction can be made between coal, epoxy, and mineral grains. Using the Tracor-Northern particle recognition and characterization program, the electron beam is programmed to scan over the field of view to locate the bright inclusions that correspond to mineral or ash species. On finding a bright inclusion, the beam performs eight diameter measurements on the inclusion, finds the center of the inclusion, and collects an EDS for two seconds. The system is set up to analyze 12 elements: Na, Mg, Al, Si, P, S, Cl, K, Ca, Fe, Ba, and Ti. The associated computer system then outputs to a storage file the following information for each particle analyzed: the size, area, perimeter, chemical composition, coordinates of location on the sample surface, frame number, and number of energy-photon counts.

Data from the CCSEM analysis is transferred simultaneously to a personal computer or the MicroVax II, where it is stored on tape or disk. Software developed at EERC classifies the minerals into categories based on size and composition.

Figure 1. Schematic of SEM/microprobe system and its operation.

2.3 Subtask A: CCSEM Testing

Three coals were chosen for CCSEM precision testing and eventual round robin testing with other labs. These coals are: 1) Beulah (lignite), 2) Eagle Butte (subbituminous), and 3) Illinois #6 (bituminous). These coals were chosen from the suite of coals being investigated by both PSI and EERC. These coals are presently being prepared by several techniques to determine the best methods for obtaining reproducible samples.

CCSEM testing on mineral standards reported in previous Quarterly reports showed fairly good precision (3). Results are reported here for precision testing of the size-fractionated Beulah test coal and bulk Beulah coal. EERC results are also compared to those obtained by PSI (4).

Table 1 shows CCSEM results for the Beulah samples. The major mineral categories of kaolinite, pyrite, and quartz are fairly consistent between all 4 analyses. Total mineral contents on a coal basis are not as consistent. The particle-size distributions of the minerals were plotted for all four samples as shown in Figure 2. There is a considerable spread in the size distribution data. More detailed examination of the raw data seems to indicate that most of the differences between samples are the result of a few, relatively large, particles. This preliminary data seems to indicate a need to analyze more particles in the larger size range. Similar work is being performed using Upper Freeport coal and will be reported in the final report.

TABLE 1
PRECISION TESTING RESULTS OF SELECTED BEULAH MINERALS
(Weight Percent)

	Run 1 *	Run 2 *	Run 3 **	PSI **
Quartz	18.00	17.61	16.3	12.0
Aluminosilicate ***	41.72	34.42	42.6	43.0
Ca-aluminosilicate	0.17	0.91	0.5	1.0
Fe-aluminosilicate	0.28	0.90	0.5	--
K-aluminosilicate	0.79	1.24	1.0	1.0
Pyrite	25.6	25.8	24.2	26.0
Gypsum	2.13	2.94	3.1	--
Barite	1.58	0.67	2.0	--
Ca-Rich	0.03	0.00	0.0	1.0
Si-Rich	0.31	0.30	0.7	--
Unknown	6.83	10.47	5.4	10.0
TOTAL Minerals Coal Basis	5.58	3.37	7.3	7.0

* 53-74 μ m coal

** Bulk coal

*** PSI mixed silicate and kaolinite contents added to get this amount

Figure 2. Reproducibility of particle size distributions determined for the samples listed in Table 1.

Discussions were held with Dr. G. P. Huffman of the University of Kentucky and Dr. W. E. Staszheim of Ames Laboratory, Iowa State University, concerning a round robin of one or more of the coals for reproducibility testing. A limited round robin of samples with these labs will be started during the next quarter.

2.4 Subtask B: CCSEM Automation and Development

Work in the area of CCSEM automation and development has focused on the automation of the present analysis and the establishment of an interface, allowing for the transfer of CCSEM field areas to the image analysis system for automated image collection and storage. Work on both of these areas is now complete, and these routines are both being tested. The automated digital image collection program was completed since the last reporting period and is briefly described below. The standard CCSEM analysis is run in the normal manner, but prior to the analysis of each frame examined, a backscattered digital image is obtained and saved to the TN8500 image analysis system. As the CCSEM analysis procedure proceeds, each particle analyzed is identified on the image. The positional data is saved to a disk along with the standard CCSEM data. These data can be recalled at a later time in order to make determinations of mineral associations and the relationships of the mineral particles to the coal matrix (juxtaposition). The data file is then appended to include any juxtapositional data. This program is seen as an intermediate step in development of the new CCSEM program which will provide juxtapositional relationships in an automated fashion.

2.5 Conclusions

Coal standards were selected and work has begun on reproducibility testing for the CCSEM analysis. Provisions are presently underway for a limited round robin of coal samples with G. P. Huffman and W. E. Staszheim. The CCSEM program is now fully automated, and the simultaneous digital image collection is in place as well.

Preliminary results of CCSEM precision testing using Beulah 53-74 μm coal revealed that the technique is not nearly at the precision level we desire. Comparison of EERC and PSI CCSEM results for Beulah and Upper Freeport coals shows some discrepancies, especially with the clay minerals and total mineral content. Based on the data, it appears we need to analyze more larger-sized minerals in a typical CCSEM run to improve counting statistics.

3.0 TASK 2: MINERAL AND ASH CHARACTERIZATION

3.1 Introduction

The important thrust of this task is to determine the inorganic constituents of coal, char, and fly ash using computer-controlled scanning electron microscopy (CCSEM), scanning electron microscopy point count (SEMPC), Auger electron spectroscopy (AES) and x-ray photoelectron spectroscopy (XPS). Samples will be generated from drop-tube furnace reactors at both the Energy and Environmental Research Center (EERC) and Physical Sciences Incorporated

(PSIT). Also included in this task is a separate 3-year study of inorganic transformations observed for the Robinson and Eagle Butte coals combusted in a down-fired combustor.

3.2 Equipment and Procedures

Computer-controlled scanning electron microscopy (CCSEM) utilizes a computer program 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 systems is the 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 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 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.

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 extraneously 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, image analysis is employed that allows for detailed examination and manipulation of stored SEI and BEI images and x-ray maps. Inherent and extraneous minerals and associations of adjacent minerals are determined easily by examining stored images of coal-epoxy polished surfaces. This technique is currently under development at the EERC.

Characterization of fly ash was performed using scanning electron microscopy and electron microscopy analysis. A technique was developed at the Energy and Environmental Research Center to determine the relative abundance of phases present in ashes and deposits (5). The technique is called SEM point count or SEMPC. The method involves microprobe analysis of about 250 random points in a polished cross section of 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 was calculated.

X-ray photoelectron spectroscopy (XPS) and Auger spectroscopy were used to characterize the surface of the fly ash and char. 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 species present on the surface and their chemical compositions. 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 one 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.

Another surface analysis technique performed at the EERC is secondary ion mass spectroscopy (SIMS). SIMS is a surface analysis and depth profiling technique that utilizes an ion beam to bombard the sample. This produces emissions 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 (include hydrogen), and the ability to provide isotopic and molecular information.

3.3 Results of SEMPC Analysis of PSIT Deposits

As part of collaborative efforts between EERC and PSIT, fourteen deposits generated by PSIT were analyzed using SEMPC. The deposits, listed in Table 2, were generated from the following coals: San Miguel, Beulah, Kentucky #11, Illinois #6, Kentucky #9, Eagle Butte, and the Upper Freeport. Table 3 summarizes the phase and oxide compositions for the deposits.

4.0 TASK 3: LABORATORY-SCALE COMBUSTION TESTING

4.1 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

TABLE 2
PSI DEPOSIT SAMPLE LABELS AND EERC SAMPLE NUMBERS

<u>Sample Label</u>
San Miguel SM-3
San Miguel SM-5
San Miguel SM-6
San Miguel SM-11
Beulah Lignite BL-19
Beulah Lignite BL-21
Beulah Lignite BL-29
Kentucky #11 KY-2
Kentucky #11 KY-5
Illinois #6 IL-4
Illinois #6 IL-5
Kentucky #9 KY-16
Eagle Butte EB-17
Upper Freeport UF-13

physical and chemical transformations of inorganic components of coals during combustion studied 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.

4.2 Equipment and Procedures

4.2.1 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 3. The furnaces are mounted on furnace bars extending through all three levels and 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.

TABLE 3

SEMP ANALYSIS OF PSIT DEPOSITS
(EDS Weight Percents)

Phase Composition	SM-3	SM-5	SM-6	SM-11	BL-19	BL-21	BL-29	KY-2	KY-5	IL-4	IL-5	KY9-16	EB-17	UF-13
Gehlenite	0.0	0.0	0.8	0.0	3.7	15.8	6.0	0.0	1.8	0.0	0.0	0.0	5.5	0.0
Anorthite	1.2	0.6	0.8	1.1	1.9	0.0	0.0	10.3	5.5	1.8	1.7	0.0	3.6	0.0
Pyroxene	0.0	0.0	0.0	0.0	0.0	1.8	0.0	0.0	0.0	0.0	0.0	0.0	1.8	1.8
Mullite	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	10.3	0.0	1.8	0.0
Calcium Silicate	0.0	0.0	0.0	0.0	0.0	0.0	2.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Quartz	7.8	6.3	47.7	8.9	33.3	0.0	14.0	15.5	29.1	5.5	8.6	26.2	12.7	35.7
Iron Oxide	0.6	0.0	1.2	0.7	18.5	3.5	2.0	19.0	7.3	5.5	8.6	7.1	3.6	7.1
Calcium Oxide	0.0	0.0	0.8	0.0	0.0	1.8	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Ankerite (Ca,Mg,Fe) CO ₃	0.0	0.0	0.4	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Aluminum Oxide	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.7	0.0	0.0	0.0
Pure Kaolinite (Amorp.)	0.6	2.5	0.4	0.7	0.0	0.0	0.0	0.0	0.0	0.0	15.5	0.0	1.8	1.8
Kaolinite Derived	0.0	1.3	0.4	0.0	0.0	3.5	0.0	0.0	7.3	25.5	1.7	2.4	5.5	0.0
Illite (Amorp.)	26.9	19.6	9.5	15.1	0.0	5.3	2.0	3.4	5.5	9.1	8.6	7.1	1.8	7.1
Montmorillonite (Amorp.)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	14.3	0.0	0.0
Calcium Derived	0.0	0.0	0.4	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Unclassified	62.9	69.6	37.4	73.4	42.6	68.4	74.0	51.7	43.6	52.7	43.1	42.9	61.8	46.4
<u>Oxide Composition</u>														
SiO ₂	70.6	70.0	82.6	72.1	51.6	37.5	37.3	49.4	63.4	55.5	44.1	56.6	45.8	65.4
Al ₂ O ₃	17.3	17.8	7.5	15.8	7.8	18.5	7.6	13.7	12.9	20.8	31.7	13.3	17.3	14.2
Fe ₂ O ₃	2.3	1.2	3.0	1.6	23.4	5.2	8.9	24.6	10.9	11.9	16.3	15.0	9.9	12.6
TiO ₂	0.9	1.2	0.7	1.2	0.5	0.9	2.1	0.5	1.1	1.0	0.4	1.1	1.0	0.5
P ₂ O ₅	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.0	0.0	0.1	0.2	0.0
CaO	3.6	4.1	3.0	3.9	10.8	21.9	33.8	6.5	6.4	4.7	3.5	6.2	18.6	1.8
MgO	0.5	0.6	0.3	0.5	2.3	6.2	1.3	1.3	0.8	1.5	0.6	0.7	4.1	0.8
Na ₂ O	1.5	1.7	0.5	1.5	0.9	5.0	0.2	1.0	0.5	0.8	0.6	0.2	0.4	0.4
K ₂ O	2.7	2.5	1.0	2.2	0.8	2.9	3.6	1.7	2.1	3.0	2.0	3.2	1.3	2.2
SO ₃	0.1	0.2	0.3	0.2	0.3	0.6	2.9	0.3	0.2	0.1	0.2	2.1	0.7	0.3
BaO	0.2	0.1	0.1	0.2	0.6	0.9	0.7	0.1	0.1	0.1	0.0	0.1	0.2	0.1
MN ₂ O ₇	0.1	0.2	0.1	0.2	0.4	0.2	0.1	0.2	0.3	0.1	0.1	0.1	0.2	0.4
ClO	0.2	0.3	0.8	0.6	0.6	0.1	1.5	0.8	1.2	0.5	0.5	1.2	0.2	1.3

Figure 3. Drop-tube furnace laboratory.

The furnace assembly consists of a series of vertically oriented tube furnaces illustrated in Figure 4. These furnaces possess a total of four 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 in the pulverized coal range at rates of 0.05 to 0.5 grams per minute and at primary carrier gas rates of approximately one liter per minute. The basic apparatus shown in Figure 5 consists of a pressurized cylinder in which a container filled with coal is placed. A rotating brush and stirrer attached to a variable speed motor feeds the coal from the container into a funnel where it is transported through the feed tubing into the furnace injector by the carrier gas.

Fly ash is cooled by means of a fly ash quenching probe shown in Figure 6. 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 (D_{50}) on a logarithmic scale within the range of 0.1-10 millimeters. 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 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 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 (Figure 7).

Figure 4. Cross-sectional diagram of the drop-tube furnace.

Figure 5. Coal feeder for the drop-tube furnace.

Fly Ash Collection System

Figure 6. Fly ash quenching probe assembly for drop-tube furnace.

Figure 7. Short residence time probe for drop-tube furnace.

The probe is inserted in the bottom of the furnace a set distance 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 impactor or multicyclone. The samples collected are analyzed by SEM.

4.2.2 Characterization of Coal, Char, and Fly Ash

The coals are carefully sized 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 inorganic 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 distributions of inorganic components as well as the size and type of mineral grains.

Chemical fractionation (6) 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 water soluble elements, followed by extraction with 1M ammonium acetate to remove elements that are associated as salts of organic acid groups. The residue from the ammonium acetate extraction is extracted with 1M 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 insoluble minerals such as clays, quartz, and pyrite.

Computer-controlled scanning electron microscopy (CCSEM) is being used to characterize coal, char, and ash samples and inorganic combustion products. 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 extraneously 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.

4.3 Char and Fly Ash Production for Kentucky #9 and San Miguel Coals

Drop-tube furnace multicyclone and impactor tests were performed using 38-53 μm , 53-74 μm , and 74-106 μm size fractions of Kentucky #9 and San Miguel coals at combustion temperatures of 1300°C, 1400°C, and 1500°C. Bulk filter tests using the 53-74 μm and bulk coal size fractions of both coals were run at combustion temperatures of 1500°C. Char production of the Kentucky #9 coal at 0.05, 0.1, 0.2, 0.5, and 0.8 second residence times also were run at combustion temperatures of 1500°C. Run conditions for the various tests are listed in Tables 4-18. The upper and lower temperatures of furnace #1 recorded in Tables 4-18 are gas temperatures derived from temperatures taken from the wall of the furnace tube. The gas temperatures have been found to be

TABLE 4
DROP-TUBE FURNACE RUN CONDITIONS FOR MULTICYCLONE COLLECTION
OF FLY ASH USING KENTUCKY #9 COAL (38-53 μm)

Run #	2290	2690	2890
Gas Flow Rates (L/min):			
Primary air	0.8	0.8	0.8
Secondary air	3.2	3.2	3.2
Quench Gas (N ₂)	3	3	3
Vacuum	7.5	7.5	7.5
Temperatures (°C):			
Injector	867	898	928
Preheat	1050	1090	1130
Furnace 1 Upper	1292	1392	1488
Furnace 1 Lower	1312	1413	1512
Coal Burned (g)	6.75	6.37	5.92
Coal Feed Rate (g/min)	0.08	0.09	0.06
Ash Collected (g)	0.9146	0.8543	0.7723
Residence Time (sec)	2.7	2.6	2.5

TABLE 5
DROP-TUBE FURNACE RUN CONDITIONS FOR MULTICYCLONE COLLECTION
OF FLY ASH USING KENTUCKY #9 COAL (53-74 μm)

Run #	2090	2490	1290
Gas Flow Rates (L/min):			
Primary air	0.8	0.8	0.8
Secondary air	3.2	3.2	3.2
Quench Gas (N ₂)	3	3	3
Vacuum	7.5	7.5	7.76
Temperatures (°C):			
Injector	871	837	932
Preheat	1050	1090	1130
Furnace 1 Upper	1292	1385	1482
Furnace 1 Lower	1312	1410	1511
Coal Burned (g)	3.83	6.48	10.49
Coal Feed Rate (g/min)	0.06	0.09	0.14
Ash Collected (g)	0.4066	0.7458	1.1419
Residence Time (sec)	2.5	2.4	2.3

TABLE 6
DROP-TUBE FURNACE RUN CONDITIONS FOR MULTICYCLONE COLLECTION
OF FLY ASH USING KENTUCKY #9 COAL (74-106 μm)

Run #	3290	3090	3490
Gas Flow Rates (L/min):			
Primary air	0.8	0.8	0.8
Secondary air	3.2	3.2	3.2
Quench Gas (N ₂)	3	3	3
Vacuum	7.5	7.5	7.5
Temperatures (°C):			
Injector	860	899	931
Preheat	1050	1090	1130
Furnace 1 Upper	1291	1388	1490
Furnace 1 Lower	1313	1410	1515
Coal Burned (g)	4.05	4.73	4.67
Coal Feed Rate (g/min)	0.09	0.1	0.16
Ash Collected (g)	0.3500	0.4941	0.4697
Residence Time (sec)	2	2	1.9

TABLE 7
DROP-TUBE FURNACE RUN CONDITIONS FOR IMPACTOR COLLECTION
OF FLY ASH USING KENTUCKY #9 COAL (38-53 μm)

Run #	<u>1990</u>	<u>2590</u>	<u>2990</u>
Gas Flow Rates (L/min):			
Primary air	0.8	0.8	0.8
Secondary air	3.2	3.2	3.2
Quench Gas (N ₂)	3	3	3
Vacuum	7.76	7.5	7.5
Temperatures (°C):			
Injector	860	833	923
Preheat	1050	1090	1130
Furnace 1 Upper	1292	1384	1489
Furnace 1 Lower	1313	1409	1514
Coal Burned (g)	6.43	6.22	4.71
Coal Feed Rate (g/min)	0.11	0.08	0.12
Ash Collected (g)	0.8357	0.8238	0.6361
Residence Time (sec)	2.7	2.6	2.5

TABLE 8
DROP-TUBE FURNACE RUN CONDITIONS FOR IMPACTOR COLLECTION
OF FLY ASH USING KENTUCKY #9 COAL (53-74 μm)

Run #	<u>1090</u>	<u>2190</u>	<u>1390</u>
Gas Flow Rates (L/min):			
Primary air	0.8	0.8	0.8
Secondary air	3.2	3.2	3.2
Quench Gas (N ₂)	3	3	3
Vacuum	7.76	7.5	7.76
Temperatures (°C):			
Injector	865	898	937
Preheat	1050	1090	1130
Furnace 1 Upper	1308	1392	1482
Furnace 1 Lower	1329	1414	1506
Coal Burned (g)	5.28	4.51	6.46
Coal Feed Rate (g/min)	0.06	0.05	0.16
Ash Collected (g)	0.5699	0.5022	0.7195
Residence Time (sec)	2.5	2.4	2.3

TABLE 9
DROP-TUBE FURNACE RUN CONDITIONS FOR IMPACTOR COLLECTION
OF FLY ASH USING KENTUCKY #9 COAL (74-106 μm)

Run #	<u>3390</u>	<u>3190</u>	<u>3590</u>
Gas Flow Rates (L/min):			
Primary air	0.8	0.8	0.8
Secondary air	3.2	3.2	3.2
Quench Gas (N ₂)	3	3	3
Vacuum	7.5	7.76	7.76
Temperatures (°C):			
Injector	861	900	928
Preheat	1050	1090	1130
Furnace 1 Upper	1288	1389	1489
Furnace 1 Lower	1309	1415	1517
Coal Burned (g)	3.4	4.8	4.58
Coal Feed Rate (g/min)	0.1	0.08	0.09
Ash Collected (g)	0.3039	0.5106	0.4182
Residence Time (sec)	2	2	1.9

TABLE 10
DROP-TUBE FURNACE RUN CONDITIONS FOR BULK FILTER COLLECTION
OF FLY ASH USING KENTUCKY #9 COAL

Run #	<u>0889</u>	<u>0990</u>
Description	<u>53-74 μm</u>	<u>Bulk</u>
Gas Flow Rates (L/min):		
Primary air	0.8	0.8
Secondary air	3.2	3.2
Quench Gas (N ₂)	3	3
Vacuum	7.76	7.76
Temperatures (°C):		
Injector	935	939
Preheat	1130	1130
Furnace 1 Upper	1491	1476
Furnace 1 Lower	1518	1503
Coal Burned (g)	2.96	3.07
Coal Feed Rate (g/min)	0.05	0.1
Ash Collected (g)	0.2289	0.3031
Residence Time (sec)	2.3	2.3

TABLE 11
DROP-TUBE FURNACE RUN CONDITIONS FOR CHAR PRODUCTION
USING KENTUCKY #9 COAL (53-74 μm)

Run #	0789	0689	0589	3790	3690
Gas Flow Rates (L/min):					
Primary air	0.8	0.8	0.8	0.8	0.8
Secondary air	3.2	3.2	3.2	3.2	3.2
Quench Gas (N ₂)	3	3	3	3	3
Vacuum	7.76	7.76	7.76	7.5	7.5
Temperatures (°C):					
Injector	933	932	930	928	928
Preheat	1130	1130	1130	1130	1130
Furnace 1 Upper	1480	1481	1484	1497	1499
Furnace 1 Lower	1493	1494	1495	1499	1483
Coal Burned (g)	3.38	2.74	2.75	2.08	2.36
Coal Feed Rate (g/min)	0.11	0.06	0.07	0.04	0.05
Ash Collected (g)	0.3697	0.3926	0.4687	0.2312	0.2650
Residence Time (sec)	0.05	0.1	0.2	0.5	0.8

TABLE 12
DROP-TUBE FURNACE RUN CONDITIONS FOR MULTICYCLONE COLLECTION
OF FLY ASH USING SAN MIGUEL COAL (38-53 μm)

Run #	0590	0390	0190
Gas Flow Rates (L/min):			
Primary air	0.8	0.8	0.8
Secondary air	3.2	3.2	3.2
Quench Gas (N ₂)	3	3	3
Vacuum	7.5	7.5	7.5
Temperatures (°C):			
Injector	858	897	929
Preheat	1050	1090	1130
Furnace 1 Upper	1290	1389	1492
Furnace 1 Lower	1313	1413	1519
Coal Burned (g)	5.1	4.75	4.69
Coal Feed Rate (g/min)	0.19	0.19	0.19
Ash Collected (g)	2.0114	1.5003	0.8940
Residence Time (sec)	2.7	2.6	2.5

TABLE 13
DROP-TUBE FURNACE RUN CONDITIONS FOR MULTICYCLONE COLLECTION
OF FLY ASH USING SAN MIGUEL COAL (53-74 μm)

Run #	1290	1590	1890
Gas Flow Rates (L/min):			
Primary air	0.8	0.8	0.8
Secondary air	3.2	3.2	3.2
Quench Gas (N ₂)	3	3	3
Vacuum	7.5	7.5	7.5
Temperatures (°C):			
Injector	835	893	925
Preheat	1050	1090	1130
Furnace 1 Upper	1297	1400	1486
Furnace 1 Lower	1305	1410	1500
Coal Burned (g)	5.07	4.29	4.84
Coal Feed Rate (g/min)	0.2	0.17	0.19
Ash Collected (g)	1.8930	1.7830	2.1392
Residence Time (sec)	2.5	2.4	2.3

TABLE 14
DROP-TUBE FURNACE RUN CONDITIONS FOR MULTICYCLONE COLLECTION
OF FLY ASH USING SAN MIGUEL COAL (74-106 μm)

Run #	1790	1090	0890
Gas Flow Rates (L/min):			
Primary air	0.8	0.8	0.8
Secondary air	3.2	3.2	3.2
Quench Gas (N ₂)	3	3	3
Vacuum	7.5	7.5	7.5
Temperatures (°C):			
Injector	860	886	922
Preheat	1050	1090	1130
Furnace 1 Upper	1290	1407	1492
Furnace 1 Lower	1305	1417	1519
Coal Burned (g)	4.69	3.57	4.64
Coal Feed Rate (g/min)	0.24	0.19	0.19
Ash Collected (g)	0.2760	0.0605	0.4891
Residence Time (sec)	2	2	1.9

TABLE 15
DROP-TUBE FURNACE RUN CONDITIONS FOR IMPACTOR COLLECTION
OF FLY ASH USING SAN MIGUEL COAL (38-53 μm)

Run #	0690	0490	0290
Gas Flow Rates (L/min):			
Primary air	0.8	0.8	0.8
Secondary air	3.2	3.2	3.2
Quench Gas (N ₂)	3	3	3
Vacuum	7.5	7.5	7.5
Temperatures (°C):			
Injector	854	893	925
Preheat	1050	1090	1130
Furnace 1 Upper	1292	1389	1490
Furnace 1 Lower	1315	1414	1517
Coal Burned (g)	0.85	0.84	1.52
Coal Feed Rate (g/min)	0.14	0.17	0.15
Ash Collected (g)	0.2828	0.2761	0.5698
Residence Time (sec)	2.7	2.6	2.5

TABLE 16
DROP-TUBE FURNACE RUN CONDITIONS FOR IMPACTOR COLLECTION
OF FLY ASH USING SAN MIGUEL COAL (53-74 μm)

Run #	1390	1490	1990
Gas Flow Rates (L/min):			
Primary air	0.8	0.8	0.8
Secondary air	3.2	3.2	3.2
Quench Gas (N ₂)	3	3	3
Vacuum	7.5	7.5	7.5
Temperatures (°C):			
Injector	834	892	923
Preheat	1050	1090	1130
Furnace 1 Upper	1298	1394	1487
Furnace 1 Lower	1308	1406	1500
Coal Burned (g)	0.78	0.89	0.9
Coal Feed Rate (g/min)	0.2	0.25	0.23
Ash Collected (g)	0.2798	0.3249	0.3980
Residence Time (sec)	2.5	2.4	1.9

TABLE 17
DROP-TUBE FURNACE RUN CONDITIONS FOR IMPACTOR COLLECTION
OF FLY ASH USING SAN MIGUEL COAL (74-106 μm)

Run #	1690	0990	1790
Gas Flow Rates (L/min):			
Primary air	0.8	0.8	0.8
Secondary air	3.2	3.2	3.2
Quench Gas (N_2)	3	3	3
Vacuum	7.5	7.5	7.5
Temperatures ($^{\circ}\text{C}$):			
Injector	865	881	926
Preheat	1050	1090	1130
Furnace 1 Upper	1290	1392	1492
Furnace 1 Lower	1303	1416	1518
Coal Burned (g)	0.95	0.83	0.91
Coal Feed Rate (g/min)	0.24	0.21	0.18
Ash Collected (g)	0.1752	0.0845	0.1051
Residence Time (sec)	2	2	1.9

TABLE 18
DROP-TUBE FURNACE RUN CONDITIONS FOR BULK FILTER COLLECTION
OF FLY ASH USING SAN MIGUEL COAL

Run # Description	2090 53-74 μm	2190 Bulk
Gas Flow Rates (L/min):		
Primary air	0.8	0.8
Secondary air	3.2	3.2
Quench Gas (N_2)	3	3
Vacuum	7.5	7.5
Temperatures ($^{\circ}\text{C}$):		
Injector	927	923
Preheat	1130	1130
Furnace 1 Upper	1483	1486
Furnace 1 Lower	1497	1500
Coal Burned (g)	0.85	1.79
Coal Feed Rate (g/min)	0.17	0.18
Ash Collected (g)	0.3136	0.6931
Residence Time (sec)	3.9	3.9

approximately 30°C lower than the wall temperatures by tests performed with a suction pyrometer.

4.4 Fly Ash Particle-Size and Composition Evolution

Introduction

Particle-size distributions of minerals and amorphous phases were determined using CCSEM for Combustion Inorganic Transformation (CIT) test coals and chars, including the Beulah lignite and Upper Freeport. Data produced on the chars were obtained by analyzing whole grain mounts of the chars on double-stick tape. The results were checked using cross-sectioned char mounts producing the same overall particle-size distribution number percent results. The number of mineral particles in each of the following size categories was determined: <1.2, 1.2-2.1, 2.1-4.4, 4.4-8.0, 8.0-11.0, and >11.0 microns. This information provides a basis for understanding the fragmentation or coalescence of minerals during combustion of these test coals.

More detailed analysis was made of the Beulah and Upper Freeport coal, char, and fly ash inorganics by observing weight percent concentrations of inorganics in different size categories. Total inorganic particles were plotted versus size using a geometric size distribution in order to observe the overall distribution particles greater than 11 microns. In addition, weight percent concentrations of selected minerals that were being transformed or produced with time during the combustion process were plotted as a function of size. In effect this gives a time-resolved look at inorganic transformations. Using this information, the interaction of different minerals and inorganics was described and inferred.

The end result of this approach to studying fly ash is that particle size and composition evolution with time can be observed through time, and this information is helpful input into models which attempt to predict fly ash size and composition.

Beulah

The whole grain mount analysis of Beulah char phases produced at selected residence times revealed that greater quantities of larger-sized particles were formed during char formation as compared to the original mineral size distribution observed in the coal (Figure 8). This is apparent evidence for coalescence of smaller inorganic particles to form larger ones. Analysis of the cross-sectioned chars revealed similar number percent distributions of Beulah fly ash particles, indicating coalescence with time (Figure 9). Comparison of cross-sectioned coal minerals, ash particles in 0.5 and 0.8-second char ash particles, and 100% carbon burnout fly ash particles was performed on a weight percent basis as shown in Figure 10. Residence time for the fly ash was about 1.5 seconds. Coalescence is evident for the inorganics, with the final fly ash showing the most mass in the >10µm fraction and the least amount of material in the <10µm range.

Quartz was reduced in quantity with time, showing an almost even degradation (Figure 11). The reduction is primarily the result of reaction, with Na and

Ca coming out of the organic bonding sites in the coal matrix. Calcium silicate, which was nonexistent in the coal, comprised nearly 4% of the ash at 0.8 seconds. Sodium silicates appear to form only as a skin on quartz particles. Although no CCSEM category currently exists to classify sodium silicate, examination of the data found that approximately 1% of the quartz grains contained 2% or more sodium. Previous work revealed the presence of Na-rich sulfates and silicates mainly on the surface layers of Beulah chars and fly ash (7,8).

Aluminosilicates derived from clay minerals such as kaolinite and halloysite reacted pervasively with organically bound Na and Ca. The most obvious evidence for this conclusion is the production of calcium aluminosilicate with time as shown in Figure 12. Reaction of CaO with aluminosilicates appears to be especially promulgated among the smaller-sized clay grains ($<10\mu\text{m}$) which are more intimately associated with the organic matrix and, though small, comprise a large reactive surface area. Figure 12 reveals that calcium aluminosilicates, which are virtually nonexistent in the coal, are more abundant in the smaller size ranges of char during early combustion, but with time coalesce to form particles that are mostly greater than 10 microns in average diameter. A plot of the aluminosilicate distribution with time, given in Figure 13, shows that initially the clays are abundant in the smaller size ranges, but upon combustion the concentrations in the smaller size ranges decrease dramatically with an increase in larger-sized grains. This is evidence again for the interaction between organically bound Ca and aluminosilicate to transform mineral aluminosilicates such as kaolinite to calcium aluminosilicates during combustion.

Reaction of sodium with clay minerals is also evident from the CCSEM data. Figure 14 illustrates that Na may have a similar reactivity with the clays as Ca does because they have concentrations that are somewhat proportional. The 0.8-second char contained about 5% Na-bearing aluminosilicates, the Na being at least 3% or more of the particle, based on CCSEM EDS levels. Approximately 2% of the 0.8-second char also consisted of Na-bearing calcium aluminosilicates, again with the sodium being at least 3% of the EDS particle composition.

Pyrite is a major constituent in the Beulah coal, comprising 26% of the coal minerals. Upon combustion, the content of pyrite decreases dramatically as displayed in Figure 15. This would be expected since pyrite readily converts to pyrrhotite and then to forms of iron oxide beginning at temperatures as low as 500°C (9). Indeed iron oxide, which was not present in the coal, was detected by CCSEM in the chars (Figure 16). The sizes of the iron oxide particles were similar to those observed for the pyrite, except there is a slight increase in material noted in the $4.6\text{--}10\mu\text{m}$ category which may be evidence for fragmentation of pyrite.

Upper Freeport

The particle-size distribution for mineral phases in the Upper Freeport chars (Figure 17) shows an initial increase in the number of particles in the smaller size categories. By 0.8 seconds, however, larger quantities of phases are found in the $>11.0\mu\text{m}$ fraction than in the coal. Weight percent distributions present evidence of coalescence of inorganic ash particles with quantities of minerals being reduced in the $<10\mu\text{m}$ range and increased in the $22\text{--}48\mu\text{m}$ range with time (Figure 18). These trends may indicate that initially fragmentation of

Figure 8. Whole-grain mount particle-size distribution of Beulah coal and char phases.

Figure 9. Cross-section particle-size distribution of Beulah coal and char phases.

Figure 10. Cross-section particle-size distribution of Beulah coal minerals, char phases and fly ash.

Figure 11. Distribution of quartz in Beulah coal and chars during combustion.

Figure 12. Distribution of Ca-aluminosilicate in Beulah coal and chars during combustion.

Figure 13. Distribution of aluminosilicate in Beulah coal and chars during combustion.

Figure 14. Scatter plot of Na quantity as a function of Ca quantity in Beulah fly ash aluminosilicates.

Figure 15. Distribution of pyrite in Beulah coal and chars during combustion.

Figure 16. Distribution of iron oxide in Beulah coal and chars during combustion.

Figure 17. Cross-section particle-size distribution of Upper Freeport coal and char phases during combustion.

Figure 18. Cross-section particle-size distribution of Upper Freeport coal and char phases.

mineral grains may be occurring with subsequent coalescence of ash particles as the combustion process proceeds.

Iron aluminosilicates have often been associated with wall slagging in boilers that fire bituminous coals such as the Upper Freeport; therefore, the formation of this phase is of prime interest. Figure 19 indicates that iron aluminosilicate particles were produced in the char mostly in the 22-48 μm size range. Some coalescence of existing iron aluminosilicate minerals in the coal may have occurred also. Sources of Fe and aluminosilicate material for the additional iron aluminosilicate phases produced were probably pyrite or iron oxide for Fe and kaolinite or illite for the aluminosilicate. Iron is also present in the illite, reaching levels of 5% of the illite chemical composition.

Illite was originally bimodally distributed in the Upper Freeport coal at 2.2-4.6 μm and 22-48 μm , but upon combustion, the smaller illite grains coalesced forming a unimodal distribution about the median of 22-48 μm (Figure 20). The shift of material from the smaller size ranges does not completely correlate or compensate in crude mass balance with the increase at the larger size range, implying that production of K-aluminosilicate may have occurred by reaction between illite and aluminosilicate, minerals such as kaolinite.

Pyrite decomposed to iron oxide in much the same manner as with the Beulah, except that by 0.8 seconds the pyrite composition was either completely destroyed or unrecognized by CCSEM (Figures 21 and 22). The iron oxide quantities produced (Figure 22) do not account for all the released iron from the pyrite. This may indicate that some of the released iron oxide has by this time reacted with aluminosilicate to form iron aluminosilicate.

Figure 19. Distribution of Fe-aluminosilicate in Upper Freeport coal and char during combustion.

Figure 20. Distribution of illite or K-aluminosilicate in Upper Freeport coal and char during combustion.

Figure 21. Distribution of pyrite in Upper Freeport coal and char during combustion.

Figure 22. Distribution of iron oxide in Upper Freeport coal and char during combustion.

4.3 Summary and Conclusions

Combustion testing of Kentucky #9 and San Miguel coals in the drop-tube furnace was nearly completed. Fly ash was generated at three temperatures for three different size fractions of both coals and collected using both the multicyclone and impactor. Bulk fly ash samples were also collected on a filter for the unsized and 53-74 μ m coal feeds. Short residence time chars were generated for the Kentucky #9. All of the samples were submitted for analysis using either CCSEM or scanning electron microscopy point count (SEMP).

Particle-size distributions of discrete mineral or amorphous phases in intermediates produced in the drop-tube furnace (DTF) for two coals were examined. Time-resolved PSD's of phases show that Beulah and Upper Freeport inorganic phases coalesce with time. The Upper Freeport shows an initial increase in the amounts of particles in the smaller size ranges due to fragmentation of minerals or the formation of smaller inorganic ash droplets from submicron minerals or inorganics. The transformation of selected inorganic components through time was also noted. Sodium and calcium organically associated in the Beulah react readily with smaller-sized kaolinitic clays and, to a much lesser degree, with quartz. Pyrite appears to undergo fragmentation during combustion in the Beulah and Upper Freeport, with a resulting increase in iron oxide. Iron aluminosilicates in Upper Freeport ash is probably the result of Fe from decomposed pyrite reacting with aluminosilicate clay material such as illite and kaolinite.

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3.3 (Combined with Section 3.2)

3.4 Liquefaction Reactivity of Low-Rank Coals

LIQUEFACTION REACTIVITY OF LOW-RANK COALS

**Quarterly Technical Progress Report
for the Period January - March 1990**

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LIQUEFACTION REACTIVITY OF LOW-RANK COALS

1.0 EXECUTIVE SUMMARY

Further characterization of silica gel zinc chloride catalyst was carried out to provide further information on the nature of this solid acid catalyst. Total acidity and type of acidity of this catalyst were determined by infrared spectroscopy and thermogravimetric analysis of the pyridine-absorbed catalyst. Acidity studies showed that the silica gel zinc chloride catalyst contains significant numbers of highly acidic sites. The number of Lewis acid sites are almost three times the number of Brönsted acid sites.

The reactions of silica gel zinc chloride catalyst with 1- and 2-methylnaphthalenes have been investigated at several time intervals to provide suitable mechanistic models for coal liquefaction. During short reaction times (5-60 minutes), isomerization of 1- or 2-methylnaphthalenes was the major reaction, but at longer reaction times (3-24 hours), hydrogenation, dealkylation, and hydrocracking occurred readily.

Reactions of bibenzyl were investigated to establish the role of molecular hydrogen in the acid-catalyzed cleavage reactions. Although cleavage reactions and reduced products were obtained in the absence of hydrogen, the presence of hydrogen is necessary to avoid coking and to improve the product yield. The results are interpreted to mean that hydrogen reduces some of the condensation products, converting them to better hydride donors. Thus the condensation products will be effectively involved in the primary reactions that give ethylbenzene, rather than progressively lose hydrogen and form coke.

Further substantiation and elaboration of the acid-catalysis mechanisms were undertaken. The reaction of diphenylpropane gave high conversion to benzene and indan, implicating free carbonium ion intermediates. With neopentylbenzene, the conversion was low, and the major products were benzene and 2-methylbutane from rearrangement of the neopentyl carbonium ion. These products are suggestive of Brönsted acid catalytic sites. Toluene, 2-methylpropane, and other linear alkanes indicated the possible involvement of the Lewis acid sites.

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, metals deposition, and inhibition of the active center by chemisorbed compounds.

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 to accommodate the coal macromolecules, yet not possessing strong acidities which 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 continued. 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, the 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 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. Wyodak coal with in situ chromia-pillared coal clays with and without incorporated hydrogenation catalysts are being prepared. Wyodak coal loaded with in situ Ni-Mo hydrogenation catalyst has also been prepared. Both these coals have been presulfided and are being tested in a two-stage coal liquefaction process.

3.1.2 Solid Acid-Catalyzed Hydrocracking

Acid-catalyzed coal conversion has been thoroughly investigated; however, the efficiencies of catalyst recovery are either 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 coal macromolecules. Chromium and aluminum cluster-pillared smectites are being tested both in the Brønsted and Lewis acid form, the latter being formed from reactions with metal chlorides. The liquefaction reactivity of Wyodak coal which has been in situ pillared with polyoxy chromium ions or metal(s)-supported will be compared with other solid acid catalysts, such as Drago aluminum chloride-silica complex and a similar zinc chloride complex. Also, reactions of silica gel-supported tin(II) chloride and zinc sulfate will be compared with silica gel zinc chloride catalyst.

3.2 Experimental

3.2.1 Catalyst Preparation

3.2.1.1 Preparation of Silica Gel Catalysts

Mixtures of silica gel with tin (II) chloride and silica gel with zinc sulfate were prepared using the same procedure as described for the preparation of silica gel zinc chloride in our previous quarterly report (1).

3.2.1.2 Preparation of In Situ Chromia-Pillared Wyodak Coal

Chromium nitrate nonhydrate (69.12 g) dissolved in 1.728 liters of deionized water was placed in a round-bottomed flask and hydrolyzed with anhydrous sodium carbonate (18.32 g). The freshly hydrolyzed chromium nitrate solution was aged at 95°C for 36 hours. At this stage, 5 g of Beulah lignite (Argonne premium coal, AR) suspended in 400 mL of deionized water (1 wt%) was added slowly at room temperature, along with vigorous stirring. The slurry was aged at room temperature for 2 hours. The solid was separated by centrifugation, and the residue was washed with deionized water until free of chromium ions. The residue was dried at 200°C.

3.2.1.3 Preparation of Bimetallic Metal-Supported Coal

A solution of nickel nitrate hexahydrate (1.07 g) and ammonium molybdate (1.51 g) in 200 mL of deionized water was placed in a 500-mL, round-bottomed flask. To this solution was added 10.0 g of Wyodak coal (Argonne premium sample, AR) and stirred overnight. The solvent was evaporated and the residue dried at 200°C.

The bimetallic, metal-supported, chromia-pillared Wyodak coal was prepared in the same manner.

3.2.1.4 Sulfidation of Metal(s) Supported on Pillared Clay Catalysts

The sulfidation of the metal-supported, chromia-pillared Wyodak and metal-supported Wyodak was carried out by placing the desired coal sample in a 75-mL tubing bomb. The tubing bomb was pressurized with a 100-psig mixture of hydrogen sulfide and hydrogen (9:1 v/v). The bomb was lowered into a fluidized-bed sand bath heated to 200°C. The bomb was heated at this temperature for 2 hours, degassed, and heating was continued for 12 hours.

3.2.1.5 Elemental Analysis

Total sulfur determination was done with a LECO model 532 sulfur analyzer, using the ASTM D1551 method. The method of Vogel (2) was used for chlorine analysis. Carbon, hydrogen, and nitrogen analyses were performed on a Control Equipment Corporation Model 240XA Elemental Analyzer.

Proton and ^{13}C NMR spectra were obtained in dichloromethane- d_2 with TMS standard on a Varian XL200 NMR spectrometer. Infrared spectra were obtained in KBr on either a Perkin Elmer Model 283 spectrometer or a Nicolet 20SXB FTIR spectrometer equipped with a mercury cadmium telluride (MCTA) detector and a Nicolet 1280 computer with a fast Fourier transform coprocessor.

Quantitative GC/FID analyses were performed with a Hewlett Packard 5880A gas chromatograph equipped with a J&W 60 m x 0.25 mm (ID), 1.0 micron DB-1701 capillary column. n-Octadecane was the internal standard. Isotope dilution GC/MS was performed on a Finnigan 800 ITD ion trap detector with an HP 5890A gas chromatograph and a J&W 30 m x 0.32 mm (ID), 1.0 micron film of DB-5. Phenol, naphthalene, and tetralin were determined with per-deuterated analogs as the respective internal standards. A 15 m x 0.25 mm (ID), 0.25-micron DB-5 film capillary column was used for the analysis of high boiling components.

3.2.2 Characterization of Solid Acid Catalysts: Acidity Measurements

The acidity of the solid acid catalyst, zinc chloride supported on silica, was further determined by pyridine adsorption and desorption methods using FTIR and thermogravimetric (TGA) methods.

3.2.2.1 Infrared Method

A small amount of sample (100 mg) was placed in a glass chamber attached to a vacuum pump, a gas inlet, and a gas outlet. The chamber was evacuated, and argon saturated with pyridine was introduced into the chamber until the weight increase ceased. At this stage the chamber was evacuated until the physisorbed pyridine was removed as indicated by the constant weight of the base absorbed sample. The infrared spectra of the pyridine-absorbed catalyst was obtained on the Nicolet FTIR spectrometer with the diffuse reflectance cell. Infrared spectral data are presented in Table I.

TABLE 1
INFRARED ABSORBANCE OF PYRIDINE-ADSORBED CATALYST

<u>Band</u>	<u>Absorbance</u>	<u>Extinction Coefficient (3)</u>
1440 cm ⁻¹ (Lewis-Pyridine Band)	0.47	0.084
1536 cm ⁻¹ (Brönsted-Pyridine Band)	0.094	0.058
Lewis/Brönsted Sites = 3.4		

3.2.2.2 Thermogravimetric Method

Total acidity of the catalyst was determined from the chemisorption of pyridine on the catalyst surface using a thermogravimetric analysis (TGA) technique.

Approximately 20 mg of catalyst were placed on the sample pan of the DuPont 951 thermogravimetric balance module, which was interfaced with a DuPont 1090 Thermoanalyzer (controller and data station). The sample was purged at ambient temperature with argon until constant weight was achieved (several minutes). The argon flow was then stopped, and the sample chamber was evacuated. The vacuum pump continued to hold the partial vacuum until constant weight was once again achieved. The pump was then turned off, and a flow of pyridine-saturated argon at ambient temperature was introduced into the sample chamber. The pyridine-argon flow continued for 180 minutes, at which time the weight gained by the sample had nearly ceased. The chamber was again evacuated, still at ambient temperature, and held under partial vacuum for 40 minutes. When constant weight was achieved, the temperature was increased at 20°C/min to 105°C, where it was held for 30 minutes. The temperature was then increased by 2°C/min to 202°C and held there for 30 minutes, followed by a temperature increase of 20°C/min to 300°C where it was held for 60 minutes. Upon reaching constant weight, the experiment was terminated. The 1090 Thermoanalyzer records time, temperature, and weight during experimentation (Figure 1). On reducing the data, dw/dt is calculated and the data are reported on a plot of wt% and dw/dt versus time and wt% and dw/dt versus temperature.

3.3 Results and Discussion

3.3.1 Characterization of Catalysts

Mixtures of silica gel with zinc sulfate, and tin(II) chloride were characterized by elemental analysis, infrared spectroscopy, and thermogravimetric methods.

Figure 1. Thermogravimetric analysis: pyridine absorption/desorption.

3.3.1.1 Elemental Analyses

Elemental analyses of the tin(II) chloride and zinc sulfate mixtures with silica gel indicated that no loss of chloride and sulfate occurred during the heating procedure. Most of the salt (99%) is present, and only a small amount of chlorine or sulfate is present as Si-O-SnCl or (Si-O-Zn)HSO₄. In the silica gel zinc chloride (SZC) catalyst, 2% of chlorine is present as Si-O-ZnCl. The catalyst is a mixture of zinc chloride, zinc chloride complexed with silica gel, and oxyzinc salt.

3.3.1.2 Infrared Method

Infrared spectroscopy of the pyridine complex was used to determine the relative proportion of Lewis and Brønsted acid sites in the silica gel zinc chloride catalyst. In the infrared spectrum of the pyridine-absorbed silica gel zinc chloride catalyst, the bands at 1440 and 1536 cm⁻¹ are assigned to pyridine-Lewis acid coordination bond, and pyridine-Brønsted acid bond, respectively. The relative intensities of these bands were converted to the concentration ratio by using the respective extinction coefficients. The ratio of the concentration of Lewis sites to Brønsted sites was 3.4 (Table 1).

3.3.1.3 Thermogravimetric Analysis

The thermogravimetric technique was used to determine the total acid sites and stability of the catalyst. In the TGA experiment, the weight of the catalyst increased from 21 mg to 29.74 mg, upon pyridine absorption followed by evacuation at ambient temperature. The weight increase is due to the chemical adsorption of the pyridine at both Lewis and Brønsted acid sites and,

therefore, is a measure of the total acidity of the catalyst. Upon slowly heating the catalyst (2°C/min.) to 300°C, all of the chemically adsorbed pyridine could be removed. In the temperature range of 105°-140°C, 2.9 mg of pyridine was lost, and the rest (5.8 mg) was lost in the range 140°-202°C. The inflection in the curve at 140 is believed to represent the onset of pyridine loss from the Brönsted acid sites, but the loss of pyridine from the Lewis acid sites continued to occur as the temperature was raised. Thus the relative amounts of Lewis and Brönsted sites could not be obtained from these data, only the total amount of acid sites (5.04 mmol/g catalyst). Heating above 300°C resulted in the loss of chlorine due to decomposition and or sublimation of zinc chloride from the catalyst surface. In the solid state the catalyst is only stable up to 300°C.

3.3.2 Catalytic Testing

3.3.2.1 Catalytic Hydrotreating of 1-Methylnaphthalene

1- and 2-methylnaphthalenes were used to investigate the relative kinetics of the hydrotreatment reactions of polynuclear aromatics with solid acid catalysts (silica gel zinc chloride). The reactions were carried out by heating 1- or 2-methylnaphthalene and silica gel zinc chloride in the presence of 1000 psig of molecular hydrogen at 300°C for reaction times ranging from 5 minutes to 24 hours. The effect of reaction time in the hydrotreating was investigated.

In a typical run, 1.0 g of 1- or 2-methylnaphthalene and 0.5 g of silica gel zinc chloride were placed in a tubing bomb (12-mL microreactor). The microreactor was evacuated, pressurized with 1000 psig of hydrogen, and placed in a rocking autoclave heated to 300°C. 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. The solid catalyst was removed by centrifugation. The liquid sample was analyzed by GC/FID and GC/FTIR/MS.

The chlorine analysis of the recovered catalyst did not indicate any loss of chlorine during reaction. Detailed characterization of the recovered catalyst to determine the possible loss of catalytic activity is in progress.

The reactions of 1- and 2-methylnaphthalenes with silica gel zinc chloride catalyst under different conditions gave the products indicated in Table 2. These products indicated that three reactions--namely, isomerization (rearrangement), hydrogenation, and demethylation (hydrocracking)--occurred during the catalytic hydrotreating of 1-methylnaphthalene. The formation of polymethylnaphthalenes is regarded as being a major part of the demethylation reaction (transmethylation).

The reaction of 1-methylnaphthalene with silica gel zinc chloride at 300°C and in the presence of 1000 psig of hydrogen for 5 minutes gave 1- and 2-methylnaphthalenes in the ratio of 5.14. Methyltetralins were the minor products from this reaction (6% yield). A 1-hour reaction time gave a ratio of 0.8, and a 24-hour reaction time gave 0.07. Under these conditions, almost 89% of the starting material was converted into products. Major products were tetralin, methyltetralins, naphthalene, and 1- and 2-methylnaphthalenes. Minor products were benzene, toluene, and decalin. Small amounts of

TABLE 2

REACTIONS OF METHYLNAPHTHALENES

(Reaction Temp. = 300°C, 1- or 2-Methylnaphthalene = 1.0 g, H₂ = 1000 psig,
Subst./Catalyst = 0.5, Catalyst = Silica Gel Zinc Chloride (SZC))

Subst.	Time (hr)	Conv. (%)	1-Menaph./2-Menaph. Ratio	Major Products
1-Menaph*	0.08	6	5.15	Methyltetralins
1-Menaph	1	6	0.8	Methyltetralins
1-Menaph	24	89	0.07	Naphthalene Tetralin Methyltetralins
2-Menaph	1	15	0.36	Naphthalene Tetralin Methyltetralins Benzene Toluene Indan
2-Menaph	3	32	0.42	Naphthalene Tetralin Decalin Benzene Alkylbenzenes
2-Menaph	24	89	0.09	Naphthalene Tetralin Methyltetralins

* Methylnaphthalene

cyclohexane, methylcyclohexane, ethylbenzene, o-xylenes, indan, and C₃-C₅ were also identified in the product. In order to determine whether the reaction actually achieves an equilibrium with respect to 1- and 2-methylnaphthalene, the reaction of 2-methylnaphthalene was also investigated. The reaction of 2-methylnaphthalene at 300°C for 1 hour and in the presence of 1000 psig of hydrogen gave 1- and 2-methylnaphthalene (85% of the starting material), and the ratio of 1- and 2-methylnaphthalenes was 0.36. Small amounts of benzene, toluene, indan, naphthalene, and methyltetralins were also produced during reaction. When the same reaction was carried out for 3 hours, 68% of the substrate was recovered as a mixture of 1- and 2-methylnaphthalenes in the ratio of 0.423. The remainder of the starting material was converted into products. Major products from this reaction were benzene, toluene, o-xylenes, ethylbenzene, decalin, naphthalene, and tetralins. Upon heating 2-methylnaphthalene and 1000 psig of hydrogen with silica gel zinc chloride for 24 hours, almost 89% of the substrate was converted into products other than methylnaphthalenes. 1- and 2-methylnaphthalenes constituted about 11% of the products in the ratio of 0.09. Product distribution was the same as that obtained in the reaction of 1-methylnaphthalene under the same conditions.

The data from the two sets of reactions at 300°C indicate that the isomerization reaction is rapid at this temperature. It apparently does not reach an exact equilibrium point, owing to different reactivities of the 1- and 2-methylnaphthalenes in the subsequent reactions (hydrogenation, hydrocracking) that occur at slower rates. This lack of steady-state concentrations makes kinetic analysis difficult. We may conclude that the isomerization reaction of 1- and 2-methylnaphthalene proceeds to an approximate equilibrium ratio (1-/2-) of 0.4 in a time of 1 hour at this temperature. Over longer periods (1 day), the ratio decreases to less than 0.1. Extensive conversion to the methyltetralin mixtures and naphthalene occurs over the extended period.

In the initial stages of the reaction, isomerization predominates as indicated by the 5-minute and 1-hour reactions. As the reaction time increases, the isomer mixture is converted into naphthalene via demethylation, and to methyltetralins via hydrogenation of either of the rings of the methylnaphthalene substrates. The demethylation is accompanied by formation of di- and trimethylnaphthalenes. Extensive hydrocracking of the tetralins resulted in a mixture of alkylbenzenes. Small amounts of cyclohexane, methylcyclohexane, decalin, and indans were formed in addition to the above products. The major reaction sequences involving the methylnaphthalenes are presented in Figure 2.

Figure 2. Hydrogenation/hydrocracking/isomerization of methylnaphthalenes.

3.3.2.2 Catalytic Hydrotreating of Cis-Decalin

The reactions of cis-decalin were carried out at 400°C for 1 hour. The reaction variables were hydrogen, catalyst, solvent, and additive (bibenzyl). The reaction conditions and conversion data are given in Table 3. The reactions were carried out in a microreactor. The reaction procedure was the

same as described for the reactions of methylnaphthalenes. The product slurry was mixed with the appropriate internal standard and extracted with methylene chloride. The solid was separated by centrifugation. The methylene chloride soluble fraction was analyzed by GC/FID and GC/FTIR/MS. The solid residue (methylene chloride soluble fraction) was weighed and analyzed by elemental analysis and infrared spectroscopy. The methylene chloride insoluble fraction was mainly recovered catalyst.

TABLE 3
CIS/TRANS CONVERSION DATA FOR REACTIONS OF CIS-DECALIN
(Reaction Temp. = 400°C, Time = 1 hr)

Catalyst	Amounts of Reactants (g)			Hydrogen (psig)	Cis/Trans Conversion (%)
	Cis-Decalin	Bibenzyl	Solvent		
None	1.00	0	None	1000	1
SZC* 0.5	1.00	0	None	1000	17.4
SZC 0.03	0.07	0	Hexadecane 2.00	1000	18.4
SZC 0.05	0.10	0.10	Hexadecane 2.00	1000	13.1
SZC 0.05	1.00	0.10	None	0	18

*SZC = Silica gel zinc chloride

Upon heating at 400°C for 1 hour in the presence of 1000 psig of hydrogen, only 1% of cis-decalin was converted into trans-decalin. However, when the same reaction was carried out by heating 1.0 g of cis-decalin with 0.5 g of silica gel zinc chloride and 1000 psig of hydrogen under the same conditions, 17.4% of trans-decalin was formed. In the reaction of 0.07 g of cis-decalin in 2.0 g of hexadecane with 0.03 g of silica gel zinc chloride in the presence of 1000 psig of hydrogen at 400°C for 1 hour the conversion of cis-decalin was 18.4%. The reaction of a solution of cis-decalin and bibenzyl (0.1 g each) in 2.0 g of hexadecane with 0.05 g of silica gel zinc chloride and 1000 psig of hydrogen at 400°C for 1 hour resulted in slightly less conversion (13.1%). When the reaction of cis-decalin (1.0 g) containing 0.10 g bibenzyl was carried out with silica gel zinc chloride at 400°C for 1 hour and in the absence of hydrogen, the conversion of cis-decalin was 18%, which is essentially the same as that observed for the reaction of cis-decalin in the presence of hydrogen and absence of bibenzyl. Almost quantitative amounts of bibenzyl and decalins were recovered at the end of the reaction.

The results are consistent with an acid-catalyzed isomerization mechanism. The very small amount of reaction in the absence of catalyst indicates that free radical reactions are not important in this system at this temperature. The catalyst (Lewis acid site) can abstract a hydride ion from the decalin to give a tertiary carbonium ion. The carbonium ion intermediate then is converted back to cis- and trans-decalin by regaining the hydride ion. The equilibrium concentration ratio for cis/trans decalin is about 0.2. The conversions obtained with this system indicate that the reaction has not progressed very far toward the equilibrium position. The most important finding is that the addition of bibenzyl does not result in any increase in the cis to trans conversion. This lack of interaction means that the carbonium ion intermediates produced in the reaction of the bibenzyl with the catalyst do not abstract hydride ions from the tertiary carbons of the cis-decalin.

3.3.2.3 Catalytic Hydrotreating of Model Compounds

The reactions of model compounds such as bibenzyl, diphenylpropane, and neopentylbenzene were carried out with solid acid catalysts such as silica gel zinc chloride, silica gel zinc sulfate, and silica gel tin(II) chloride. The reactions were carried out at 350°C for 3 hours both with and without hydrogen. These reactions were carried out in the manner described for the reactions of methylnaphthalenes. At the end of the reaction, the microreactor was cooled in dry ice/acetone slurry, degassed, and opened. The product slurry from the reaction was mixed with the appropriate internal standard, transferred into a centrifugation tube with methylene chloride, and the solid catalyst was separated by centrifugation. The liquid product was analyzed by GC/FID and GC/FTIR/MS analyses. The solid product was washed with methylene chloride, vacuum dried, and weighed. The elemental analysis of the methylene chloride insoluble product indicated this product to be essentially the recovered catalyst.

Reactions of bibenzyl with silica gel tin(II) chloride and silica gel zinc sulfate indicated a very small conversion of bibenzyl into products. Traces of benzene and toluene were the only products from these reactions. The elemental analysis of the methylene chloride insoluble fractions indicated these products to be the same as the original catalyst.

The effect of hydrogen on the conversion of bibenzyl and the product distribution was investigated by carrying out reactions both in the presence and the absence of hydrogen. The percent conversion measured as the disappearance of the substrate was almost the same in both these reactions. However, the product distribution was significantly affected by the presence of hydrogen (Table 4). The reaction with no hydrogen produced 7% of coke which is formed due to retrograde condensation reactions. Also, the amount of condensation products (substituted bibenzyls) increased from 18% to 27% in the absence of hydrogen. In the presence of hydrogen, the amount of benzene was only slightly higher, but the amount of ethylbenzene increased considerably. It is believed that the reaction of bibenzyl involves ipso protonation followed by the cleavage of an aryl-methylene bond, leading to the formation of benzene and the phenylethyl carbonium ion. The phenylethyl carbonium ion can undergo a variety of reactions (Figure 3) to give products. The overall mechanism of the acid-catalyzed hydrocracking of bibenzyl is depicted in Figure 4. The fact that ethylbenzene forms even in the absence of molecular hydrogen indicates that hydride transfer from Scholl intermediates or

TABLE 4

CATALYTIC HYDROCRACKING OF BIBENZYL
(350°C, 3 hrs, 5.49 mmols bibenzyl, 0.5G SZC catalyst)

Reductant Amount	Conversion (%)	Major Products (mmols)	
None	83	Benzene	(3.2)
		Toluene	(0.2)
		Ethylbenzene	(0.8)
		Cond. Prod.	27%
		Coke	7%
Hydrogen 1000 psi	80	Benzene	(3.54)
		Toluene	(1.35)
		Ethylbenzene	(0.15)
		Cond. Prod.	18%
		Coke	0%

Figure 3. Reactions of phenylethyl carbonium ion.

Figure 4. Mechanism for hydrodealkylation of bibenzyl.

hydroaromatic condensation products is the major mechanism for formation of ethylbenzene. Hydrogen may be indirectly involved through reductions of these condensation products.

Diphenylpropane and neopentylbenzene were used to investigate the catalysis mechanism of silica gel zinc chloride. The reactions were carried out at 350°C for 3 hours in the presence of 1000 psig of hydrogen. The reaction procedure and product work-up have been described earlier. The product slurry was separated into methylene chloride soluble and insoluble fractions. The methylene chloride soluble fraction was mixed with the appropriate internal standard and analyzed by quantitative GC using a petrocol column. The methylene chloride insoluble fraction was analyzed by elemental analysis and was found to be essentially the recovered catalyst. The product distribution and the percent conversion for these reactions are presented in Table 5.

Diphenylpropane gave benzene and indan as the major products. The formation of benzene may be due to the ipso protonation of the aromatic ring followed by aryl-methylene bond cleavage. The phenylpropyl carbonium ion then undergoes rearrangement in the presence of the acid catalyst to give indan as the second major product. The minor products from this reaction were C_1 - C_3 benzenes. Possible mechanisms leading to the formation of these products are shown in Figures 5 and 6.

The conversion of neopentylbenzene was much smaller than that of diphenylpropane, and a variety of products was obtained. The major product from this reaction was benzene, which is formed due to the ipso protonation of the aromatic ring followed by aryl-methylene bond cleavage. The neopentyl carbonium ion rearranges to produce 2-methylbutane (Figure 7). Toluene and 2-methylpropane may have been formed from the Lewis acid catalyzed cracking of neopentylbenzene (Figures 8 and 9).

4.0 REFERENCES

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TABLE 5

CATALYTIC HYDROCRACKING OF DIPHENYLPROPANE AND NEOPENTYLBENZENE
(350°C, 3 hrs, Subst./Cat. = 2, H₂ = 1000 psig)

<u>Catalyst (g)</u>	<u>Substrate (mmols)</u>	<u>Conversion</u>	<u>Major Products (mmols)</u>	
SZC 0.25	DPP (2.6)	76	Indan	(1.39)
			Propylbenzene	(0.08)
			Ethylbenzene	(0.06)
			Toluene	(0.05)
			Benzene	(2.43)
			Cond. Prod.	0%
			Coke	0%
SZC 0.25	NPB (3.5)	26	Benzene	(0.29)
			2-Methylbutane	(0.08)
			2,2-Dimethylpropane	(0.003)
			Toluene	(0.06)
			2-Methylpropane	(0.04)
			Butane	(0.003)
			Pentane	(0.001)
			Ethylbenzene	(0.03)

SZC = Silica gel zinc chloride
DPP = Diphenylpropane
NPB = Neopentylbenzene

Figure 5. Mechanism for hydrodealkylation of diphenylpropane (Brønsted Site).

Figure 6. Mechanism for hydrodealkylation of diphenylpropane (Lewis Site).

Figure 7. Mechanism for hydrodealkylation of neopentane (Brönsted site--ipso cleavage).

Figure 8. Mechanism for hydrodealkylation of neopentane (Brönsted site--alpha cleavage).

Figure 9. Mechanism for hydrodealkylation of neopentane (Lewis site--alpha cleavage).

3.5 Gasification Ash and Slag Characterization

GASIFICATION ASH AND SLAG CHARACTERIZATION

**Quarterly Technical Progress Report
for the Period of January - March 1990**

by

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GASIFICATION ASH AND SLAG CHARACTERIZATION

1.0 EXECUTIVE SUMMARY

This report summarizes the accomplishments for the period of January through March 1990.

Task A: Construction of the pressurized drop-tube furnace system that will be used to simulate gasification conditions has been completed, and operation will begin when the necessary permits have been approved.

Task B: The computer code PHOEBE was tested against the Al_2O_3 - SiO_2 binary phase diagram. A typographical error in the data base was discovered and eliminated. Graphical results will be presented in following monthly reports.

Task C: Determination of physiochemical effects present during interfacial surface tension measurements were studied.

- 1) **Effect of Time:** The data shows that there is an increase in the interfacial surface tension in the first 30 minutes of measurement, the time required to achieve uniform, steady-state conditions in the molten slag droplet.
- 2) **Effect of Atmosphere:** The data show that measurements conducted in a CO/CO_2 atmosphere are less than those conducted in an H_2/N_2 atmosphere.
- 3) **Effect of Temperature:** The data show significant changes for temperatures below the temperature of critical viscosity, T_{cr} , and no significant changes for temperatures above T_{cr} . This effect is attributed to the presence of surface active phases and polymerization of silicates in the slags. Please refer to the Results and Discussion section of this report for further information.

2.0 OBJECTIVES

2.1 Task A: Inorganic Reactions

This task involves determining the reactions and interactions that coal inorganic constituents undergo during gasification processes. Two coals: Sufco, a Utah bituminous coal, and Jacob's Ranch, a Wyoming subbituminous coal, will be studied. The chemical and mineralogical transformations will be studied under simulated gasification conditions using a modified version of the pressurized drop-tube furnace system at the EERC. The coals will be characterized using chemical fractionation, computer-controlled scanning electron microscopy (CCSEM), and scanning electron microscopy point count (SEMPC). SEMPC data can be used to determine the viscosity and relative reactivity of the liquid phases as well as the bulk chemical composition of the sample. This data will show both the partitioning of the ash species as

well as the effect of char formation on the ash species with respect to potential sintering behavior.

2.2 Task B: Partitioning of Ash Components

The relative quantity and composition of the amorphous phases on char and ash particles provide an indication of the deposition propensity of coal ash under gasification conditions. The reactivity between individual char and ash particles is also determined by the nature of the amorphous phase. The reactivity propensity is based on the base-to-acid ratios of individual ash components. Understanding the role of the amorphous phase will aid in the understanding of partitioning and deposition phenomena. The data may also be used to develop a scale, index, or empirical equation to measure the degree of reactivity between amorphous phases. Task B will involve the detailed comparison of the ash species formed in the pressurized drop-tube furnace system with the parent coal. The gas-entrained species will be determined by on-line sampling in the furnace. Work will also continue in the development of a vapor-liquid-solid thermochemical equilibrium code. Data from this code will be used to theoretically predict ash partitioning.

2.3 Task C: Ash Sintering Under Gasification Conditions

Sintering is an ash characteristic that can be used to predict ash behavior. The behavior of mineral matter in coal gasification is different than that in the combustion systems and is generally characterized by lower temperatures, more reducing conditions, and longer residence times. The goal of Task C is to study sintering mechanisms in coal ash systems to determine the effects of various additives on sintering phenomena.

2.4 Associated Task

As this project involves development of methodologies to predict ash behavior in gasification systems, we plan to enhance our relationship with industrial-scale operators such as DOW, Shell, and Texaco. This will ensure that our approach to studying ash behavior in gasification systems can be validated as they are developed.

3.0 RESULTS AND DISCUSSION

3.1 Physiochemical Effects Determining the Accuracy of Interfacial Surface Tension Measurement of Coal Ashes

The sessile drop technique has been used to determine the interfacial surface tension of Beulah Blend, Illinois #6, and Pittsburgh #8 coal ashes in various atmospheres. The following is a discussion of the physiochemical effects determining the accuracy of the measurement. The data shows that the interfacial surface tension measured below the temperature of critical viscosity, T_{cr} , are lower than those determined above T_{cr} . This effect is attributed to the nonequilibrium state of the liquid-vapor surface tension, η_{LV} . The difference in the chemical composition of the molten drop surface

and the bulk chemical composition of the drop creates a nonequilibrium state. The difference in chemical composition between the surface and bulk can be attributed to evaporation of sodium, the random distribution of surface active phases such as silica-rich clusters, and the polymerization of silicate structures in the slag. Interfacial surface tensions measurements did not vary significantly with temperature above T_{cr} .

Ordinarily, surface tension is an intensive thermodynamic property that should be measured on the systems that are free from extraneous mechanical, electrical or chemical interactions. Surface tension measured in the presence of an interacting gas is termed interfacial surface tension. The calculation of surface tension employs procedures which permit fitting of measured drop profile to a theoretical profile by varying two parameters, β and b , using a nonlinear regression program. The shape factor, β , and the radius curvature, b , at the drop apex are related by the equation:

$$\beta = \frac{b^2 * g}{\gamma} * (d_m - d_{gas}) \quad [1]$$

where γ is the surface tension, g is the gravitational acceleration which depends on the drop size, and d_m and d_{gas} are the densities of liquid slag and gas, respectively. Two principle errors based on the measurement of the drop profile and density were discussed in the article (1). The purpose of this task is to determine all possible physiochemical effects that influence the accuracy of interfacial surface tension and viscosity measurements of coal ash slags under reducing atmospheres corresponding to gasification conditions.

3.2 Experimental

Beulah lignite, Pittsburgh #8, and Illinois #6 coals were pulverized to -60 mesh and ashed in air at 800°C for 24 hours. The resulting ashes were slagged at 1500°C and kept in a homogeneous state by rotating the viscometer bob. Controlled atmospheres of air, 8% H_2 -92% N_2 , and 60%CO-40% CO_2 were used in the interfacial surface tension and viscosity measurements. The samples used in the measurements were first slagged, quenched in air at room temperature, and finally ground to -38 mesh. This procedure produced a homogeneous sample with a uniform distribution of all coal ash components. Therefore, errors in the determination of interfacial surface tension due to a nonequilibrium state caused by a nonuniform distribution are theoretically avoided. Homogenation of samples increases the required sample preparation time. Thus the evaporation of light elements such as sodium from the surface of a sessile drop over a long duration may occur, affecting the measured values of interfacial surface tension. During evaporation, the chemical potential of surface atoms is varied from those in the bulk. As a consequence of that, the interfacial surface tension also changes.

Two kind of pellets were used: pulverized glassy slag and small pieces of the crashed slag. The pulverized glassy coal ash was pressed by hand into

a pellet with diameter about 1 cm, centered on a plane surface of vitreous carbon, and placed in the horizontal tube furnace preheated to 900°C. Previous work showed that for drops with diameters greater than 2 cm, the surface tension of mercury increased progressively with drop diameter and decreases slightly with diameters less than 1 cm (2). For the work conducted in the Gasification Ash and Slag project, the sessile drops were exposed to various mixtures of gases, air, H_2/N_2 (8/92), and CO/CO_2 (60/40). A continuous flow of gas (60 cc/min) was maintained throughout the experiment. The profile of a sessile drop was photographed at designated temperatures and times.

The coordinates of sessile drop were measured both directly from the film using an optical microscope and from the image projected onto graph paper. Calculation of the surface tension was performed by a computerized nonlinear curve-fitting procedure. Chemical compositions of coal ashes were determined after surface tension measurements by x-ray fluorescence analysis. The compositions of the ashes on a sulfur-free basis are listed in Table 1.

Raask (3) has suggested that in iron-rich slags, iron carbide might be formed at the slag-vitreous carbon interface, causing carbon monoxide evolution above 1400°C. The reaction between iron oxide bearing slags and solid carbon was significant in $FeO-SiO_2$ slags. Lime-containing slags were found to react more slowly with carbon (4). These important side reactions created difficulties in the interpretation of the experimental work.

During the Gasification Ash and Slag work, the process of gas generation inside the slag droplet caused changes in the sessile drop shape. This effect was determined by the calculation of slag density from the sessile drop coordinates. A number of experiments have shown a significant change of density for slag droplets exposed to air at temperatures above 1350°C. To study this effect, interfacial surface tension measurements determined below 1350°C were made after the sample had been held at constant temperature for at least 30 min. It should be pointed out that the temperature of sessile drop formation is a characteristic one and occurs below 1350°C for most coal ashes. Thus the temperature of sessile drop formation was selected as a reference temperature. For homogenated slags in CO/CO_2 , the interfacial surface tension measured above 1400°C did not show a significant change in slag droplet density. Table 2 illustrates examples of density variation as the function of temperature for several slags exposed to CO/CO_2 atmosphere. All results of interfacial surface tension with density error larger than 5% were rejected.

Viscosity was measured using a rotating bob viscometer in CO/CO_2 (60/40) atmosphere to determine the temperature of critical viscosity. Measurements were started at the highest temperature and stepped down to lower temperatures until the upper limit of the viscometer was approached.

Table 3 lists some of the interfacial surface tension data for Illinois #6 slags prepared in CO/CO_2 atmosphere (Runs No. 13-15), which were held at temperatures for complete spherical formation in CO/CO_2 for 0-40 min. The data shows evidence that there is an increase of interfacial surface tension within 30 min, likely due to the stabilization of η_{LV} . This amount of time is required to achieve steady-state conditions in the molten slag.

TABLE 1

COMPOSITION OF COAL ASHES (WEIGHT PERCENT EXPRESSED AS EQUIVALENT OXIDE) USED IN THE INTERFACIAL SURFACE MEASUREMENTS

Run No.	Coal Ash	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	CaO	MgO	Na ₂ O	K ₂ O
A. Prepared in air									
1	Beulah	37.5	15.1	11.3	1.6	21.6	6.1	5.7	0.8
2	Pittsburgh #8	50.9	20.2	19.1	1.2	4.7	1.1	0.0	2.6
3	Illinois #6	46.7	20.7	21.1	1.3	6.4	1.1	0.0	2.7
B. Prepared in H ₂ /N ₂ (8/92)									
4	Beulah	37.9	15.3	11.1	1.6	22.2	5.5	5.7	0.7
5	Pittsburgh #8	51.2	20.7	18.0	1.2	4.8	1.2	0.0	2.6
6	Illinois #6	47.7	19.6	20.7	1.3	6.5	1.2	0.0	2.8
C. Prepared in CO/CO ₂ (60/40)									
7	Beulah	38.0	15.3	10.9	1.6	22.4	5.1	5.8	0.7
8	Beulah + Limest.	33.1	23.0	10.1	1.3	26.1	2.9	2.8	0.7
9	Beulah + Dolom.	34.2	16.2	9.7	1.5	25.8	8.0	4.2	0.5
10	Pittsburgh #8	51.1	20.6	18.2	1.2	4.9	1.2	0.0	2.6
11	Pitt. + Limest.	43.1	20.7	16.2	1.1	16.0	0.8	0.0	2.2
12	Pitt. + Dolom.	45.9	20.3	16.6	1.1	10.1	3.6	0.0	2.2
13	Illinois #6	47.9	19.5	20.6	1.3	6.7	1.2	0.0	2.8
14	Ill. + Limest.	40.9	18.6	18.9	1.1	17.5	0.7	0.0	2.3
15	Ill. + Dolom.	42.4	20.2	18.0	1.1	12.4	3.5	0.0	2.3

TABLE 2

DENSITY OF SLAG DROPLETS CALCULATED FROM THE SESSILE DROP

Temperature °C	Density, g/cm(3)		
	Beulah Run No.7	Pittsburgh #8 Run No. 11	Illinois #6 Run No. 13
1300	3.08	2.80	2.51
1325	3.13	NA	2.48
1375	3.07	2.84	2.41
1425	3.12	2.78	2.55
1475	3.07	2.78	2.50
Average	3.09 + 0.04	2.80 + 0.04	2.49 + 0.08

Atmosphere: CO/CO₂ (60/40)

TABLE 3

INTERFACIAL SURFACE TENSION OF ILLINOIS #6 COAL ASH
VERSUS ANNEALING TIME, DETERMINED AT TEMPERATURE OF
SESSILE DROP FORMATION

Surface Tension, dyne/cm			
Time (min)	Run No. 13 T = 1275°C	Run No. 14 T = 1250°C	Run No. 15 T = 1250°C
0-5	205	NA	238
15	244	339	255
30	278	318	259
40	249	329	278

Atmosphere: CO/CO₂

It is worth noting that the interfacial surface tension of coal ash exposed to reducing atmospheres is much less than those measured in air and 8%H₂-92%N₂ as shown in Table 4. This is likely to be caused by the structural complexity of a melt in the surface layers of the sessile drop due to the reducing of oxygen content in a slag;

where O_o represents an oxygen site in a silicate system, and V_o represents an oxygen deficiency. The structural reasons for the variation is not yet conclusively established. It should be noted that the interfacial surface tensions differ depending on the atmosphere in which the coals are heated.

The effect of temperature is generally noted by the increase of droplet area. In the multicomponent silicate system, nonhomogeneity is a very important factor that may change the droplet interfacial surface tension. Therefore, all experiments were performed on homogenized slags after measuring viscosity in a CO/CO₂ (60/40) atmosphere. Figures 1-3 show viscosity-temperature relationships along with the interfacial surface tension values. Temperature has a significant effect on the changes of the interfacial surface tension below the temperature of critical viscosity. This effect may be attributed to a nonequilibrium state due to the random distribution of surface active phases in the slag and polymerization of the silicate structure. However, there is not significant variation of η_{LV} with temperatures above T_{cr} .

Chemical composition of tested coal ashes was varied with addition of small amounts of limestone or dolomite which are used as sulfur capture agents in gasification facilities. To obtain a uniform distribution of chemical composition, coal ashes with additives underwent the same procedure described in the experimental section.

TABLE 4

INTERFACIAL SURFACE TENSION OF BEULAH, PITTSBURGH #8, AND ILLINOIS #6 MEASURED IN VARIED ATMOSPHERES, DETERMINED AT TEMPERATURE OF SESSILE DROP FORMATION

Temperature of Sessile Drop Formation (°C)	Surface Tension, dyne/cm			*Base/ Acid Ratio
	Air	H ₂ /N ₂ (8/92)	CO/CO ₂ (60/40)	
Beulah				
1285	802			0.84
1275		615		
1200			408 + 18	
Pittsburgh #8				
1275	483			0.38
1275		358		
1200			261 + 5	
Illinois #6				
1200	531			0.45
1175		334		
1275			259	

* $\frac{\text{Base}}{\text{Acid}} = \frac{\text{Na}_2\text{O} + \text{K}_2\text{O} + \text{CaO} + \text{MgO} + \text{Fe}_2\text{O}_3}{\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{TiO}_2}$

Figure 1. Viscosity-temperature relationship of Beulah slag (Run no. 7) and the values of interfacial surface tension determined for selected temperatures. Under CO/CO₂ atmosphere.

Figure 2. Viscosity-temperature relationship of Pittsburgh #8 slag (Run no. 11) and the values of interfacial surface tension determined for selected temperatures. Under CO/CO₂ atmosphere.

Figure 3. Viscosity-temperature relationship of Illinois #6 slag (Run no. 13) and the values of interfacial surface tension determined for selected temperatures. Under CO/CO₂ atmosphere.

Table 5 compares the values of interfacial surface tension with the base-to-acid ratio. Generally, the interfacial surface tension decreases as the base-to-acid ratio decreases. The base-to-acid ratio has been demonstrated as a useful measure of slag viscosity. Usually, viscosity decreases with the increase of the base-to-acid ratio.

TABLE 5

INTERFACIAL SURFACE TENSION OF BEULAH, PITTSBURGH #8, AND ILLINOIS #6 COAL ASHES WITH ADDITIVES, DETERMINED AT TEMPERATURE OF SESSILE DROP FORMATION

Temperature (°C)	Interfacial Surface Tension, dyne/cm			*Base/ Acid Ratio
	Coal Ash	Coal Ash + Limestone	Coal Ash + Dolomite	
Beulah				
1200	408 + 18			0.79
1300		267 + 4		0.72
1275			419	0.90
Pittsburgh #8				
1200	261 + 5			0.34
1250		329 + 20		0.50
1300			389 + 34	0.44
Illinois #6				
1275	259			0.41
1250		328 + 10		0.60
1250			269 + 20	0.52

Atmosphere: CO/CO₂ (60/40)

$$* \frac{\text{Base}}{\text{Acid}} = \frac{\text{Na}_2\text{O} + \text{K}_2\text{O} + \text{CaO} + \text{MgO} + \text{FeO}}{\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{TiO}_2}$$

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3.6 Coal Science

**COAL SCIENCE
EARTH RESOURCE EVALUATION AND MANAGEMENT**

**Quarterly Technical Progress Report
for the Period January-March 1990**

by

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COAL SCIENCE EARTH RESOURCE EVALUATION AND MANAGEMENT

1.0 Goals and Objectives

The general "Coal Science" objectives and goals are based on the desire of the North Dakota Mining and Mineral Research Institute (MMRRI) to 1) more fully utilize coal and related geologic data currently available for integration and analysis, and 2) base interpretation of these data on well controlled test cases or examples. The focus of the first phase of the project is to setup the computerized basis for reevaluating, or evaluating for the first time, North Dakota's lignite resource in its stratigraphic and paleontologic context.

2.0 Accomplishments

During this reporting period, each component of the first year objectives were augmented including 1) acquisition, ordering, and review of computer-related hardware and software, 2) review and acquisition of field and laboratory equipment, 3) data base design evaluation, 4) computerization of a variety of coal and related geologic data, 5) geologic and paleontologic preparation of test area and related samples, 6) review and submission of applications for permission to drill in test areas on U.S. Forest Service property, and 7) preparation of papers and talks that utilized data base designs so far implemented (see Appendix 1). These accomplishments included completion of Milestones E.1, E.2, and F.1. Milestones E.1 and E.2 represent the assessment and characterization of the stratigraphic and paleontologic data base designs and procedures for Year 1. Milestone F.1 includes the augmentation of the data base for Bowman and Slope Counties in southwestern North Dakota.

2.1 Computer Hardware and Software

Hardware. A video-capture system is now operational and will become an important part of the analysis of the stratigraphic and paleontologic context of coal. This system runs on the main data management computer (Gateway 2000-386), utilizing a PCVISIONplus framegrabber from Imaging Technology. This video system consists of a high-resolution SONY Trinitron monitor, Cohu CCD camera and lens, and a SONY thermal printer. The system uses specialized programming, such as Jandel's JAVA program, to "capture" black and white images for digitizing and numerical analysis. Initial hardware system incompatibility problems consisted of memory conflicts between video cards, capture programming, and the EVEREX cassette tape backup system. These problems were resolved by establishing protocol to reconfigure the hardware for different applications. Thus the video system runs under its own configuration to resolve its hardware specific requirements. The video system will capture images for analysis at three scales or levels of magnification: 1) macro (large objects from 10 to 500 mm in length) 2) micro (small three-dimensional objects from 1 to 50 mm in length), and 3) micro (effectively two-dimensional objects less than 1 mm in size). With the Cohu lens (12.5-73 mm

zoom) and TOYO diopters, the video system can capture a wide range of macroscale images. Experimental work continues to determine the best configuration to maximize depth of the field for close-up work of large three-dimensional objects. Relatively small specimens, or close-up study of large specimens, require macrophotography. The Cohu camera can be fitted for this type of application, and study is currently underway to acquire a low power dissecting-type microscope for this purpose. The third size range of objects is studied after thin-section type preparation with high-powered stereomicroscopes. A Zeiss microscope is available at UND-EERC for this purpose. Study is underway to adapt this microscope for video image analysis of palynomorphs from samples collected in the test areas of western North Dakota. This work represents, in part, the Ph.D. studies of Tim Kroeger, a student in the Department of Geology and Geophysics at the University of North Dakota.

Software. Video-capture and analysis programs that have been acquired for use with the hardware described above include Jandel's JAVA program and a University of California-Berkeley program known as MORPHOSYS. During the winter quarter, initial testing began to develop morphometric applications. These applications have focused mainly on paleontological specimens to determine methods for improving the accuracy and speed of taking standard measurements. In addition, video imaging provides the opportunity to effectively take "instant" photographs of objects of interest. This photographic technique saves a tremendous amount of time over conventional photography for sample documentation. Like conventional photography, but in its own peculiar way, video photography is extremely light sensitive. To facilitate the control of lighting during video photography, a standard MP3-type copy stand was rewired so that each of the four high-intensity lamps could be individually regulated. Although use of the video-capture system has just begun, it offers great promise in the numerical analysis of a variety of samples and in the incorporation of video images into other programs for display or additional analysis.

Data base design and management is founded on Symantec's program "Q&A." As has been noted previously, this program is essentially unique in its application power versus ease of use and cost effectiveness. The program is intended to be utilized for complex retrieval in various routines that provide immediate flexibility for data acquisition and reporting. Q&A is capable of using multiple external files in data management and reporting that permits data base design to employ relational-type data processing. Compared to major market data base systems, such as dBASE, rBASE, and PARADOX, Q&A provides the on-line users with the opportunity to control their data environment without elaborate ritual or protocol. In addition, Q&A provides a word-processing environment that can be employed to utilize information from constructed data bases within its "file" environment. Thus text and data can be merged in any number of formats without redesigning files. Enhancement features (e.g., bold, italics, font selection), available to word-processors, can be added to "data" to clarify and augment data presentation. During the winter quarter, additional time was spent to improve the output design of data to Hewlett-Packard laserjets. Bitstream fontware was acquired to permit the construction of PRESTIGE fonts of any size and style (e.g., bold, italic, etc.). Data base programming and desktop laserjet systems are currently undergoing major

changes in their ability to display data and images easily. "Traditional" (a few years old) techniques for displaying laserjet output will be outdated as programs (e.g., Borland's spreadsheet program QUATRO PRO) will automatically download desired fonts, and/or the laserjet itself (e.g., HP Laserjet III) will provide a wider variety of font choices. This discussion is presented to stress that data management is inextricably bound to its adequate display for analysis, interpretation, and reporting.

During the winter quarter, programming was acquired for basic data analysis, including Borland's spreadsheet QUATRO PRO and Applied Biostatistics' NTSYS-pc, which is a numerical taxonomy and multivariate analysis system of programs. QUATRO PRO is a LOTUS 123-type spreadsheet for numerical data management and display. QUATRO PRO was acquired, in part, because it provides greater data reporting control and better graphics. NTSYS-pc was acquired for numerical analysis of paleontologic data and will be used in conjunction with data obtained through video imaging.

During the fall quarter, the geologic program STRATIFACT by GRG was acquired (through other funding) for the display and analysis of geologic section data and their correlation. This version of STRATIFACT had severe limitations on importing and exporting data and in other geologic-specific functions. UND-EERC-MMRRI has a standing order for the new version when it is available (the stated date of publication has long since passed). In any case, most geologic programs, like STRATIFACT, fill particular application needs. However, most are not inherently good data managers and do not provide the flexibility of data base systems such as Q&A. My approach to data management and manipulation is to utilize data systems that, if not inherently compatible, can be modified to permit the exchange of data for specific applications. Rockware's program LOGGER was acquired to facilitate the exchange of geologic section data. LOGGER is in essence a data management system of geologic section information. Files are maintained in ASCII format, and thus data can be manipulated outside of the program. This program was received at the end of the winter quarter and has received only limited study, but it is believed that data managed in Q&A will be available for use in LOGGER for graphic display of section information. In addition to LOGGER, a module was acquired from GRG to permit the up- and downloading of NCRDS section data into STRATIFACT. The use of this module awaits the arrival of the new version of STRATIFACT.

2.2 Other Equipment Considerations

During the fall and winter quarters, consideration was given to the procurement of certain pieces of field and laboratory equipment. Decisions based on immediate needs predicated the acquisition of a RAYTECH 10-inch rock slab and trim saw for the preparation of geologic cores, lithic samples, and paleontologic specimens. In addition, acquisition of a stereomicroscope was reviewed for use with the video system.

2.3 Database Design Assessment and Characterization

During the fall and winter quarters, data base design features were considered relative to potential applications. Data bases were designed and

frequently modified for use with stratigraphic and paleontologic data. I believe a general approach has been determined. The assessment and characterization were, in part, summarized in the fall quarterly report, and are included here as part of the fulfillment of specific milestones for the winter quarter.

At present, four major file-types are employed to handle geologic and paleontologic resource information. Additional files permit access to related data of a unique nature, such as map information (e.g., publication, revision, contour interval) and coding information, such as words, abbreviations, or terms that have special meaning for sort routines. The four main file-types include: 1) geologic section or observation location information (*MNOS), 2) geologic section unit descriptions (*UNIT), 3) paleontologic location and stratigraphic information (*LOC), and 4) taxon identification information (*SPP). The prefix "*" denotes a specific file name, such as WB or PRB for the Williston or Powder River Basins. Both data files with these prefixes have the same data base design and can be automatically merged into one large data base if required.

The *MNOS files contain information on the location of geologic observations, such as surface and subsurface measured sections. The *MNOS form contains six general field categories in 99 fields, including 21 code fields for specialized sort routines. *MNOS field categories include: 1)-reference information, 2) numbering systems associated with record, 3) location and land owner information 4) section thickness and elevation information, 5) litho- and chronostratigraphic information, and 6) sample/specimen information. Reference information fields contain data on the source of the information (i.e., citation), including: 1) authorship, 2) source of data, 3) project chief, 4) institutional or agency affiliation of the project chief, 5) location of observation in cross section panels, and 6) type of observation (e.g., surface measured geologic section). Numbering systems associated with the record include: 1) UND-EERC-MMRI "M-number," 2) a reference number, associated with the source of information, such as a number specifically associated with the publication of the geologic section, 3) field number, usually referring to the original number used during field work, and 4) institutional number, referring to numbering systems employed by various agencies or institutions (e.g., NDSWC 4252 = North Dakota State Water Commission number 4252), and 5) section name, if any (e.g., Tepee Buttes section). Location fields contain information ranging in scale from general political boundaries to site specific coordinate systems: 1) nation, 2) region, 3) field area, 4) state, 5) county, 6) map reference, 7) township and range location, 8) footage from section lines, 9) longitude and latitude, 10) UTM coordinates, 11) state grid coordinates, 12) property owner information, and 13) general location comment field. *MNOS files use the MAPS file as an external lookup table to import map reference information. Section thickness and elevation information is contained in fields that automatically convert metric to English measurements, error associated with elevation interpretation, and initials of interpreter of elevation. Litho- and chronostratigraphic information is contained in fields that reference: 1) the geologic age of the measured section or observation, 2) the formations represent in the section, 3) the thickness of the formations represented in the section, 4) the completeness of the formation at this location, 5) a

general listing of the named beds in the section, 6) specific reference to a particular bed, its original name (revision from field or published identification), and unit number in the section, and 7) general stratigraphic comment field. This form also contains sample and photographic information concerning the entire section, including reference numbers for: 1) fossil localities, 2) lithic samples, 3) photographs of the section.

The corresponding or companion *UNIT file has 46 fields specific to geologic section unit reference, measurement, and description. A "unit" is a stratigraphic interval, identified by the geologist, that is sufficiently distinct from lithologies above and below to represent a discrete portion of the overall geologic section. Reference fields include: 1) M-number, 2) source of information, 3) unit number, 4) unit (bed) name, 5) original bed description, 6) formational assignment of unit, 7) and sample number(s) pertaining to the unit. Measurement fields record individual unit thicknesses and permit calculations to be made to derive unit thicknesses from a variety of original information types, depending on the nature of how the section was measured. Methods of deriving unit thickness include: 1) simple inputting of original data from described measured sections (with conversions between feet and meters), 2) calculation of unit thicknesses by measuring illustrations of geologic sections for which original data no longer exists, and 3) calculation of unit thicknesses from surface geologic sections constructed by pace and compass techniques (utilizing dip control). Description fields contain information derived from the original description or illustration of the geologic section. As noted, this data base includes a large field that permits the quotation of the description of the unit as originally interpreted. The remaining fields contain information specific to different aspects of the description of the units. Standard field types include: 1) primary rock type, 2) rock-type modifiers, 3) fresh and dry colors (GSA rock color chart), 4) sedimentary structures, 5) grain size sequences, 6) weathering profile, 7) depositional environment, and 8) fossil-indicated environment. Other fields are added as needed to manage information for specific projects or to set up data (through internal lookup tables) for loading into other programs (e.g., coding for the illustration of geologic sections).

*LOC files contain records on the location of fossil localities and is specifically designed for micro- and macro-fossil specimens. The *LOC file is similar to *MNOS files in general design, containing the nearly the same fields for reference and location data. Like the *MNOS form design, *LOC files contain a number of coding fields used for sort routines of age-related information and uses the file MAPS for map reference information. Specialized locality fields include information on: 1) litho- and chronostratigraphy, 2) collecting history, and 3) the fauna. Stratigraphic fields contain information concerning: 1) the formation and member to which the locality can be assigned, 2) the original formation used by the discoverer of the locality, 3) the elevation of the locality, 4) the footage determination of the horizon of the locality within the formation (e.g., from top or bottom), 5) the level or interval of the locality relative to other formational contacts and marker beds, 6) the measured section and unit numbers (*MNOS, *UNIT) to which the locality belongs, 7) the age of the locality, and 8) an extended comment field for additional stratigraphic considerations. Information concerning the

collecting history of the locality includes: 1) the discoverer(s) and date of discovery, 2) collector(s) and date of collecting, 3) field party chief and institutional or agency affiliation, and 4) the repository for the collections. Faunal information about the locality includes: 1) fossil groups represented at the locality (e.g., mammals, microfossils, mollusks, etc.), 2) a faunal list of identified taxa, 2) name of the individual identifying the fossils, and 3) faunal comment field concerning the preservation of the fossils.

The companion *SPP file records information on the identification of taxa at a particular locality. Field types include: 1) taxon identification, 2) a simplified classification of the taxon, 3) repository and specimen numbers, and 4) number of specimens and identification comments. Both old and revised identifications are recorded to provide a history of study on specific specimens and taxon names. The file *SPP uses the *LOC file and MCLASS files as external lookup files. Using *LOC files, the stratigraphic range of a taxon can be determined through a merge of the components of the two files. Using the MCLASS file, a simplified classification of a taxon can be automatically imported into *SPP to provide a means to summarize stratigraphic data on higher taxonomic categories.

2.4 Data Input

Substantial amounts of data have been entered in all of the four main file types (i.e., *MNOS, *UNIT, *LOC, and *SPP). External lookup files have also been constructed that maintain information on map reference data (MAPS) and fossil-classification (MCLASS). Other files record information on related information and include the following files: 1) overall locality register (LOCREG), 2) type-specimen data (TCKZOIC), 3) specimen numbers and institutional repositories (SPEC-NO), 4) taxon coding (TAXON-NO), and 5) reference bibliography (BIB). Measured section and other geological observations (*MNOS and *UNIT files) have been and continue to be entered for western North Dakota and adjacent Montana, focusing on the Slope County test area, but also in Bowman County and in the area of Fort Union in the vicinity of the Nesson Anticline in Williams and McKenzie Counties. Locality (*LOC and *SPP files) information has also been inputted for these areas and continues to be augmented. Locality information has also been inputted for the Powder River Basin for the purposes of determining the age relations between the coal-bearing strata of this basin with that of the Williston Basin. MAP data has been entered for North Dakota, Montana, Wyoming, and portions of southernmost Saskatchewan. Additional MAP file management is underway. USGS map data is being downloaded from magnetic tapes into Q&A files for greater ease of use.

2.5 Sample Preparation

Geologic and paleontologic samples of importance to interpreting the geologic context of coal-bearing strata in western North Dakota were and continue to be prepared for study. Sample analysis will include traditional and recently available techniques (video-capture) to provide stratigraphic, environmental, and biochronologic information.

2.6 Drilling-related Activity

Two sites have been proposed for drilling and geophysical logging. These sites are in northwestern Slope County and southwestern Golden Valley County, North Dakota. Data derived from drilling at these sites will add significantly to our ability to correlate and interpret the coal-bearing strata of the lower and middle Paleocene of easternmost Montana and western North Dakota. Both sites are on federal Forest Service property and require permits for access and drilling. Appropriate permit forms have been completed and will be submitted in April. An "invitation for bids" has also been drafted. This document includes the specifications and requirements for the drilling process. The bid invitation is modeled after documents used for this purpose by the North Dakota State Water Commission.

2.7 Papers & Presentations

During the winter quarter, papers and talks were prepared that utilized data inputted into the data base structure described above (see Appendix 1 for titles). The flexibility of data retrieval and reporting permitted data to be organized for convenient interpretation and construction of illustrations. Additional contributions are planned for talks and papers due during spring quarter that will serve as additional tests for the adequacy of current data base designs.

3.0 Summary and Conclusions

Substantial progress continues to be made toward establishing MMRRI geologic and paleontologic data base designs in regards to coal and its geologic context. The milestone "E. Data base assessment and characterization" has been completed for stratigraphy (E.1) and paleontology (E.2). In addition, "Data base augmentation (F.1)" for the Slope/Bowman County test area has been completed. Drill hole data for this area, however, continues to be inputted for research on coal stratigraphy and correlation. The data bases described above permit the computerization of large amounts of quantitative and descriptive geologic data and yet are relatively easy to use. Besides myself, data has been inputted by undergraduate and graduate students and support staff. Although some training is required, inputting of data that does not require interpretation is relatively straightforward. Individuals with a geologic background can input data requiring some interpretation (e.g., stratigraphic and descriptive information) using customized help information available with all fields in all files. As previously noted, the goal is to make computerized coal resource data available to the researcher as part of the analysis phase of their work. This permits a far wider range of choices in manipulating and displaying available data. The next step is to make the data available through a computer network system that allows all researchers to utilize the same data bases conveniently.

4.0 Appendix 1: Papers and Abstracts Prepared and Submitted during the Winter Quarter

Kihm, A.J., and HARTMAN, J.H., 1990, Chronostratigraphic implications of the mammal and nonmarine mollusk record of the Paleocene Fort Union Group in North Dakota: North Dakota Academy of Science, v. 44, p. 70. [accepted; to be presented and published in April].

HARTMAN, J.H., and Kihm, A.J., 1990, Chronostratigraphy of Paleocene strata in the Williston Basin, in Finkelman, R.B., Daly, D.J., Tewalt, S.J., eds., Geology and utilization of Fort Union Region lignites [submitted and accepted; to be published in Fall, 1990].

HARTMAN, J.H., 1990, Paleocene and lower Eocene nonmarine molluscan biostratigraphy of the Powder River Basin, Wyoming-Montana: Geological Society of America, Rocky Mountain Section [submitted and accepted; to be presented and published in May].

4.0 COMBUSTION RESEARCH

4.1 Fluidized-Bed Combustion

FLUIDIZED-BED COMBUSTION OF LOW-RANK COALS

**Quarterly Technical Progress Report
for the Period January - March, 1990**

by

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1.0 BACKGROUND

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 industrial-scale units of both types are currently in operation. 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 interrelating those problems generic to bubbling, circulating, and pressurized fluidized-bed combustion systems. The 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, and
 - 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 importantly, the economics involved in having fuel flexibility for the FBC.
- Agglomeration/sintering of bed material and deposition on tubes, support surfaces, and refractory has been identified as a problem by both manufacturers and users of FBC technology. The problem cases have been documented for both bubbling and circulating beds, using a variety of fuels, including coal. The EERC has extensive experience in this area to help understand and solve this operational problem.
- Scale-up effects need to be addressed so that vendors and users can take pilot-scale data and be assured that the large-scale system will perform as anticipated. This data base has been growing rapidly with all of the

new units starting operation; however, much information is still required. The University of North Dakota will have an opportunity to observe scale-up effects for CFBC when the University includes a CFBC as a part of its steam system expansion. 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, and
 - 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 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 specifications in addition to NSPS.

These problems and concerns could limit FBC from reaching its full potential. Special efforts should be taken to perform the necessary research to help FBC evolve to a mature technology meeting the technical, economic, and environmental needs of the future.

2.0 GOALS AND OBJECTIVES

A number of major issues have been identified that warrant further research. EERC has the capability to investigate several issues in atmospheric bubbling FBC. Some of these issues are proposed in this work plan. Other FBC research should be funded, at least partially, by the industrial sector, either through EPRI or private companies. Efforts should continue to transfer the expertise gained under previous Cooperative Agreements to the private sector.

The overall goal of the low-rank coal (LRC) fluidized-bed combustion (FBC) program at EERC is to develop a technology data base so that industry can introduce economically and environmentally acceptable coal technology options to the marketplace. Research will address those areas where data gaps exist in fuel flexibility and performance, potential operating problems, environmental compliance, advanced concepts, and system simplification.

2.1 Three-Year Objectives (7/89 - 6/92)

EERC has developed an extensive data base on corrosion and erosion of boiler tubes, agglomeration and sintering of bed material, fuels and sorbent characterization, and particulate emissions through testing funded under the Cooperative Agreement. To successfully transfer this information to the private sector, EERC will continue to publish results from this work at conferences and in refereed journals. The existing data base will be supplemented by low level experimentation, paper studies, economic evaluations, and surveys of operating plants and other researchers' data to fill gaps that may exist.

Pilot-scale work has been performed evaluating the corrosion and erosion of boiler tube surfaces in bubbling beds. EERC has done extensive analysis and characterization of samples generated from this testing. Over the next three years, available samples from industrial and utility-scale boilers will be analyzed and results correlated to bench- and pilot-scale work as well as to each other. EERC will also attempt to obtain funding from non-DOE sources to perform more work on large-scale systems.

Efforts in corrosion and erosion will switch focus to CFBC during this time period. A pilot-scale CFBC is being constructed as a part of another project. Initial work on this unit will involve system, coal, and sorbent characterization. During the characterization testing, an assessment will be made to determine if any meaningful corrosion and/or erosion data can be obtained. If meaningful data can be generated, EERC and METC personnel will discuss the possibility of incorporating CFBC corrosion and erosion work into this program.

Work will continue on the coal pretreatment cell currently being developed at EERC. After each phase of the project, an assessment will be made to determine if the concept is still technically and economically feasible. The end result of this effort is expected to be a design of the pretreatment cell in conjunction with a bubbling and circulating FBC and an economic evaluation of the concept. Testing will be done at the pilot-scale, with no demonstration planned as part of this program.

As part of the advanced concepts task and other noncooperative agreement work, EERC will work toward simplifying the control and operation of the FBC. As a part of this task, users of FBC technology will be polled to identify operational problems with fuel and sorbent feed and ash removal systems. Based on priorities identified from this poll and results of other work, EERC will work toward the simplification of control and operation of the FBC. Specific systems will be identified in either the second- or third-year work plans.

First generation PFBC technology has reached commercialization, as indicated by the two recent Clean Coal awards for utility-scale plants. Second generation concepts are now being developed. The success of these concepts will depend, in part, on an understanding of the effects of fuel properties on performance. The EERC will consult with developers of second generation technology on how fuel properties affect drying, pyrolysis, combustion, and topping cycles. The EERC is in the process of designing and constructing a pilot-scale CFBC as a part of a multiclient-funded program.

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This unit will be used to investigate the impact of CFBC design and coal properties on performance. The test unit would not be available to this program for at least one year. Once the CFBC is available for testing, the current status of the technology will be assessed to determine if and how the unit should be incorporated into this test program.

Atmospheric fluidized-bed combustion has become an acceptable option for the generation of steam and electricity. A number of units are currently on-line in both the industrial and utility sector. Great market potential exists for the use of AFBC technology in both commercial and industrial sectors; however, to increase the acceptability of this technology, low cost, reliability, and ease of operation must be inherent to the system. The purpose of this task is to simplify the control and operation of the FBC for boilers in the range of 10,000 to 200,000 lbs/hr. The goal of this system simplification is to make the unit easier to operate, reduce capital and operating costs, and increase the overall reliability of the system.

2.2 Proposed First-Year Research (7/89 - 6/90)

Specific objectives of the Fluidized-Bed Combustion Project for Year One of this three-year period are as follows:

Task 1. Coal Characterization Reference Guide

To transfer information generated at EERC during the characterization studies, a reference guide will be prepared that discusses the performance, operational, and economic issues related to fuel quality. This guide will rely on information generated at EERC, with supplemental data from other researchers, vendors, and operating facilities. The guide will be directed toward users of FBC technology who need to know the impact of fuel switching on the operation of their unit.

Task 2. Corrosion/Erosion of Boiler Tubes

Samples of boiler tubes and deposits from full-scale units, both industrial and utility, will be obtained. Detailed metallographic analysis will be performed to enable a better understanding of the mechanisms of metal wastage and to extend the data base so that metal wastage between units and coal types can be better correlated. The impact of stress corrosion will also be examined. The success of this task will depend on the availability of samples and the cooperation from FBC users. EERC will also collaborate with Lawrence Livermore Laboratories on sample availability and analysis.

Task 3. Advanced Concepts - Coal Pretreatment Cell

Work will continue on the coal pretreatment cell currently under development at the EERC. Work during the year will focus on pilot testing the pretreatment cell. Information generated during pilot testing will be used

to improve the design concept and to generate information for a more detailed economic evaluation of the concept.

Task 4. PFBC Consulting

The EERC will provide consulting services to Foster-Wheeler and MW Kellogg. The focus will be on the effects of fuel properties on the design and performance of their second generation concepts.

Task 5. System Simplification

The general approach to this work will be, first, to identify the most troublesome, complicated, and costly system components. A second step will evaluate the cost of improving each of the components identified, and the resulting benefits of the said improvement. Based on the cost/benefit analysis, a prioritized list of components for study will be developed. Before any work will begin on the component development phase, the EERC will make recommendations to the METC COTR to obtain approval of the test plan for developmental work. It is anticipated that the developmental work will focus on control systems.

3.0 RESULTS AND DISCUSSION

3.1 Corrosion/Erosion of Boiler Tubes - Deposit Analyses from MDU Heskett Station

The 80-MW FBC unit at the Montana Dakota Utilities Heskett Station has experienced deposition on both in-bed and convective pass heat transfer surfaces, causing significant reduction in overall heat transfer. The unit is fired with Beulah lignite with a bed material of river sand. Deposits from this unit were collected and analyzed using x-ray fluorescence, x-ray diffraction, scanning electron microscopy (SEM), microprobe analysis, and scanning electron microscopy point count (SEMP). The last technique was developed at the EERC specifically to characterize ash-related phenomena. The river sand used as the bed material and a sample of spent bed material were also analyzed by SEMPC. Also a sample of ash coating from the spent bed material was analyzed. The focus of the analysis was to establish the mechanism of deposit formation and growth. The results of the analysis are as follows.

Table 1 compares the bulk chemical composition of the virgin bed material (river sand), the coal ash chemistry (ASTM ash prepared at 750°C), and the bulk chemical compositions of the in-bed tube and convective pass tubes. Table 2 shows the chemical composition of the samples on an SO₃ free basis. The coal ash was typical of Beulah lignite with high alkali and alkaline earth elements. On an SO₃ free basis, the Na₂O content of the ash was about 8.0 wt%. The virgin bed material was also high in alkaline earth and alkali elements. The spent bed material was surprisingly low in SO₃. This may be

TABLE 1

CHEMICAL ANALYSIS OF SAMPLES FROM THE 80-MW HESKETT STATION

wt% Oxides	Beulah Coal	Virgin Bed Material	Spent Bed Material	Bed Material Ash Coating	In-Bed Tube Deposit	Convective Pass Deposit
SiO ₂	27.7	61.8	54.3	16.3	6.0	7.6
Al ₂ O ₃	11.9	12.3	16.9	10.9	4.5	5.1
Fe ₂ O ₃	8.3	0.6	2.5	9.9	8.2	28.4
TiO ₂	0.7	0.0	0.3	1.0	0.6	0.7
P ₂ O ₅	0.5	0.1	0.1	0.1	1.9	1.1
CaO	17.1	10.2	7.2	28.2	24.7	16.0
MgO	5.5	8.6	2.0	8.6	6.7	3.5
Na ₂ O	6.3	5.3	7.9	6.2	7.4	10.2
K ₂ O	0.6	1.0	4.6	0.8	0.4	0.3
SO ₃	19.7	0.0	4.2	17.8	39.6	27.0
Total	98.3	99.9	100.0	99.8	100.0	99.9
% Ash	7.3	--	--	--	--	--
LOI	--	--	--	--	--	--

TABLE 2

CHEMICAL ANALYSIS OF SAMPLES FROM THE 80-MW
HESKETT STATION ON AN SO₃ FREE BASIS

wt% Oxides	Beulah Coal	Virgin Bed Material	Spent Bed Material	Bed Material Ash Coating	In-Bed Tube Deposit	Convective Pass Deposit
SiO ₂	26.5	61.8	56.7	19.8	9.9	10.4
Al ₂ O ₃	15.6	12.3	17.6	13.3	7.5	7.0
Fe ₂ O ₃	11.4	0.6	2.6	12.0	13.6	38.9
TiO ₂	1.3	0.0	0.3	1.2	1.0	1.0
P ₂ O ₅	1.6	0.1	0.1	0.1	3.1	1.5
CaO	27.3	10.2	7.5	34.3	40.9	21.9
MgO	6.5	8.6	2.1	10.5	11.1	4.8
Na ₂ O	9.6	5.3	8.2	7.5	12.3	14.0
K ₂ O	0.4	1.0	4.8	1.0	0.7	0.4
SO ₃	--	--	--	--	--	--
Total	100.2	99.9	99.9	99.7	100.1	99.9

due to the high bed turnover rate used at the unit to prevent agglomeration and the high amount of finely dispersed ash which would tend to be elutriated. The Ca/S molar ratio for the spent bed material is 2.44, indicating free Ca available. The spent bed material was also rich in SiO_2 and Al_2O_3 . However, the Si/Al molar ratio of the spent bed was much lower than that of the virgin bed (2.73 compared to 4.27). This would indicate a contribution of coal ash material (Si/Al molar ratio for the coal ash is 1.98). Just based on the Si/Al molar ratio, the bed inventory appears to be 35% river sand and 65% coal ash.

The ash coating was rich in SO_3 , compared to the spent bed. The Ca/S molar ratio was 2.26, indicating an excess of Ca in the coating. Based on the SO_3 free chemical composition, the ash coating was slightly enriched in Ca and Mg, compared to the coal ash, and very enriched (compared to the spent bed chemistry) in Ca, Mg, and Fe. The Si/Al molar ratio was 1.27, indicating that the aluminosilicate component was formed from kaolinite-derived species (Si/Al molar ratio of about 1) with some quartz.

The two deposits had very high sulfate levels. Indeed, the Ca/S molar ratios for the deposits were less than 1.0, indicating that there was no free Ca in the deposits. The deposits had very similar levels of Si and Al. The Si/Al molar ratios were close to that of the ash coating, indicating that the aluminosilicate material originated from the kaolinite clay with some quartz. The in-bed tube deposit was richer in Ca and Mg compared to the convective pass tube deposit. Of interest is that the Na_2O levels for the two deposits were similar. Furthermore, the chemical composition of the ash coating on an SO_3 free basis was similar to the in-bed tube deposit. The notable exceptions were the SiO_2 and Al_2O_3 levels. The convective pass was very rich in Fe_2O_3 . The ash coating and in-bed tube deposit had Fe_2O_3 levels similar to the coal ash. Of interest is that as the spent bed was depleted in Fe_2O_3 , compared to the coal ash, indicating a large portion of the Fe_2O_3 was elutriated during combustion.

X-ray diffraction analysis was performed on the in-bed tube deposit and the convective pass deposit. The in-bed tube deposit was shown to contain CaSO_4 (anhydrite) and hematite (Fe_2O_3). The convective pass tube deposit, however, contained hematite, anhydrite, and glaucoberite ($\text{Na}_2\text{Ca}(\text{SO}_4)_2$).

The examination of the morphology and spatial distribution of the major elements in the deposit samples was determined using SEM and electron microprobe techniques. The samples in cross section appeared to be a dense matrix with low porosity. Individual fly ash particles were difficult to discern. The matrix material was predominantly calcium sulfate. Examination of the cross sections using backscattered imaging showed that the iron oxide was dispersed through the sulfate matrix as discrete grains. This showed that the iron oxide does not take part in the deposit growth mechanism or contribute to the overall strength. The composition of the matrix material was confirmed by selected point analyses performed using the electron microprobe. The analyses showed that the matrix was almost pure calcium sulfate or sodium calcium sulfate. Some points were almost pure sodium sulfate.

The results of the SEMPC analysis of the various samples are listed in Table 3. The results are listed in terms of volume percent of each of the phases. The virgin bed material contained albite ($\text{NaAlSi}_3\text{O}_8$), quartz, dolomite ($(\text{Ca}, \text{Mg}) \text{CO}_3$), illite, and trace amounts of kaolinite and unclassifieds. The unclassified phases are those which don't meet the chemical criteria of the technique. For our purposes, these were assumed to be amorphous. The analysis showed that while the virgin bed material had a high sodium composition, the sodium was bound chemically to Si and Al. Furthermore, there was some available sorbent in the form of dolomite in the bed material. The SEMPC analysis of the spent bed material showed that the bed material contained approximately the same amount of albite, but was significantly depleted in quartz. There was some anhydrite observed in the spent bed, along with traces of nepheline ($\text{NaAlSi}_3\text{O}_8$), akermanite ($\text{Ca}_2\text{MgSi}_2\text{O}_7$), and anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$). The spent bed also contained kaolinite, illite, and montmorillonite, as well as a high level of unclassified (amorphous) material.

The ash coating was shown by SEMPC analysis to be rich in unclassified material, kaolinite, and anhydrite. Nepheline, akermanite, anorthite, and iron oxide were detected. Of significance was the absence of albite, illite, quartz, and dolomite (i.e., the phases in the virgin bed) within the ash coating. Based on this analysis, it appears that the ash coating was formed from the coal ash with no contribution from the bed material.

With respect to the in-bed tube deposit, only sodium calcium sulfate and unclassified phases were observed. The bulk of the unclassifieds were, on further analysis, sulfate phases mixed with other components. The iron oxide was shown by microprobe analysis to be finely dispersed discrete grains too small for spatial resolution by the SEMPC technique. The major phases observed in the convective pass tube deposit were iron oxide, sodium calcium sulfate, and unclassifieds. Some calcium sulfate and gehlenite ($\text{Ca}_2\text{Al}_2\text{SiO}_7$) were observed. Once again the unclassified material was shown to be predominantly rich in calcium and sulfur.

The results of the analysis showed that the Beulah coal ash has a definite propensity for deposition. The formation of ash coating on the surfaces of the bed material is a precursor to agglomeration. It has been shown that the ash coating is derived from the coal ash, in particular, the calcium and sulfur. The deposits, including the ash coating, had chemical compositions very different than the spent bed material. This indicated further that the deposition mechanism was a selective process. In all cases the predominant enrichment was observed with respect to the Ca and S. Significant Fe enrichment was observed in the convective pass tube deposit. However, the Fe did not appear to be responsible for the deposit growth.

The evidence suggested that the cause of the deposit growth was due to the formation and presence of sodium calcium sulfate in the bed. This material was formed from the organically bound sodium and calcium in the Beulah coal reacting with sulfur. There was no free calcium observed in the deposits. The fine-grained sulfate mixture appeared to have an affinity for the cooled surfaces, including the bed particles. Furthermore, there appeared to be a distinct tendency of sulfate species to sinter. The matrix was too fine-grained to establish the presence of a melt phase. It should be noted that sulfate species crystallize readily on cooling. It is suggested that the mode of growth may be a molten sulfate phase. Certainly the presence of sodium

SEMPC ANALYSIS OF SAMPLES FROM THE 80-MW HESKETT STATION

	<u>Coal</u>	<u>Virgin Bed Material</u>	<u>Spent Bed Material</u>	<u>Ash Coating</u>	<u>In-Bed Tube Deposit</u>	<u>Tube Deposit Morphology</u>	<u>Convective Pass Deposit</u>
Silicates							
Nepheline	--	--	0.8	4.0	--	--	--
Aakermanite	--	--	0.4	2.0	--	--	--
Gehlenite	--	--	--	--	--	--	1.2
Pyroxene	--	--	--	--	--	--	0.8
Albite	--	32.6	39.9	--	--	--	--
Anorthite	--	--	0.4	2.0	--	--	--
Oxide or Carbonate							
Quartz	x	28.1	7.7	--	--	--	0.4
Iron Oxide	--	--	0.8	4.0	--	x	14.5
Ankerite	--	--	--	--	--	--	0.8
Dolomite	--	28.1	--	--	--	--	--
Sulfate and Sulfide							
Barite	x	--	--	--	--	--	1.2
Anhydrite	x	--	3.7	14.0	--	x	4.1
Sulfated Ankerite	--	--	--	--	--	--	1.2
Sodium Calcium Sulfate	--	--	--	--	35.4	x	12.8
Pyrrhotite	--	--	--	--	--	--	1.2
Pyrite	x	--	--	--	--	--	--
Unclassified or Amorphous							
Unclassified	x	1.1	38.7	64.0	64.6	x	71.5
Kaolinite	x	1.1	4.5	12.0	--	--	0.4
Kaolinite-Derived	--	--	--	--	--	--	0.4
Illite	--	9.0	2.5	--	--	--	0.4
Montmorillonite	--	--	0.8	--	--	--	0.8
Calcium-Derived	--	--	--	--	--	--	--
Amorphous	*						
SiO ₂	27.7	NA	NA	NA	9.3	10.2	28.8
Al ₂ O ₃	11.9	NA	NA	NA	7.2	10.5	16.9
Fe ₂ O ₃	8.3	NA	NA	NA	11.6	12.4	25.8
TiO ₂	0.7	NA	NA	NA	0.7	1.4	1
P ₂ O ₅	0.5	NA	NA	NA	0	0	0.1
CaO	17.1	NA	NA	NA	36.7	30.9	10.9
MgO	5.5	NA	NA	NA	14.9	14.6	4.6
Na ₂ O	6.3	NA	NA	NA	17.4	14.8	8.7
K ₂ O	0.6	NA	NA	NA	1.1	1.3	2.3
SO ₃	19.7	NA	NA	NA	0	0	0

* Sulk Ash Analysis for Coal

NA Data Not Available

-- Phase not detected

x Phase detected, but not quantified

with the calcium would be expected to lower the melting point. The presence of such phases as nepheline, anorthite, and gehlenite would suggest relatively high transient temperatures being reached within the bed. The silicate phases, while showing melting behavior, were not present in significant quantities to have a significant effect on the deposition phenomena.

The deposits formed are very similar to the dense fouling deposits observed with high alkaline earth and alkali fuels in large-scale conventional combustors. These deposits also tend to be predominantly calcium sulfate with the presence of fluxing components such as sodium or potassium. Here a significant amount of ash component partitioning within the combustor occurs to form an ash stream rich in calcium sulfate. These deposits grow relatively slowly, but are usually dense, hard-bonded, and in areas difficult to soot blow.

The analysis of the pilot-scale data and that from the 80-MW Heskett Station indicate that there is a tendency of certain coal ash to form deposits in a fluidized-bed combustor. The mechanism of adherence and growth, for the case with the Beulah coal, appears to be via a molten sulfate matrix, due to the fluxing action of sodium with the calcium sulfate matrix. The bed material plays no significant role in the deposition mechanism. This is in concurrence with the pilot-scale results and demonstrates the effect that ash chemistry can have on a fluid-bed system.

3.2 PFBC Consulting

A visit was made to Foster Wheeler Development Corporation to discuss ways in which the EERC DOE cooperative agreement program could meet the mutual goals of the two organizations. Foster Wheeler is currently working on a second generation PFBC which uses a pyrolysis step to produce a char burned in a circulating PFBC. The flue gas from the PFBC is combined with the low Btu gas from the pyrolysis step and burned in a topping cycle to raise the temperature of the gas going into the turbine. They propose a system efficiency of 45% and a reduction in the cost of electricity by 20%. The preliminary feasibility study was based on data generated at EERC on the entrained carbonizer. No tests have been done to date at the conditions proposed for the system.

Phase I of the Foster Wheeler program, which was all done on paper, has been completed. Phase II will involve testing each of the separate components to resolve problems and to develop the final design of a 5-MW demo plant. Phase III will involve the demo.

Some of the problem areas identified include hot-gas cleanup, performance of the carbonizer, alkali, and sorbent utilization. We discussed ways in which EERC could contribute technically to these areas. Since no data is available on operating the carbonizer at conditions proposed for the cycle, any data that EERC could generate on the mild gasification unit would be helpful. Some modifications will be required so that the system can operate up to 1700°F and 14 atmospheres. Pressure should be sacrificed if both conditions cannot be met. This will take some modification of the EERC mild gasification system. Testing should be done on one common coal to establish the scalability of the data between systems. After that, EERC could tack on additional run time to planned mild gasification runs. This would allow

testing in a cost-effective manner and would expand the data base on the number and types of coals tested at the carbonizer conditions.

Discussions were held concerning using a bench scale reactor to look at kinetics and reactions of alkali release and gettering, sorbent utilization, and N_2O formation. FWDC felt these were all valid and important topics for the development of a second generation PFBC. One point discussed was whether there would be a problem sulfating the CaS from the carbonizer once it was introduced into the PFBC. Data from KRW indicated that a coating formed on the limestone particles, preventing sulfation when introduced into an oxidizing atmosphere. If there is sintering or deadburning occurring, this may limit the utilization of available Ca from the limestone and may make disposal a problem. Therefore, it was agreed that more work needed to be done on sorbent testing.

Information on several subjects generated at EERC under the Cooperative Agreement was requested and sent to FWDC. This included in-bed heat transfer; corrosion, erosion, and deposition in FBC; combustion efficiency vs. operating conditions; results from the 1-lb/hr mild gasification unit; SEM capabilities; and high-temperature ceramic bags. EERC will continue dialogue with FWDC as the next year's EERC Cooperative Agreement program plan is developed.

3.3 System Simplification

The technology assessment of control systems has been completed. The results of this assessment are currently being compiled and will be included in the next quarterly report. An experimental approach for the development of expert control systems is also being developed. This plan will be discussed with METC personnel upon completion.

4.2 Beneficiation of Low-Rank Coals

BENEFICIATION OF LOW-RANK COALS

**Quarterly Technical Progress Report
for the period January - March 1990**

by

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1.0 GOALS AND OBJECTIVES

The overall objectives of the Low-Rank Coal Beneficiation project are to study methods of reducing the inorganic content and increasing the heating value of low-rank coal (LRC) to produce high quality dry coal products and/or coal/water fuels (CWF). The University of North Dakota Energy & Environmental Research Center (EERC) has demonstrated that high-energy content dry or slurry fuels can be produced from lignite and subbituminous coal using the hot-water drying process (HWD), and that low-ash, coal-based fuel can be produced using a combination of physical and chemical cleaning. The processes were integrated to achieve a greater than 400-lb/hr pilot-scale throughput for producing clean, energy-dense coal and/or CWF from low cost, highly reactive LRC feedstocks. These pilot-scale capabilities continue to supply fuels to DOE-sponsored combustion, gasification, and heat engine programs running concurrently with the Low-Rank Coal Beneficiation Program.

Current year LRC beneficiation project research will be conducted at the bench-scale level using the EERC's cold-charge autoclave and laboratory coal processing equipment. Analytical characterization of appropriate samples will be performed by UNDEERC's coal analysis and water analysis laboratories. Significant contributions in this year's work will be provided by the Fuels & Process Chemistry Group in support of the oil agglomeration process on lignites and subbituminous coals.

Current-year objectives for the EERC LRC Beneficiation project are to:

1. Evaluate oil agglomeration with acid leaching, as a combined process.
2. Investigate colloidal coal cleaning (CCC) based on previous efforts.
3. Explore pressurized hot-water drying (HWD) with direct air injection (partial oxidation) heating.

Initial emphasis has been placed on the oil agglomeration task. The CCC technique will be investigated later in the year at the conclusion of the oil agglomeration matrix testing and data reduction. The partial oxidation hot-water drying (PO-HWD) is being coordinated with similar testing for an outside client.

Near-term project objectives for the period January through March 1990 were to:

1. Evaluate the statistical results from the oil agglomeration matrix design to determine the optimal conditions for agglomeration of a North Dakota lignite.
2. Perform partial oxidation hot-water drying on a North Dakota lignite along with the same studies for another client.

2.0 INTRODUCTION

This report describes progress towards goals and objectives established previously (1), as well as those listed in section 1.0. Attention was devoted to evaluation of the statistical results from the central composite factorial design and PO-HWD of Beulah, ND, lignite.

3.0 BENEFICIATION OF LOW-RANK COALS

3.1 Oil Agglomeration Of Beulah Lignite

3.1.1 Statistical Results

The factors (independent variables) that were studied using the matrix design were feed coal particle size (X_1), acid mix time (X_2), acid mix speed (X_3), oil mix time (X_4), and oil mix speed (X_5). The responses (dependent variables) that were investigated were agglomerate ash content (Y_1), agglomerate yield (Y_2), recoverable oil--the oil retained in the agglomerates (Y_3), performance value--the general agglomerate quality (Y_4), ash efficiency index (Y_5), and ash reduction (Y_6). The numbers in parentheses are the identifier (variable name) for each respective independent or dependent parameter.

The data from the test matrix are given in Table 1. It should be noted that the X's were coded to be between -2 and +2 in order to facilitate the regression analysis that was performed. The actual values of the X's for each coded value (-2, -1, 0, +1, +2) are given in Table 2.

The matrix of runs performed was a central composite design for five independent variables, and it required 32 runs (2). The 33 runs actually performed included the matrix and one repeat run (Run 33). This matrix allowed the fitting of a full quadratic equation to describe the impact of the factors (X's) on each respective response. The quadratic equation for each response can be represented as:

$$\begin{aligned} F_i = & b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_4X_4 + b_5X_5 \\ & + b_6X_{12} + b_7X_{22} + b_8X_{32} + b_9X_{42} + b_{10}X_{52} \\ & + b_{11}X_1X_2 + b_{12}X_1X_3 + b_{13}X_1X_4 + b_{14}X_1X_5 + b_{15}X_2X_3 \\ & + b_{16}X_2X_4 + b_{17}X_2X_5 + b_{18}X_3X_4 + b_{19}X_3X_5 + b_{20}X_4X_5 \end{aligned}$$

TABLE 1. CODED INDEPENDENT VARIABLES AND RESPONSES

RUN	X ₁	X ₂	X ₃	X ₄	X ₅	Y ₁	Y ₂	Y ₂ *	Y ₃	Y ₄	Y ₅	Y ₆
12	-1	-1	-1	-1	1	1.21	82.65	82.65	57.94	2	5821.58	82.39
19	1	-1	-1	-1	-1	2.12	22.94	22.94	42.34	1	1030.61	79.50
17	-1	1	-1	-1	-1	1.37	96.67	96.67	47.64	2	5703.78	80.06
8	1	1	-1	-1	1	2.20	48.92	48.92	46.78	3	1987.80	78.72
22	-1	-1	1	-1	-1	1.12	100.00	99.80	44.10	2	7443.59	83.70
5	1	-1	1	-1	1	1.89	4.24	4.24	37.56	0	222.47	81.72
32	-1	1	1	-1	1	0.92	100.00	99.80	39.52	4	9448.53	86.61
30	1	1	1	-1	-1	2.27	3.41	3.41	27.34	0	148.92	78.05
27	-1	-1	-1	1	-1	1.40	92.57	92.57	39.04	3	5367.64	79.62
31	1	-1	-1	1	1	2.62	69.37	69.37	38.82	3	2181.70	74.66
25	-1	1	-1	1	1	1.76	90.89	90.89	47.52	3	3976.92	74.38
3	1	1	-1	1	-1	2.64	15.71	15.71	58.90	1	570.69	74.47
6	-1	-1	1	1	1	2.35	100.00	99.80	39.74	5	2795.59	65.79
10	1	-1	1	1	-1	2.53	7.53	7.53	59.98	0	292.76	75.53
7	-1	1	1	1	-1	1.24	92.25	92.25	36.58	4	6191.44	81.95
24	1	1	1	1	1	3.37	0.70	0.70	17.53	0	20.81	67.41
16	-2	0	0	0	0	0.97	100.00	99.80	31.54	2	8812.83	85.69
1	2	0	0	0	0	3.88	2.10	2.10	43.86	0	53.73	70.63
18	0	-2	0	0	0	1.85	98.14	98.14	44.62	4	4211.52	78.88
23	0	2	0	0	0	1.45	91.30	91.30	40.90	3	5349.93	83.45
21	0	0	-2	0	0	1.85	94.41	94.41	42.86	5	4093.60	78.88
26	0	0	2	0	0	1.77	97.05	97.05	40.98	4	4396.96	79.79
13	0	0	0	-2	0	1.57	97.70	97.70	42.16	3	5132.06	82.08
2	0	0	0	2	0	1.66	98.38	98.38	44.12	5	4831.55	81.05
29	0	0	0	0	-2	3.02	29.95	29.95	34.14	1	888.27	65.53
20	0	0	0	0	2	1.23	88.22	88.22	43.26	4	6290.58	85.96
33	0	0	0	0	2	1.59	94.28	94.28	44.50	4	5077.89	81.85
4	0	0	0	0	0	1.79	91.60	91.60	51.24	4	4153.15	79.57
9	0	0	0	0	0	2.23	98.53	98.53	49.44	4	3303.78	74.54
11	0	0	0	0	0	1.33	99.48	99.48	49.56	4	6340.38	84.82
14	0	0	0	0	0	1.71	98.62	98.62	45.34	3	4648.71	80.48
15	0	0	0	0	0	2.80	98.49	98.49	45.64	3	2404.96	68.04
28	0	0	0	0	0	2.33	78.17	78.17	39.88	3	2661.87	73.40

X₁ Feed Coal Particle Size
X₂ Acid Mix Time
X₃ Acid Mix Speed
X₄ Oil Mix Time
X₅ Oil Mix Speed
* Normalized values of Y₂

Y₁ Agglomerate Ash
Y₂ Yield
Y₃ Free Oil
Y₄ Performance Value
Y₅ Efficiency Index
Y₆ Ash Reduction

TABLE 2. CODING USED FOR INDEPENDENT VARIABLES

X_i = Coded Factor i	Values of Coded Factors					Units
	-2	-1	0	1	2	
i=1) Coal Mesh Size	-30x60	60x100	100x200	200x325	-325	mesh
i=2) Acid Mix Time	10	22.5	35	47.5	60	min
i=3) Acid Mix Speed	4	6	9	13.5	20.25	1000 rpm
i=4) Oil Mix Time	2	6.5	11	15.5	20	min
i=5) Oil Mix Speed	0.1	0.2	0.4	0.8	1.6	1000 rpm

In fitting this equation to the responses, any terms that were not statistically significant (at the 5% significance level) were deleted, so that, in all cases, a much smaller equation was finally obtained. The reduced equations are given in Table 3. Two summary statistics are also given in Table 3: a) the overall significance of the equation [which was always very high] and b) the amount of variation in the data explained by linear regression (called R^2). The R^2 varied from 0.26 for the percent ash reduction (Y_6), indicating a large amount of scatter around the equation, to a high of 0.87 for the yield (Y_2), indicating a good level of agreement between the data and the model.

TABLE 3. STATISTICAL REGRESSION SUMMARY

Response	Significant Terms	Overall Significance	R^2
Y_1 = Agglomerate Ash	$Y_1 = 1.94 + 0.59X_1 + 21X_4$	99.99%	0.60
Y_2 = Yield(*)	$Y_2^T = -3.1 + 2.8X_1 + 0.8X_1^2 - 0.5X_5 + 0.7X_5^2 + 1.4X_1X_3 + 0.7X_2X_4$	99.99%	0.87
Y_3 = Free Oil	$Y_3 = 42.9 - 1.9X_2 - 3.3X_3 + 3.0X_1X_4 - 4.1X_1X_5 - 5.2X_2X_3 - 4.5X_4X_5$	99.99%	0.67
Y_4 = Performance Value(#)	$Y_4 = 3.53 - 0.88X_1 - 0.8X_1^2 + 0.38X_4 + 0.60X_5 - 0.34X_5^2 - 0.80X_1X_3 - 0.44X_2X_4$	99.99%	0.84
Y_5 = Efficiency Index	$Y_5 = 3810 - 2410X_1$	99.99%	0.67
Y_6 = Ash Reduction	$Y_6 = 78.15 - 2.27X_1 - 2.46X_4$	98.64%	0.26

* $Y_2 = \frac{100\%}{1 + \exp(Y_2^T)}$

Equation shows lack of fit at 4% significance level

The regression equations generated in Table 3 were used to draw conclusions about optimum operating conditions. To facilitate this data interpretation, the equation models were graphed for the predicted values, along with the actual data, shown in Figures 1-5. All the responses are depicted, except for Y_4 , the performance value, which had lack of fit.

All responses were best at the lowest level of X_1 (-30 x 60 mesh). In addition, a low level of X_4 (oil mix time = 2 minutes) was best for Y_1 (agglomerate ash content) and Y_6 (ash reduction), while it did not adversely affect the other responses. With these two factors set, the best values for X_2 , X_3 , and X_5 are found via examination of responses Y_2 , Y_3 , and Y_4 . The high level for X_3 (acid mix speed) was best based mainly on its affect on improved yields (Y_2), but it also accounted for higher free recoverable oil (Y_3) and performance values (Y_4). Mid to high values of X_5 (oil mix speed) were found to be best for all responses with too high or too low an oil mix speed, causing lower agglomerate yields, etc. The only factor giving mixed results was X_2 (acid mix time), which gave the best yields and performance values at high mix times, but the most recoverable free oil at low mix times. The impact on the recoverable oil was the greatest; therefore, low acid mix times were judged the best condition according to the statistical results.

Figure 1. Ash content vs. oil mix time and particle-size fraction.

Figure 2. Agglomerate yield vs. agglomerate mix speed and particle-size fraction.

Figure 3. Free recoverable oil vs. acid mix time and acid mix speed.

Figure 4. Ash efficiency index vs. oil mix time and particle-size fraction.

Figure 5. Ash reduction vs. oil mix time and particle-size fraction.

3.2 Partial Oxidation Hot-Water Drying

3.2.1 Objectives

The purpose of the testing was to determine if partial oxidation during hot-water drying would a) enhance the cleanability of the coal, b) improve the rheology of CWFs made from LRC, and c) improve the economics of hot-water drying by direct particle heating.

3.2.2 Experimental Procedure

Partial oxidation hot-water drying was performed in the EERC 7.6-liter externally heated, stirred autoclave. The autoclave was equipped with a dip tube in order to sparge oxygen through the agitated slurry. A metal frit was fastened to the bottom of the dip tube to facilitate oxygen dispersion within the slurry.

A 3.8-liter autoclave, filled from a cylinder tank, was used as an accumulator for oxygen charging. The volume of the accumulator was accurately determined by measuring the mass of water needed to fill the accumulator. The pound-moles of oxygen in the accumulator, as a function of pressure and temperature, were determined from Van der Waal's equation (3).

Approximately 2000 to 4000 grams of a 50% Beulah/50% water slurry was used in each test. After charging the slurry, the autoclave was evacuated of residual air, and the heaters were turned on. Heat-up to 200°C took approximately 1.5 hours, whereupon the contents of the autoclave were allowed to stabilize at 200°C.

Prior to charging oxygen to the 7.6-liter reactor, the pressure and temperature in the accumulator were recorded. The oxygen was then metered from the accumulator into the 7.6-liter autoclave until the desired slurry temperature was achieved. The final oxygen pressure and temperature in the accumulator were then recorded.

After completing the test, the autoclave and contents were allowed to cool overnight. The product gas was metered and vented, and the product slurry was recovered and weighed. Product gas sampling was performed for two tests. The process water was separated from the solids by filtering. The filter cake was washed with deionized water to help remove any cations loosely adhered to the coal surface.

The filter cake from each test was diluted with deionized water to produce slurry for rheological testing. Apparent viscosity was determined for the slurry at three different solid contents. Presently, Certigrav washability testing is being performed on the raw and hot-water dried coals for inclusion in the next Quarterly report.

3.2.3 Results

Combustion of the slurry was instantaneous upon addition of the oxygen, and temperature rise was rapid. Temperature control, however, in the batch autoclave system was limited by an unsuitable oxygen charge system. The

maximum charge pressure for the accumulator was 2000 psig, as set by the pressure transducer. As a consequence, the tests usually required multiple charges of oxygen to approach the desired temperature. The temperature of the slurry in the 7.6-liter autoclave usually decreased before the accumulator could be recharged with oxygen. The temperature drop was rapid because the autoclave was absorbing heat from the slurry. Additionally, as the steam pressure in the 7.6-liter autoclave increased and as combustion gases were produced, subsequent charges delivered less oxygen, producing a progressively lower temperature increase. This shortcoming was somewhat alleviated by decreasing the mass of slurry in the last PO-HWD test.

The conditions for the three PO-HWD tests and one HWD test are presented in Table 4. The oxygen requirements, in pound-moles of oxygen charged per gram of slurry per Celsius degree temperature rise, are presented in Table 5. The oxygen utilization, as a percentage of the original oxygen charge, has not been determined because product gas analysis has not yet been performed. Selection of which test to perform gas analysis on is pending results of the Certigrav washability testing. The solids recovery per test is also presented in Table 5.

TABLE 4. CONDITIONS FOR HWD AND PO-HWD TESTS

Test #	Test Type	Temperature (°C)	Slurry Charge (grams)	Oxygen (lb-moles)
1	HWD	303	3984	NA
2	PO-HWD	239	3988	0.0195
3	PO-HWD	282	3989	0.0190
4	PO-HWD	303	1991	0.0227

HWD Hot-Water Dried
PO Partial Oxidation
NA Not Applicable

TABLE 5. OXYGEN REQUIREMENTS AND SOLIDS RECOVERY

Test #	Temperature Rise (dC°)	Oxygen (lb-mole/g-dC°)	Solids Recovery (wt%)
1	NA	NA	90.8
2	36	1.36×10^{-7}	93.4
3	75	6.35×10^{-8}	91.6
4	96	1.19×10^{-7}	80.5

NA Not Applicable

Preliminary calculations indicated that the lb-moles of O_2 necessary to raise one gram of slurry one degree Celsius via partial oxidation varies by only about 2% over the range of 300°C to 320°C. Similarly, over the range of 282°C to 303°C, the oxygen requirements should be nearly equal. However, the measured oxygen requirements varied by nearly 100% over the range of 282°C to 303°C. The large discrepancy may indicate overcharging of oxygen in order to achieve temperature.

The solids recovery for the HWD test at 303°C was approximately 91 wt%, while the solids recovery for the PO-HWD test at 303°C is approximately 81 wt%. The loss of solids in the HWD test is attributed to decarboxylation and mild pyrolysis reactions. The additional loss of solids in the PO-HWD test is presumably due to combustion reactions.

The large difference in solids recovery between the 282°C and 303°C PO-HWD tests also seems to substantiate the overcharging of oxygen in order to achieve 303°C.

The apparent viscosity at 100 sec^{-1} versus solids content is presented in Figure 6 for slurries produced from the raw, HWD and PO-HWD Beulah coal. The slurry with the highest solids content was achieved with the 303°C HWD coal. Partial oxidation hot-water drying at 303°C, however, did not produce a slurry with comparable solids content and viscosity. The variation may be due to insufficient residence time at temperature and consumption of combustible material during PO-HWD. The PO-HWD did, however, improve slurry solids content above that of a raw Beulah slurry.

Figure 6. Apparent viscosity vs. solids content for raw, HWD and PO-HWD Beulah lignite.

3.2.4 Washability Testing

The Certigrav washability testing is currently being performed. Theoretically, the partial oxidation during hot-water drying will liberate ash material from the coal structure and, consequently, enhance ash removal via gravity separation. Results of the washability testing will determine if gas proximate, ultimate, and heating value analyses should be performed.

3.2.5 Economic Benefits

Presently the economic benefits of PO-HWD over HWD have not been determined. Most certainly an electrical cost savings will be realized by supplying a portion of the thermal requirements by direct (internal) heating. However, additional product gas and PO-HWD coal analysis (proximate, ultimate, and heating value) will have to be performed to determine the cost differential. The results of the cost savings calculations will be presented in the next quarterly.

4.0 CONCLUSIONS

1. The results indicate that finer particle sizes were not as successful in agglomeration or ash reduction as larger particle sizes were, which is probably due to the fact that the sizes were sieve fractions of the parent coal, instead of the parent coal being pulverized to smaller sizes.
2. Ash efficiency indexes of greater than 6,000 were attained for a few of the agglomerates and represent excellent agglomeration performance.
3. Autoclave testing has proven that heat for hot-water drying of Beulah coal slurry can be supplied internally by partial oxidation (combustion) of the coal.
4. Combustion of a 50/50 Beulah coal/water slurry is instantaneous at temperatures as low as 200°C.
5. The batch processing method is not reliable for temperature control and oxygen charging for partial oxidation testing.

5.0 RECOMMENDATIONS

1. Additional testing of acid strength needs to be performed on the oil agglomeration process in order to optimize the acid cleaning conditions.
2. Oil/coal ratios have to be investigated further for Beulah lignite because some agglomerate products were large clumps, instead of several smaller agglomerates.

3. Further statistical matrix testing of acid strength and oil strength will provide scale-up information for the developing oil agglomeration process data bank.
4. Future partial oxidation work, to accurately determine oxygen utilization and temperature control, should be performed in a continuous unit such as the EERC 10-lb/hr CPU or 600-lb/hr PDU.

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4.3 Combustion Characterization of Low-Rank Coal Fuels

COMBUSTION CHARACTERIZATION OF LOW-RANK COAL FUELS

**Quarterly Technical Progress Report
for the Period January-March 1990**

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COMBUSTION CHARACTERIZATION OF LOW-RANK COAL FUELS

1.0 INTRODUCTION

Coal research by the Pittsburgh Energy Technology Center (PETC) of the U.S. Department of Energy (DOE) is directed toward both increasing coal usage in existing markets and introducing new, premium quality coal-based fuels to markets currently dependent on oil or natural gas. Accordingly, the work concentrates on coal cleaning, fuel formulation and handling, combustion, and flue gas cleanups, 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.

The industrial and utility sectors are major consumers of oil and gas. Many of these oil and gas systems could be converted to coal-fired systems, resulting in a significant reduction in the oil and gas needs of this country. As an example, oil- and gas-generating systems in the utility sector have a nameplate generating capacity of 156 gigawatts (GW). Of this, 91.6 GW have the potential for conversion to coal, based on remaining years of service. This represents 4.8 quads of energy per year. There are similar opportunities to reduce U.S. dependency on oil and gas in the industrial sector.

A number of critical factors need to be examined to determine the success of switching from oil or gas to coal. Significant differences exist in burner designs, furnace plan areas, heat release rates, tube spacing in convective passes, number and location of soot and wall blowers, and others. Combustion characterization of replacement fuels is needed to assess the impact of the new fuel's properties on the existing design. This characterization should help assess any equipment modifications or derating necessary as a result of switching fuels.

2.0 GOALS AND OBJECTIVES

The purpose of this project is to expand the scientific and engineering data base on the combustion characterization of advanced low-rank coal fuel types for combustion systems in the industrial and utility markets currently using oil or gas as the primary fuel. To accomplish this overall objective, specific objectives are to use existing and new laboratory-, bench-, and pilot-scale techniques to characterize various dry and slurried coals and coal blends. Results of these enhanced characterization tests will be used to assess the effect of switching fuels on the ignitability and stability of the flame, fouling and slagging, emissions, and carbon burnout as compared to the design fuel.

Work during the three-year period April 1986 through June 1989 focused on the development of a small-scale combustion device suitable for the residential and commercial marketplace, followed by characterization of coals and coal/water slurries as replacement fuels for oil and gas. The direction of the project has shifted, with the new emphasis on the industrial and

utility marketplace. Low-rank coals and slurries, alone or in blends, with the potential to replace oil and gas will be characterized in the next three years (7/89 - 6/92).

The University of North Dakota Energy and Environmental Research Center (UNDEERC) has been involved in the characterization of coal for over 20 years. This work was initially developed to study fouling in the convective pass and has been expanded to also study boiler slagging and particulate emissions. A number of analytical techniques and bench- and pilot-scale tests have been developed. These techniques will be used as a part of the proposed work. EERC does not currently have the capabilities to study flame stability and ignitability; therefore, part of the three-year objectives will be to add this capability. The capability for flame stability testing will be combined with existing techniques for studying slagging, fouling, and emissions and new techniques being developed under other parallel DOE and EPRI programs to produce an "enhanced" combustion characterization program. This program will be used to characterize low-rank coals and slurries, alone or in blends, to determine their potential as replacements for oil and gas.

UNDEERC is also a subcontractor to Combustion Engineering, Inc. for work under DOE Contract No. DE-AC22-89PC88654, which was awarded in March 1989. This contract is for the combustion characterization of beneficiated coal-based fuels; the primary focus will be on fuels derived from eastern bituminous coals. In the subject three-year Cooperative Agreement, the intention is to expand the data base on selected, advanced, low-rank coal fuels in a manner generally parallel to the contract noted above. To achieve this objective, UNDEERC will develop a cooperative program with the Coal Combustion R&D Division at PETC. UNDEERC will perform laboratory analyses and bench-scale tests (similar to the work for CE) as far as practical and appropriate for the selected fuels. Atomization and combustion testing of these fuels will be performed at PETC.

It is not anticipated that the cooperative UNDEERC/PETC program will duplicate all aspects of the CE contract. The intention is to characterize the combustion properties of advanced LRC fuels (in both dry and slurry forms) by means broadly similar to those employed by CE and its subcontractors, within the constraints of the funding level of the Cooperative Agreement and the work priorities of the PETC staff and facilities.

Specific three-year objectives include:

1. Combustor Modifications and Development.

Several modifications will be made to the EERC 550,000-Btu/hr test combustor to enhance its capabilities for characterizing fuels. These modifications include adding a data acquisition and control system, pressure transducers, thermocouples, control valves, and flow transmitters (this equipment is available from the residential-scale packed-bed combustion system). An adjustable swirl burner similar to that used by PETC will be purchased and installed. Modifications to the coal feed system are needed to allow accurate metering of the fuel and to eliminate problems with uneven feeding. Coal-sizing equipment will be upgraded to allow more control over the size of the feed of the coal. An existing tubular

ESP will be installed. Additional viewports will be added to the combustor.

2. Characterization of Combustion Performance.

The performance of various fuels, including coal blends, coal (both dry and slurried), and oil (for comparative purposes) will be characterized. These characterization tests will be designed to determine combustion performance, mineral matter behavior, and emissions.

Aspects of combustion performance to be measured will include flame stability, ignitability, and carbon burnout. Mineral matter observations will include slagging on furnace walls, deposition on convective pass tubes, fly ash formulation, and mineral matter transformations. Gaseous emissions, including NO_x, SO₂, CO, and particulates, will be measured. Fly ash particle size and resistivity will help evaluate ESP performance.

3. Comparison to Commercial-Scale Demonstrations.

Results from the enhanced characterization tests performed under this project will be compared to results (where available) of existing DOE and EPRI large-scale demonstration projects.

3.0 PROPOSED WORK FOR THE FIRST YEAR (7/89 - 6/90)

To achieve the specific goals for the third year, a five-task program has been developed. The tasks include modifications to the 550,000-Btu/hr test furnace, system shakedown, and baseline testing of a western subbituminous coal and three characterization studies of various coals and coal blends.

3.1 Task A. Combustor Modifications

Several modifications will be made to the EERC 550,000-Btu/hr test combustor to enhance its capabilities for characterizing fuels. These modifications include adding a data acquisition and control system, pressure transducers, thermocouples, control valves, and flow transmitters (this equipment is available from the residential-scale packed-bed combustion system). An adjustable swirl burner similar to that used by PETC will be purchased and installed. Modifications to the coal feed system are needed to allow accurate metering of the fuel and to eliminate problems with uneven feeding. Coal-sizing equipment will be upgraded to allow more control over the size of the feed of the coal. An existing tubular ESP will be installed using non-DOE funds.

3.2 Task B. Shakedown and Baseline Testing

Procedures for measuring flame stability and ignitability will be refined. Equipment that has been modified will be tested to ensure it operates properly. The data acquisition and control system and new instrumentation will be tested.

A baseline test will be performed. The baseline coal will be a western subbituminous coal. Baseline testing will include flame stability testing and an extended ash fouling and slagging test. Funding for this task will be split 60%/40% Cooperative and non-Cooperative Agreement funding.

3.3 Task C. Characterization of a Lignite and Petroleum Coke Blend

This task is not part of the Cooperative Agreement, but will be performed in conjunction with this cooperative program.

A blend of a northern Great Plains lignite will be blended with petroleum coke in blends ranging from 60:40 lignite:petroleum coke to 100% lignite. The purpose of this blending is mainly to improve the energy density of the lignite so that it can be competitively marketed and used in the industrial sector. Results will be applicable to utility customers. It is expected that the blending will also improve the fouling characteristics of the lignite. The characterization will include a detailed analytical screening, carbon loss and deposition studies on the drop-tube furnace, and an extended fouling and slagging test on the ash fouling furnace, including flame stability. All work will be performed at EERC.

3.4 Task D. Characterization of a Subbituminous and Petroleum Coke Blend

This task is not part of the Cooperative Agreement, but will be performed in conjunction with this cooperative program.

A blend of a western subbituminous coal with high fouling tendencies will be blended with petroleum coke to a maximum blend ratio of 60:40 subbituminous:petroleum coke. The purpose of the blending in this case is primarily to reduce fouling and also to increase the energy density, while disposing of by-product from an associated industry. The target of this blending exercise is the utility industry; however, results will be applicable to users in the industrial sector. The test protocol will be the same as outlined in Task 4. All work will be performed at EERC.

3.5 Task E. Characterization of a Low-Sulfur Subbituminous Coal and a High-Sulfur Bituminous Coal Blend

This task assumes a carryover of \$35,000 from the 1988-1989 Cooperative Agreement year.

A low-sulfur western subbituminous coal will be blended with a high-sulfur bituminous coal for this task. The target market would be utility customers in the Midwest. The main purpose of the blending is for sulfur control from the viewpoint of the bituminous coal. From the perspective of the subbituminous coal, the blending will increase the energy density and may improve the fouling tendencies.

EERC will perform a detailed analytical screening of the parent coals and various blends. The blend ratio will vary from 100:0 to 0:100 subbituminous:bituminous. Following the analytical characterization, drop-tube work to characterize carbon burnout and depositional characteristics will be performed by EERC. Combustion tests of this blend will be performed by the

Coal Combustion R&D Division of PETC. EERC and PETC personnel will work together to combine the results into a detailed package characterizing the blending of the two test coals.

4.0 PROJECT STATUS

Activities during the third quarter were scheduled to complete construction of new equipment (coal feed hoppers, sampling cyclones, and baseline heat flux probe), modifications to existing equipment, installation of purchased equipment (adjustable secondary air swirl burner, coal feeder, and coal-sizing equipment), installation of existing tubular ESP, and subsequent piping changes on the ash fouling furnace (AFU) at EERC. These changes were essential to completing the work load described in the annual project plan. Equipment shakedown was scheduled to be completed by March 1990; however, shakedown testing has been rescheduled to begin during the second or third week in May. Acquisition of equipment and supplies, questions regarding the compatibility of the swirl burner, and manpower availability were the factors that contributed most to the delays encountered.

4.1 Task A. Combustor Modifications

Modifications to the AFU and auxiliary systems were broad in scope and covered all aspects of the combustion system from the mill to the particulate control device. Many of the activities occurred simultaneously; however, most were dependent upon completion of one or more areas. This interdependence delayed the completion of combustor modifications, prompting the rescheduling of shakedown testing. System modifications completed during the third quarter included: the rearrangement of heat exchangers to accommodate the tubular ESP and sampling cyclones that were installed; the installation of the mechanical-aerodynamic coal sizer, the coal feeder, meters and control valves for the furnace wall slag probes and the data acquisition system; construction of the baseline heat-flux probe; and modifications to the probe bank and associated cooling air system. A schematic of the combustion test system prior to modification can be seen in Figure 1, and a schematic of the system showing some of the changes can be seen in Figure 2.

4.1.1 Coal Feed Characterization and Control

Changes in the particle size of the pulverized coal entering the combustion system can skew combustion results by decreasing the stability of the flame under a given set of conditions, lowering the rate of carbon burnout. This type of change cannot be tolerated for a series of tests on the same fuel. For the low-rank coal fuels test program, control of feed size will be accomplished using the mechanical-aerodynamic separator shown in Figure 3. The separator will allow a consistent particle size of approximately 75% less than 200 mesh for each combustion test. The separator was installed on a 400-lb/hr pulverizer in EERC's coal preparation facility and will be calibrated prior to shakedown testing.

Also purchased was a microprocessor-controlled weight-loss coal feeder. The new feeder, which can be seen in Figure 4, will allow on-line monitoring of the feed rate and will be used to maintain combustion conditions such as

Figure 2. Schematic of EERC's combustion test system showing some of the completed modifications.

Figure 1. Schematic of EERC's combustion test system prior to modifications.

Figure 3. Schematic of 30" double whizzer mechanical separator.

Figure 4. Schematic of microprocessor-controlled coal feeder.

air/fuel ratio and furnace exit gas temperature. Because of the sensitivity of the weight mechanism, the feeder has a small hopper (two cubic foot volume) and requires an additional hopper for coal storage. The microprocessor controls a pneumatic valve that will be opened to fill the feed hopper when the fuel level is below a given set point. The additional hopper will be constructed prior to shakedown next quarter.

4.1.2 Combustion Characterization

To aid in the characterization of the flame and the combustion environment, an adjustable secondary air swirl burner was installed, a high velocity thermocouple was constructed, and a baseline heat flux probe was also constructed. During flame stability testing, the swirl burner (shown in Figure 5) will be adjusted to determine the level of swirl required to achieve the proper backmixing of secondary air. Flame characterization will be performed during the first 3 to 5 hours of each combustion test. Visual observation of the flame will evaluate flame standoff as a function of swirl setting. Combustor sight ports were modified to give a better view of the burner cone and flame, and photographs (standard 35 mm and 35 mm infrared) will be used to record the results at each condition. In addition, a high-velocity thermocouple (HVT) and a baseline heat flux probe will be used to evaluate the furnace temperature profile and heat flux to the furnace wall, respectively.

Figure 5. IFRF adjustable swirl burner.

A high-temperature extraction probe, designed by Northwest Research, Inc. in conjunction with EERC, is under construction and may be available for use during this test program. The extraction probe uses nitrogen to quench ash intermediates as they are collected and will be used to characterize carbon burnout as a function of residence time and swirl setting.

4.1.3 Fly Ash Characterization

Changes made to the combustion furnace's particulate collection and control systems were accomplished to increase fly ash characterization capabilities. The newly installed tubular ESP, which can be operated under cold-side (350°F) or hot-side (750°F) conditions, adds a degree of flexibility previously unavailable for particulate control testing. The rearrangement of heat exchange equipment allows the flue gas to bypass a pair of heat exchangers to achieve the higher gas temperature. The ESP has electric heaters to maintain gas temperature and will be operated at a flue gas velocity of 50 ft/sec. Excess flue gas (if any) will be bypassed through one of the cyclones. This arrangement should also give EERC the capability of testing ESP collection efficiency as a function of rapping frequency and/or flue gas conditioning at a constant SCA (standard collection area). The ESP is instrumented to monitor current through the collected ash layer to aid in determining the optimum rapping frequency.

Two cyclones were also added to the particulate control section of the furnace: a bypass cyclone and a sampling cyclone. The bypass cyclone will be used during heatup to prevent moisture from accumulating in the sampling cyclone or the ESP. The sampling cyclone will be used to collect a high-volume sample for resistivity testing and other analyses (SEMPC, XRF, XRD, ESCA, etc.). During sample collection, the sampling cyclone will be operated at a pressure drop of 4 inches of water column to achieve a cut size of 2.5 microns. Each cyclone will also be calibrated to measure flue gas flow rate as a function of pressure drop.

4.2 Task B. Shakedown and Baseline Testing

Shakedown testing of the ash fouling combustion system will begin immediately following the completion of all construction and modification activities. The initial shakedown schedule consists of four combustion tests to evaluate the effectiveness of the coal feeder, swirl burner, data acquisition system, sampling cyclone, and tubular ESP. Each test will include one standard 5.25-hour ash fouling test. Ash deposit samples will be collected for strength tests using EERC's drop impactor. A readily available coal will be used for the comparison of results between tests.

The first test will evaluate the operation of the coal feeder and the data acquisition and control system. The furnace slag probes will be maintained between 500° and 800°F by computer-controlled valves, and heat flux through the probes will be computed using the inlet and outlet water temperatures in conjunction with electronic flow meters. The temperature of the flue gas entering the ESP will also be monitored to establish the need for additional heat exchange equipment to achieve desired operational parameters. The combustion system will also be checked for any piping leaks during the first test. The newly constructed HVT will also be tested. The natural gas heatup will be monitored to determine natural gas and air flows in

an attempt to characterize combustor preheating during a standard 8-hour preheat cycle. The standard burner gun will be used to fire the pulverized coal at a rate sufficient to achieve a furnace exit gas temperature (FEGT) of 2,200°F. Combustion air will be maintained at about 21.5% excess air, and a deposit will be collected on the air-cooled convective pass deposition probes for strength evaluation.

Objectives for the second shakedown test are to evaluate the effectiveness of the sampling cyclone in obtaining a high-volume sample for fly ash characterization and to establish a baseline combustion test as a reference for future testing. The cyclone will be calibrated for air flow as a function of pressure drop and will be operated at 4 inches of water column during sampling. Three EPA method 5 (dust loading) tests will be run at the cyclone inlet and outlet to determine collection efficiency.

Based on results from the initial shakedown test, the combustor preheat cycle will be altered to achieve an appropriate air/fuel ratio (approximately 10%-15% excess air). Using this information, the firing rate may be increased to shorten the combustor preheat cycle. Prior to testing, a 2-inch refractory liner will be installed to reduce heat transfer through the combustor walls in preparation for future testing on the unit. The FEGT will be maintained at 2,000°F with 21.5% excess air. A standard 5.25-hour combustion test will be run to collect a deposit for strength evaluation, and results will be compared to those obtained in the first shakedown test to determine the effect of FEGT on deposit strength. Photographs of the combustion test furnace and the auxiliary systems will be taken to highlight modifications. Photographs of the flame will also be taken in preparation for the third shakedown test in which flame stability will be monitored as a function of swirl number.

The third shakedown test will use the adjustable swirl burner during the natural gas preheat cycle and combustion testing. The heating rate of the combustor will be compared to that obtained with the standard burner used in the second shakedown test. After the switch to coal, flame stability will be monitored as a function of swirl during the first 3 to 5 hours. Flame standoff will be monitored by visual observation and photography of the flame under varying swirl conditions, while combustion conditions will be monitored by the HVT, the slag probes, and the flue gas analyzers. Upon completion of flame stability testing, a standard 5.25-hour combustion test will be run at a FEGT of 2,000°F and an excess air level of 21.5%. A deposit will be collected on the air-cooled convective pass probes to determine the effect of using the swirl burner on deposition rate. Because the swirl burner uses only primary and secondary air, the potential exists for more ash to be carried out of the furnace proper into the probe bank duct, increasing the rate of deposition on the air-cooled probes. A multicyclone sample will also be obtained at the sampling cyclone inlet and compared to the sample obtained in the cyclone. Results will determine the effectiveness of the cyclone in obtaining a representative fly ash sample for characterization studies.

A fourth shakedown test will be run to determine the effectiveness of the tubular ESP for the collection of gas-borne particulate. Dust loading samples will be taken at the inlet and outlet of the ESP, and a standard procedure will be set for testing on the unit. ESP testing may require more than one shakedown to establish the optimum operational voltage and rapping frequency. The FEGT will be maintained at 2,000°F, and the excess air level

will be maintained near 21.5%. Again, deposit samples will be obtained for strength evaluation, and the baseline heat flux probe will be used to monitor combustion conditions.

Baseline testing of a Great Plains lignite will begin when system shakedown is complete.

4.3 Task C. Characterization of a Lignite and Petroleum Coke Blend

A commitment has been made by Manalta Coal, Ltd. to participate in a blending study using a Great Plains lignite and a petroleum coke blend. The actual work on the project was expected to start in June 1990. This scope of work for the program includes detailed analytical characterizations of the coal and coke, drop-tube furnace tests of a range of blends and operating conditions, and a 32-hour combustion test on the optimal blend to determine combustion characteristics.

4.4 Task D. Characterization of a Subbituminous and Petroleum Coke Blend

Final fuel selections for the upcoming year for Detroit Edison did not include petroleum coke. Therefore, Detroit Edison decided not to fund this task.

4.5 Task E. Characterization of a Low-Sulfur Subbituminous Coal and a High-Sulfur Bituminous Coal

Due to funding limitations, no work has been performed on this task.

5.0 SUMMARY AND CONCLUSIONS

Modifications to the ash fouling combustor at EERC were nearly completed during the third quarter. Equipment shakedown was scheduled to be completed by March 1990; however, shakedown testing has been rescheduled to begin during the second or third week in May. Acquisition of equipment and supplies, questions regarding the compatibility of the swirl burner, and manpower availability were the factors that contributed most to the delays encountered. A schedule for shakedown testing has been completed and will include at least four combustion tests. Each test will contain a standard 5.25-hour combustion test using air-cooled probes to collect a convective pass deposit sample for strength evaluation. The operating conditions during combustor preheat will be varied to determine the optimum level of preheating required prior to the switch to coal. Furnace exit gas temperature (FEGT) will be varied between 2,000° and 2,200°F to compare the strength of deposits formed as a function of temperature. The first test will consist of system monitoring functions and will evaluate the operability of the newly installed equipment. The second test will evaluate the effectiveness of the sampling cyclone in obtaining a representative high-volume sample. The third test will evaluate the use of an adjustable swirl burner for flame stability testing, while the effect of using the swirl burner on the deposition rate observed for the same coal on the convective pass fouling probes will be monitored. Operation of the tubular ESP for fly ash collection testing will be evaluated in the final shakedown test(s).

Baseline testing will begin when shakedown is completed.

6.0 NEXT QUARTER ACTIVITIES

Combustor modifications and shakedown testing are scheduled to be completed next quarter.

4.4 Diesel Utilization of Low-Rank Coals

DIESEL UTILIZATION OF LOW-RANK COALS

**Quarterly Technical Progress Report
for the Period January - March 1990**

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DIESEL UTILIZATION OF LOW-RANK COALS

1.0 INTRODUCTION

Lignite chars have a higher reactivity than higher-rank coals, indicated by particle burning rates four to five times higher than those 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 may be used in higher-rpm diesel applications, if ash concentrations are reduced to limit engine wear and particulate emissions.

The utilization of coal slurry fuels in medium-speed diesel engines offers the opportunity to replace premium petroleum-derived distillate fuels with more economical and abundant coal. Recent advances in coal technologies, such as the ability to prepare satisfactory coal/water slurry fuels and the efforts to reduce the mineral content of the parent coals in coal beneficiation processes, suggest that coal-derived fuels with low mineral contents soon may be technically feasible and utilized 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 over 35 wt%. However, with the advent of UNDEERC's hydrothermal drying 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. With the availability of a slurry with an adequate heating value, it is now possible to take advantage of a main characteristic of low-rank coals, namely the higher reactivity of their nonvolatile carbonaceous components. 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.

New coal utilization technologies designed to produce gaseous and carbonaceous products are currently under development. However, these processes also produce small quantities of minimally processed tars and coal-derived liquids which must be utilized in some manner. These "mild gasification" liquids just might provide a reasonable replacement for petroleum-derived diesel fuel.

2.0 GOALS AND OBJECTIVES

The overall objective of this program is to develop a scientific and engineering data base on the use of low-rank coals (LRC) in diesel engine applications. Research will be directed toward understanding characteristics of LRC fuels produced from advanced beneficiation processes which affect their use in diesel engine applications. Combustion studies will be performed to provide functional relationships between fuel properties and subsequent products of

combustion, including release and deposition of alkali metals and other ash constituents. The formation of nitrogen and sulfur oxides and other potentially detrimental species will be investigated, and methods to reduce their emission levels will be studied. The impact of LRC fuels on diesel engine components will also be studied, especially fuel injection systems and engine internals. Special emphasis will be placed on characterizing the LRC fuel atomization and its effect on combustion behavior.

2.1 Three-Year Project Objectives

Task A. Revise Technology and Market Assessment.

This task will update the diesel engine technology and market assessment made three years ago at the start of this program. With the expanded interest and significant research funding currently in the coal-fueled diesel area, several reports about this research have recently been published.

Task B. Diesel Injector Atomization Study.

This task evaluates the effects of various slurry properties on the atomization quality of the fuels. Slurry properties will include fuel type, particle-size distribution, solids loading, additive package, and high-shear rheology, while atomization quality will be measured using still photography and a Malvern 2600 particle-size analyzer at atmospheric pressure. In addition, the effect of different injection pressures and types of injectors will be investigated for their effect on atomization.

Task C. Evaluation of Atomizer Combustion Behavior.

This task involves combustion testing of the slurry fuels evaluated in Task B to determine the effects of atomization quality on various combustion characteristics such as ignition delay, burn time, and heat release rates as determined by pressure traces and light emissions. Statistical analysis of this data will highlight the relative importance of atomization on combustion.

Task D. Evaluation of Injector Life and Performance in a Diesel Engine.

This task will evaluate the combustion efficiencies and emissions of these fuels in a 4-cycle diesel engine. This task will also measure the amount of deposition, erosion, and corrosion experienced by the cylinder liner, piston rings, and injectors. Particular attention will be given to the effect that injection pressure has on the erosion problems experienced in fuel injectors. Ash characterization will be performed on several western coals to determine the main parameters relating to wear rates, including ash composition, size distribution, shape factor, etc. The product of combustion (POC) particulate in the exhaust stream and the lube oil (from blowby of the rings) will be also be compared. This characterization will also compare these

properties to an eastern bituminous coal currently being used in one of the proof-of-concept coal-fueled diesel engines. Remedial steps to improve injector life will be evaluated and, where possible, tested in the diesel engine to determine their effectiveness.

Task E. Diesel Engine Facilities Upgrade.

This task will upgrade the current diesel engine facility with the addition of a one- or two-cylinder, large bore, higher rpm, four-stroke diesel engine to perform combustion testing with the more reactive low-rank coal fuels. The decision of which engine to acquire will be based on the desire to operate the engine at speeds as high or higher than the other DOE diesel programs to investigate whether the reactivity of the LRC fuels allow higher engine rpms at comparable combustion efficiencies. A large bore is also desired to reduce the spray impingement on the cooler metal surfaces, and the four-stroke engine design will make the test data more comparable to other DOE coal-fueled diesel engine programs. The cost of the engine will also be a factor in its selection.

2.2 Proposed First Year Research

Task A - Revise Technology and Market Assessment.

This task will update the previous literature assessment made at the beginning of the program.

Task B - Diesel Injector Atomization Study.

This task will compare LRC and bituminous fuel injector sprays using a Malvern 2600 droplet-size analyzer and still photography at atmospheric pressure and in a pressurized spray chamber. This investigation will examine the effects of different fuel and injector types and the effects of different slurry properties on atomization quality. These properties will include high-shear rheology as determined by an extrusion viscometer, particle-size distributions, solids loading of the fuel, and additive package.

Task C - Evaluation of Atomizer Combustion Behavior.

This task will evaluate ignition delay, duration, intensity, and heat release rates in the diesel simulator and correlate them to the atomization characteristics determined in Task B.

Task D - Evaluation of Injector Life and Performance in 70-hp Diesel Engine.

This task will evaluate the effects of the fuels and the atomization properties measured in task B on their combustion efficiencies. In addition, longer term continuous erosion tests will be run to evaluate injector life and potential methods or materials to improve injector life.

Task E - Diesel Engine Facility Upgrade.

This task will upgrade the current diesel engine facility with the addition of a one- or two-cylinder, large bore, higher rpm diesel engine to perform testing with the more reactive low-rank coal fuels. This engine will more closely represent the mainstream of current contract research, thus making data obtained with the LRC fuels more useful for potential engine manufacturers.

3.0 RESULTS AND ACCOMPLISHMENTS

3.1 Diesel Engine Upgrade

A Caterpillar 1Y540 single cylinder research engine was purchased from the research department of Caterpillar, Inc. This engine is a 1-G2 lubricant test engine. Table 1 lists the operating characteristics of the selected engine.

TABLE 1
OPERATING CHARACTERISTICS OF CATERPILLAR 1Y540 DIESEL ENGINE FOR
COAL/WATER FUEL TESTING

Bore (inches)	5.4
Stroke (inches)	6.5
No. Cylinders	one
RPM (min/max)	600/2100
Power (hp)	72 @2100
Compression Ratio	14.5:1
Engine Orientation	vertical
Nozzle Location	central
Valves	four

As seen from Table 1, this engine has the capabilities to operate at considerably higher speeds than the 1050 rpm currently being used in the General Electric coal-fueled locomotive program. This higher rpm range will allow the higher reactivity of the LRC fuels to be investigated by operating the engine at higher rpms, until a significant degradation in carbon burnout is measured.

Construction activity for the quarter included the arrival of the diesel engine by the end of January 1990 and its installation on a concrete slab designed to dampen excessive vibration from the engine. This slab was designed to weigh approximately 8000 pounds and was built from 12" H beams located down the middle of the slab with 12" channel iron used to form the outside edge of the slab. Lord lattice mounts were used to isolate the slab from the ground. Figure 1 is a photograph of the diesel engine and the structural steel/concrete slab on which the engine was mounted. This photograph also shows the air surge tank and the high-pressure steam air preheater. A 1.5" integral flow orifice assembly (IFOA) is used to measure the incoming air flow rate. A one-inch air regulator

is used to control the intake manifold air pressure and a 1-ft³ pressure vessel is used as an air surge tank to dampen the air pulses entering the air preheater and engine manifold. This air preheater was manufactured with seventy-six 3/8 OD tubes on which the high-pressure steam would condense. This preheater was rated for 150 psig on both the tube and shell side at 350°F. The steam-heated air preheater uses 110 psig steam to preheat the inlet compressed air up to 280°F at a maximum air flow rate of 240 scfm of compressed air. To obtain better control of the air temperature, a bypass line was added to allow unheated air to mix with the preheated air. Flexible high-temperature, metal-braided hoses were used to isolate the intake and exhaust piping from the engine skid. A 2.5" gate valve was included in the exhaust line for backpressuring the engine to simulate a turbocharger.

An Ingersoll-Rand air starter with a reversed direction drive is used to start the engine. Compressed air is used to engage the drive gears before a pressure switch trips a solenoid valve which feeds air to the turbine in the starter. A Dana-Spicer drive shaft was ordered to couple the engine to the dynamometer. The dynamometer is an Eaton Model 1014 which is currently being rebuilt to match up better with the rpm and horsepower range of the diesel engine. This dynamometer should arrive back at the UNDEERC by the end of April. Load cells for measuring diesel and CWF fuel flow into the engine have been received.

A mobile gas analyzer is being constructed for the diesel program. This panel consists of O₂, SO₂, NO_x, CO, CO₂, and hydrocarbon analyzers which can be used to sample from two different locations. All of the analyzers have been ordered and received except for the SO₂ and O₂ analyzers. Installing, plumbing, and wiring these analyzers into a mobile panel was started during the quarter.

Figure 2 is a photograph of the diesel engine head bottom showing where the pilot and main injectors will be located. The main injector, capable of injecting approximately 750 mm³/stroke, is located in the center of the cylinder to reduce the amount of CWF spray impingement, while the diesel pilot injector is located to the right of the main injector and the exhaust port valves.

3.2 Diesel Injector Atomization Study

Figure 3 is a schematic showing the design of the high-pressure intensifier currently under construction at the UNDEERC. The pressure intensifier is being fabricated from a hydraulic cylinder and high-pressure tubing. This intensifier will be used to conduct atomization tests at more uniform injection pressures. The pressure intensifier and accumulator should also provide a continuous spray for between 0.5 to 1 second. The longer spray duration will enable the pulsed spray option ordered with the Malvern 2600 to acquire more sweeps during a single injection and eliminate more of the initial and final spray patterns, thereby providing more consistent atomization results. Compressed nitrogen is fed into the large piston accumulator at a controlled pressure which displaces the large shaft through the packing rings. This shaft displaces the CWF out of the high-pressure accumulator. This vessel will intensify the regulated pressure from a gas cylinder approximately ten times, thus injection pressures up to 15,000 psig can be obtained using regulated bottle N₂. This data will also be compared to high-shear rheology data generated under a different program.

Figure 1. Photograph of single cylinder Caterpillar 1Y540 diesel engine test skid for CWF testing.

Figure 2. Photograph of modified diesel engine head including a diesel pilot fuel injector.

Several atomization tests were conducted using a water/soluble oil mixture. A nitrogen cylinder was used to supply a pressure of 2400 psig to a piston-type accumulator. The accumulator had a 25 mL volume which would be discharged in less than two seconds. The pressure delivered to the multihole nozzle was 2200 psig, while a constant pressure could not be maintained to the pintle-type nozzle due to the relatively large orifice diameter. Droplet-size data was collected with a Malvern 2600 and a PS-51 pulsed spray synchronizer. The mean droplet-size was found to be approximately 50 μm using the pintle-type injector. These tests allowed the operation of the pulsed spray synchronizer to be checked out under spray durations typical of the pressure intensifier.

Figure 3. Diagram of pressure intensifier for CWF diesel injector atomization tests

4.0 FUTURE PLANS

Future plans for the project include installing the Eaton 1014 dynamometer when it arrives and to start engine testing with diesel fuel to establish a baseline performance curve. Then the modified head will be installed to establish a diesel fuel baseline with the new pilot injector position. Slurry fuel combustion work will be started using Spring Creek and Kemmerer subbituminous fuels already available along with an Otisca Industries Taggart seam CWF available at the UNDEERC. These fuels will be evaluated at different engine timings and injection pressures along with different pilot fuel quantities. Engine rpm will also be examined for the effect it has on carbon burnout and engine emissions. Diesel injector atomization work will be performed to determine what effect injection pressure, particle size/fuel type, and fuel rheology have on droplet-size distributions.

4.5 Produce and Characterize HWD Fuels for Heat Engine Applications

PRODUCTION & CHARACTERIZATION OF CWF FOR HEAT ENGINE APPLICATIONS

Quarterly Technical Progress Report for the Period
January-March 1990

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NOMENCLATURE

τ shear stress, lb_f/ft^2 τ_w shear stress at the wall, lb_f/ft^2 ΔP pressure difference between two capillary ends, lb_f/ft^2 ΔP_f frictional pressure loss between capillary ends, lb_f/ft^2 γ shear rate, sec^{-1} γ_w shear rate at the wall, sec^{-1} μ coefficient of viscosity, $\text{lb}_f\text{-sec}/\text{ft}^2$ μ_a apparent viscosity, $\text{lb}_f\text{-sec}/\text{ft}^2$ α kinetic energy correction factor, D diameter of the capillary tube, ft R radius of the capillary tube, ft P_1 pressure above the liquid level, lb_f/ft^2 P_2 pressure at the exit of the capillary tube, lb_f/ft^2	r distance from the center of the tube, ft L length of capillary tube, ft L' height of liquid above the capillary tube, ft V velocity in the axial direction, ft/sec Q volumetric flow rate, ft^3/sec d density, lb_m/ft^3 k flow index, k_c coefficient of sudden contraction, n power law flow coefficient, n' Rabinowitsch-Mooney coefficient, N_f length equivalent for frictional pressure loss equal to entrance losses, ft g acceleration due to gravity, ft/sec^2 g_c conversion factor, $32.174 \text{ lb}_m\text{-ft}/\text{lb}_f\text{-sec}^2$
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PRODUCTION & CHARACTERIZATION OF CWF FOR HEAT ENGINE APPLICATIONS

1.0 GOALS AND OBJECTIVES

The overall objectives of the Production & Characterization of Coal/Water Fuel (CWF) for Heat Engine Applications are to improve current capabilities to supply and characterize clean CWFs from low-rank coals (LRCs) for METC-sponsored heat engine combustion utilization programs. The University of North Dakota Energy & Environmental Research Center (EERC) has demonstrated that high-energy content dry or slurry fuels can be produced from lignite and subbituminous coal using the hot-water drying process (HWD), and that low-ash, coal-based fuel can be produced using a combination of physical and chemical cleaning. These processes were integrated to maintain a greater than 200-lb/hr pilot-scale capability for producing clean, energy-dense coal suitable for clean solid or CWF product preparation from low-cost, highly reactive LRC feedstocks. The pilot-scale capabilities will continue to supply fuels for DOE-sponsored Combustion, Gasification, and Heat Engine programs running concurrently with the Low-Rank Coal Beneficiation and CWF Programs, as needed.

Current year CWF production and characterization efforts will be focused on 3 tasks:

1. Increasing the throughput of the continuous HWD pilot plant from 200 to a maximum of 600 lbs/hr by updating the equipment and instrumentation, thus reducing the cost of supplying clean, HWD CWF from low-rank coals to heat engine combustion researchers.
2. Renovating the laboratory support facilities to improve characterization of CWF produced in the pilot plant facilities.
3. Developing the capability to determine the high-shear rheology of CWF at the conditions expected in heat engine combustion systems, such as turbines and diesels.

Near-term objectives of the project for the period January through March 1990 were to:

1. Install new equipment and finish modifications for the HWD pilot plant throughput expansion.
2. Monitor contractor renovations of the pilot plant laboratory facilities.
3. Complete fabrication of a high-shear rheometer for rheology determinations of CWF at shear rates up to 200,000 1/sec.
4. Develop methods for rheological data analyses and finalize the test matrix.

2.0 INTRODUCTION

This report describes progress towards goals and objectives related to those listed in section 1.0. Efforts have concentrated on improving the capabilities to support heat engine research by producing clean CWF from low-rank coals and reducing the costs of the fuels produced. Hot-water drying, when integrated with wet coal cleaning techniques, such as dense-media cone separation and dilute acid leaching, has produced drum quantities of CWF from LRCs with less than 2.0 wt% ash on a dry basis at solids contents up to 55 wt% and at micronized particle size (100% < 45 microns, 12 microns average) (1, 2). These fuels have shown excellent combustion characteristics in the General Electric Research and Development diesel engine and the EERC Turbine Simulator programs, achieving higher average carbon burnouts than bituminous fuels with a much smaller mean particle size (3,4).

The efficient operation of advanced heat engine combustion systems depends on the high carbon burnout of CWF. Atomization quality of CWF is an important parameter related to a high carbon burnout in these systems. It is well known that the apparent viscosity of CWFs at a high-shear rate has a dominant effect on the size distribution of atomized fuel droplets (5). Further background information has been given previously (6). This investigation will attempt to determine if CWFs that are pseudoplastic at low-shear rates remain pseudoplastic at high-shear rates, and if CWFs that are dilatant at low shear remain dilatant at high shear.

3.0 PRODUCTION & CHARACTERIZATION OF CWF FOR HEAT ENGINES

3.1 Pilot Plant Throughput Expansion

Modifications to the current pumping system, the condensing Dowtherm preheater section, and the pressure letdown station of the HWD pilot plant were continued and completed during the past quarter. The throughput increase was achieved according to the plan outlined in the previous Quarterly report (6). The revised configuration of the pilot plant at the planned throughput of 600 lbs slurry/hr is shown in Figure 1.

3.2 Pilot Plant Laboratory Facility

Laboratory renovations were essentially completed through a local company, Community Contractors of Grand Forks, ND, by March 15, 1990.

3.3 High-Shear Rheology Program

3.3.1 Background

Rheological studies of CWF are needed to aid the formulation and utilization of CWF suitable for heat engine applications. Efficient operation of an advanced heat engine combustion system depends on high CWF carbon burnout. Previous studies have shown atomization quality to be a critical parameter influencing combustibility of CWF in turbine and diesel engine applications. The apparent viscosity of CWFs at the high-shear rates present

Figure 1. Revised flow sheet of the HWD pilot plant.

during atomization was found to have a dominant effect on atomization quality as measured by the size distribution of atomized droplets (7).

Coal/water rheology is complex and composition dependent. Different variables like particle-size distribution, solids concentration, and additive package influence flow properties (2). In general, CWFs can be classified as non-Newtonian and typically exhibit shear dependent flow behavior which can be either pseudoplastic or dilatant.

The objective of this study is to determine the flow behavior of CWF at the high-shear rate region characteristic of the point of atomization. The relationship between high-shear and low-shear flow behavior and apparent viscosity as well as variables such as coal type, particle size, solids concentration, and additive package will be studied. Additionally, a correlation between high-shear flow behavior and apparent viscosity with droplet size distribution during atomization may be established. Atomization and droplet size data will be generated by tests conducted for the EERC turbine test program.

To determine the flow behavior, viscometers measure the deformation which occurs to the fluid when a force or a shearing action is applied to the given fluid. Shear stress is defined as the ratio of this force to the area on which it is applied. The apparent viscosity is defined as the ratio of wall shear stress to the rate of shear applied to the fluid.

Measurement of flow properties at high-shear rate with rotational viscometers such as the Haake concentric cylinder viscometer become very cumbersome as the frictional heat buildup becomes significant. Capillary tube viscometers, such as extrusion rheometers, avoid this problem by once-through flow of the fluid which carries out the built-up heat. Extrusion rheometers use a pressurized vessel to force the fluid through a long, smooth cylindrical capillary tube of known dimensions. The frictional pressure drop associated with the laminar flow of the fluid and the corresponding flow rate is measured. For determination of the flow curve, several measurements are necessary at different pressures and length to diameter ratios of the capillary.

Previous studies at UNDEERC found various CWFs exhibited pseudoplastic flow behavior at the low-shear rate region of up to 450 sec^{-1} (8). Apparent viscosity of various CWFs appeared to be a function of the solids concentration. Use of a dispersant additive (nonionic surfactant type) was found very effective in decreasing apparent viscosity at low-shear rates (100 sec^{-1}) by almost one order of magnitude (8). However, flow behavior was found to be adversely affected by the use of a dispersant and changed to shear thickening behavior. Mannheimer also reported shear thickening behavior of a low solids content micronized CWF with dispersant additive at shear rates of up to $10,000 \text{ sec}^{-1}$ (9).

Yu and others (7) considered that atomization quality predictions can be made using effective viscosity measurement at a shear rate range of $10,000$ - $100,000 \text{ sec}^{-1}$, calculated to arise at atomization. They reported linear relationships between mean droplet size and apparent viscosity at this shear region.

3.3.2 Discussion

For a fluid in steady laminar flow within a tube of radius R and length L , with a pressure difference between the ends of the capillary tube, ΔP_f , a viscous force tending to retard flow will be exactly balanced by a force resulting from the ΔP_f . Therefore, the shear stress at any point in the capillary is directly proportional to the distance from the center of the tube and to the pressure gradient.

$$\tau = (\Delta P_f \cdot r)/2L \quad (1)$$

Shear stress at the center of the capillary is zero and becomes maximum at the wall. This linear relation of shear stress with tube radius is valid regardless of the nature of the fluid. At the wall, the shear stress is proportional to the radius R .

$$\tau_w = (\Delta P_f \cdot R)/2L \quad (2)$$

The rate of shear also varies with the radius and is dependent on the nature of the fluid. For a Newtonian fluid, shear rate decreases linearly with the radius.

$$\gamma = (-dV/dr) = 8V/D = (32Q/\pi D^3) \quad (3)$$

However, for a non-Newtonian fluid the relationship is more complex. The shear rate at the wall is determined by applying the Rabinowitsch correction to the average rate of shear calculated from the volumetric flow rate.

$$\gamma_w = (8V/D)(3n'+1)/4n' \quad (4)$$

where

$$n' = (d \ln \tau / d \ln \gamma) \quad (5)$$

For non-Newtonian fluids, shear rate and shear stress are related by the coefficient of proportionality known as the apparent viscosity. Unlike Newtonian viscosity, this apparent viscosity is not a constant and is a function of the shear rate.

$$\mu_a = \tau/\gamma \quad (6)$$

Apparent viscosity is determined from measurement of the pressure drop in the capillary tube and the associated flow rate. Shear rate and shear stress are calculated at the same point in the capillary, i.e. the wall, so that:

$$\mu_a = \tau_w/\gamma_w = [(\pi \cdot \Delta P_f \cdot D^3)/(128 L \cdot Q)](3n'+1)/4n' \quad (7)$$

A power law model, where the shear stress is proportional to the power of the shear rate, describes flow behavior of many non-Newtonian fluids and has been successfully applied to CWF. When the shear rate increases more than in proportion to the shearing stress, the fluid is called pseudoplastic or

shear-thinning. For the case of a dilatant or shear thickening fluid, the shear rate increases less than in proportion to the shearing stress.

$$\tau = k \cdot \dot{\gamma}^n = k(-dv/dr)^n \quad (8)$$

where k = flow coefficient and n = flow index.

The volumetric rate of flow is determined from this relationship by integrating the velocity distribution over the cross section of the tube.

$$Q = \pi(\Delta P_f/2k \cdot L)^{1/n} [n/(3n+1)] R^{(3n+1)/n} \quad (9)$$

For $n=1$ (Newtonian fluid), this equation reduces to the Hagen-Poiseuille relation.

$$Q = \pi R^4 \cdot \Delta P / 8\mu \cdot L \quad (10)$$

Three general correction terms must be added to obtain the frictional pressure drop from the applied pressure on the fluid (P_1) and the pressure of the liquid exiting from the capillary tube (P_2). These correction terms account for the head of fluid above the tube exit, kinetic energy effects due to velocity head of the exiting liquid and entrance effects due to sudden contraction.

$$\Delta P_f = P_1 - P_2 + (L + L') d \cdot g / g_c - (d \cdot V^2 / g_c) (1/2\alpha + k_c/2) \quad (11)$$

The values of α and k_c are not firmly established for non-Newtonian fluids. Combined corrections for kinetic energy and entrance effects may be taken to be the same as Newtonian material (10).

$$\Delta P_f = P_1 - P_2 + (L + L') d \cdot g / g_c - 1.12(d \cdot V^2 / g_c) \quad (12)$$

Combined correction factors may also be obtained as a function of flow index as given by Bogue (11). Uncertainties regarding the correction term may be minimized by making the L/D ratio for the capillary tube as large as possible. L/D ratio of the order of 200 to 1000 has been used by some investigators.

Alternatively, Bagley's empirical method may be used to eliminate entrance effects from obtained pressure drop. Entrance losses are expressed in terms of effective capillary length ($L + N_f$), such that measured pressure drop is equal to pressure drop over the effective capillary length for fully developed flow.

$$\tau_w = \Delta P \cdot R / 2(L + N_f \cdot R) \quad (13)$$

$$L/R = -N_f + \Delta P / 2\tau_w \quad (14)$$

For non-Newtonian fluids, τ is a unique function of apparent shear rate at the wall ($4Q/\pi R^3$). A series of measurements of pressure drop on capillary tubes of different L/D ratios at constant values of apparent shear rate is required. A plot of L/R versus ΔP will be linear and intercept the L/R ordinate at ΔP equal to zero. A slope of the line will give N_f . From a set of

data at different values of $4Q/\pi R^3$, a plot of N_f versus $4Q/\pi R^3$ can be obtained. Shear stress at the wall can then be calculated using the effective capillary length to exclude the entrance effect.

3.3.3 Data Analysis

From experimental measurement of frictional pressure drop ΔP_f and the mass flow rate W , the power law parameters k and n can be calculated by regression analysis. Equation 9 can be written in the form of a straight line equation.

$$\log Q = \log[(1/2k)^{1/n} \pi n/(3n+1)R^{(3n+1)/n}] + (1/n)\log(\Delta P_f/L) \quad (15)$$

For each experimental run, shear stress at the wall is calculated using equation 2 while shear rate at the wall is calculated using equations 3, 4 and 5. Apparent viscosity at the experimental shear rate is calculated from these data. Using a set of shear stress and shear rate data at different shear rates, the power law parameters can also be estimated by regression.

3.3.4 Test Program

At least one coal of each type, i.e., bituminous, subbituminous, and lignite will be included in the test matrix. Flow behavior at high- and low-shear rates of CWF prepared from each type of coal will be determined at two levels of solids concentration and mean particle sizes.

Physically cleaned, acid cleaned, and hot-water dried coal with and without additives will be used to prepare CWF from lignitic and subbituminous coal. Bituminous CWF from Otisca Industries will be used for comparison. Both combustion grind and micronized samples will be included for the studies. The essential feature of any capillary tube viscometer is the measurement of the frictional pressure drop associated with the laminar flow of fluid at a given rate through a long, smooth, cylindrical tube of known dimension. The bench-scale unit consists of an autoclave vessel, Magna-drive stirrer, an actuated 1/16" valve and various flow, pressure, and temperature instrumentation, as depicted in Figure 2. Rheology tests will consist of first charging the slurry to the autoclave vessel, adjusting the operating temperature, and back pressuring the system with nitrogen up to 1200 psi. The CWF is forced through the capillary tube, at which time the flow rate and the pressure drop are measured simultaneously. The shear rate and viscosity data will be determined by computer calculation from the flow rate and pressure drop on-line data acquisition. Further experimental description was given in the previous Quarterly report (6). Fabrication of the system is nearly complete, and testing will begin during the April to June Quarterly period.

The high-shear data will be correlated with low-shear data obtained using a Haake RV100 viscometer to extend the validity of the Yield Power Law curve fit for the flow behavior of non-Newtonian CWFs. Data generated will also be compared to pressurized atomization spray testing to be conducted concurrently by the Turbine Combustion Phenomena and Diesel Utilization of Low-Rank Coal program.

Figure 2. High-shear viscometer.

4.0 CONCLUSIONS

1. The HWD pilot plant modifications are essentially completed in accordance with intended designs. No major alterations of intended throughput expansion plans were needed.
2. The high-shear viscometer apparatus is nearly complete. Initial testing of various coal/water slurries, along with design of test matrix, will be completed for April to June Quarterly.

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5.0 LIQUEFACTION RESEARCH

5.1 Low-Rank Coal Direct Liquefaction

LOW-RANK COAL DIRECT LIQUEFACTION

**Quarterly Technical Progress Report
for the Period January - March 1990**

by

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LOW-RANK COAL DIRECT LIQUEFACTION

EXECUTIVE SUMMARY

During the January-March 1990 quarter, studies of low-severity pretreatment to enhance the direct liquefaction of low-rank coals (LRCs) continued. Gas analyses were completed for the products of the low-severity pretreatment screening tests performed as part of Task 1. The Task 2 pretreatment tests using hydrogen-donating solvents were initiated according to the experimental matrix.

Two of the Task 3 mechanistic studies of retrograde reactions during LRC direct liquefaction were performed. A few observations were made based upon the engineering data available to date. At the low-severity conditions used to achieve a conversion of 8.6%, very little decarboxylation or cracking of the coal occurred. The information available for the 93.7% conversion test indicated that the water/gas shift reaction played a role in the production of CO_2 during the conversion activities. In addition, some cracking and decarboxylation of the coal were noted during this test. Because it is suspected that H_2S acts as a reaction promoter, H_2S was added to the gas reactants of the tests. It was found that virtually the same quantity of H_2S per gram of MAF (moisture- and ash-free) coal fed was consumed during both tests, suggesting that the sulfur is incorporated into the coal structure early in the reaction. Mechanistically, this may have implications in either pretreatment or staged processing reaction pathways.

1.0 INTRODUCTION

To expand the scientific and engineering data base of LRC liquefaction, investigations of direct liquefaction processes that produce the most competitive feedstocks or liquid fuels must be investigated. Coal can be converted to very high yields of oils with increasing levels of efficiency using a two-stage processing approach. To obtain even higher yields, however, it may be necessary to control the processing conditions to which coal is subjected in a manner that significantly reduces the role that repolymerization, recombination, and/or coking reactions play in the conversion process.

2.0 GOALS AND OBJECTIVES

2.1 Three-Year Program Beginning FY'89-90

The primary objective of the three-year Low-Rank Coal Direct Liquefaction program is to develop an LRC liquefaction process that will result in increased levels of conversion to distillable liquids. The work effort associated with meeting this objective includes an investigation of low-severity preconversion treatment of LRCs and a mechanistic study of the retrograde reactions which occur during processing as a function of conversion. Through mechanistic inference, the results of this work may be applicable to higher-rank coals.

The potential role of preconversion treatment of LRCs will be evaluated empirically by determining which systems can successfully prepare LRCs for the thermal first-stage conversion during two-stage processing. The initial work will screen various proposed systems for their effect on first-stage conversion. Second-year work will focus on promising systems identified during the initial screening in an effort to understand the mechanisms that produce improved yield structures. Once a mechanism has been hypothesized, it may be possible to suggest improvements that can be made in the pretreatment step. Additional batch and semi-batch testing will take place during the third year to test and evaluate the conclusions drawn from the second-year studies. The batch testing will be followed by limited validation on the continuous process unit (CPU).

It has been shown that, during most liquefaction conversion processes, the mechanism of hydrogen transfer to the coal occurs primarily between the solvent and the coal. It may be possible to take advantage of the higher reactivity of LRCs to enhance processing oil yields if hydrogen-donating solvents are employed during a preconversion step. This type of treatment may extend the range of low-severity processing to very low pressures as well as low temperatures. Preliminary evaluation of this preconversion treatment method will take place on the batch scale. The products from the batch-scale tests will be treated in a two-stage batch system to determine the effect of the preconversion reactions on the total system yield structure. The results will be compared to the results of previous tests performed with and without the preconversion treatment. After the batch testing is completed, a verification test will be performed on the CPU to confirm the batch data.

The feed coal and product streams will be characterized to define the relative importance of lignite structure and solvent composition to the success (or lack thereof) of low-severity processing. During this effort, which will extend throughout the three-year period, analyses will define important reactions taking place, including cracking, hydrogen transfer, hydrodeoxygenation, hydrodealkylation, solvolysis, product stabilization, and retrograde reactions. Analytical results will also enable comparisons to be made between the low-rank feed streams and the products of the low-severity processing.

A preliminary mechanistic study of the retrograde reactions that occur as a function of conversion will be performed. This study will require the production of samples at low-severity processing conditions with conversions of 10%, 50%, and 95%. An additional test will be performed at more severe conditions to produce a coked product. Analyses of the products of the tests will indicate if changes occur in the products with respect to increasing conversion to soluble material. ^{13}C NMR analyses will be used to provide a relatively detailed examination of the fate of the chemical functional groups present in the coal. This technique may make it possible to observe and follow specific retrograde trends, allowing the development of functional-group-specific pretreatment processes.

2.2 Third Quarter of FY'89-90

Work which was scheduled for the third quarter of FY'89-90 originally included performance of both the Task 2 CPU validation of the most promising preconversion treatment using hydrogen-donating solvents and the Task 3

mechanistic study batch tests. Due to the fact that the autoclave system was unavailable for the Task 2 studies in the fall, the CPU validation test was postponed.

3.0 ACCOMPLISHMENTS

3.1 Task 1--Preconversion Treatment of Low-Rank Coals

Gas analyses were performed for the Task 1 screening tests. The liquid product analyses for the autoclave tests (Matrix Test Points 7-12) have not yet been completed. When available, the analytical results will be combined with the mass and material balance data, and a determination of the most promising preconversion treatment method will be made.

3.2 Task 2--Preconversion Treatment of LRCs With Hydrogen-Donating Solvents

The autoclave system was set up for the preconversion treatment tests using hydrogen-donating solvents. Testing was initiated according to the experimental matrix.

3.3 Task 3--Mechanistic Studies of Retrograde Reactions During Liquefaction

Two tests were performed to produce noncoked product with conversions to THF-soluble material of 8.6% and 93.7%, respectively. The analytical data are not yet available for these tests, but some inferences into reaction mechanism may be made based upon the material balance data presented in Tables 1 and 2.

Due to the low reaction temperature, the water/gas shift reaction was not expected to be a factor during the 8.6% conversion test. The data shown in Table 1 seem to confirm this as there is no evidence of the reaction taking place; i.e., water was not consumed and hydrogen was not produced. It may, therefore, be assumed that the CO_2 produced during the test was due to the decarboxylation of about 14 wt% of the MAF coal fed to the system. There was very little evidence of cracking of the coal (as shown by the production of hydrocarbon gases), indicating that virtually no gasification of the coal occurred at these conditions.

Some cracking was evident at the more severe conditions (i.e., the test in which 93.7% conversion was achieved), as shown by the production of hydrocarbon gases equaling approximately 1.3 wt% of the MAF coal fed to the system. As Table 2 shows, almost 190 gm of CO_2 were produced during the reaction. Production of CO_2 was probably from two sources: the water/gas shift reaction and decarboxylation of the coal. Calculations involving the water/gas shift reaction during these tests are summarized in Table 3. The expected CO_2 production due to the water/gas shift reaction was calculated to be about 2.75 gm-moles, or 121 gm. Assuming that decarboxylation of the coal was responsible for the production of the remaining 1.55 gm-moles (68 gm) of CO_2 , approximately 34.3 wt% of the MAF coal fed was involved in the decarboxylation reaction. This is more than twice as much of the MAF coal as was involved in decarboxylation during the 8.6% conversion test.

TABLE 1
MATERIAL BALANCE DATA FOR MECHANISTIC STUDIES TEST
RESULTING IN 8.6% CONVERSION

Component	In (gm)	Out (gm)	Corrected Product Slate ^a (gm)	Product Slate (wt% MAF coal fed)
Gas				
CO	208.83	201.77	-7.06	-3.51
H ₂	0.00	0.00	0.00	0.00
CO ₂	0.00	28.36	28.36	14.09
Cl-C3	0.00	0.50	0.50	0.25
H ₂ S	35.19	17.90	-17.29	-8.59
Product Slurry				
H ₂ O	95.28	95.30	0.86 ^b	0.43
Ash	21.21	22.72	1.71 ^b	0.85
MAF Coal	201.26	182.30	183.92 ^b	91.38
Solubles	596.35	601.28	10.25 ^b	5.09

^a Positive values indicate production of the component; negative values indicate consumption.

^b All losses were assigned to the product slurry.

TABLE 2
MATERIAL BALANCE DATA FOR MECHANISTIC STUDIES TEST
RESULTING IN 93.7% CONVERSION

Component	In (gm)	Out (gm)	Corrected Product Slate ^a (gm)	Product Slate (wt% MAF coal fed)
Gas				
CO	211.55	103.06	-108.49	-54.55
H ₂	0.00	2.07	2.07	1.04
CO ₂	0.00	189.36	189.36	95.22
Cl-C3	0.00	2.56	2.56	1.28
H ₂ S	34.77	18.21	-16.56	-8.33
Product Slurry				
H ₂ O	94.17	44.77	-48.64 ^b	-24.46
Ash	20.97	19.70	-0.93 ^b	-0.47
MAF Coal	198.87	12.41	12.62 ^b	6.35
Solubles	596.59	750.72	166.88 ^b	83.91

^a Positive values indicate production of the component; negative values indicate consumption. These values include contributions made by the water/gas shift reaction.

^b All losses were assigned to the product slurry.

TABLE 3
SUMMARY OF WATER/GAS SHIFT (WGS) REACTION^a
DURING MECHANISTIC STUDIES TESTS
(gm-moles)

Component	In	Out	WGS ^b	Coal-Derived ^c
8.6% Conversion				
CO	7.45	7.20	0.00	-0.25
H ₂ O	5.29	5.29	0.00	0.00
CO ₂	0.00	0.64	0.00	0.64
H ₂	0.00	0.00	0.00	0.00
93.7% Conversion				
CO	7.55	3.68	-2.75	-1.12
H ₂ O	5.23	2.48	-2.75	0.00
CO ₂	0.00	4.30	2.75	1.55
H ₂	0.00	1.02	2.75	-1.73

^a $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$

^b Assumed for these calculations that H₂O is the limiting reactant and that all H₂O consumption during the reaction was due to WGS reaction.

^c Positive values indicate production of a component; negative values indicate consumption.

It is suspected that H₂S acts as a reaction promoter; therefore, H₂S was added to the gas reactants of these tests. Virtually the same quantity of H₂S was consumed during both tests. This suggests that the sulfur is incorporated into the coal structure early in the reaction. Mechanistically, this may have implications in either pretreatment or staged processing reaction pathways. For instance, to achieve favorable yield structures using H₂S as a promoter, the H₂S may need to be present prior to the beginning of the conversion reactions. During continuous processing, it would therefore be necessary for the H₂S to contact the feed slurry at elevated temperatures prior to the actual conversion activities.

3.4 Task K, FY'88-89--Low-Severity Staged Liquefaction Tests

GC/MS analyses were completed on the product slurries of these tests. Reduction of the results is continuing.

4.0 FUTURE OBJECTIVES

- All remaining Task K (FY'88-89) data reduction and interpretation will be completed.

- The analysis of the samples generated during the Task 1 autoclave tests will be completed and the results interpreted.
- The Task 2 autoclave testing of preconversion treatment using hydrogen-donating solvents will be completed, the products analyzed, and the results interpreted.
- The Task 3 mechanistic studies batch testing will be completed, the products analyzed, and the results interpreted.

6.0 GASIFICATION RESEARCH

6.1 Production of Hydrogen and By-Products from Coal

PRODUCTION OF HYDROGEN AND BY-PRODUCTS FROM COAL

**Quarterly Technical Progress Report
for the Period January-March 1990**

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PRODUCTION OF HYDROGEN AND BY-PRODUCTS FROM COAL

1.0 INTRODUCTION

Coal gasification products consist of char solids, condensables, and gases. A flexible processing system that allows variation of products to meet market demand would substantially improve the marketability of coal. Such a processing system could integrate catalytic gasification and mild gasification of coal. Operating temperatures range from 500° to 800°C, at nominally atmospheric pressure. A hybrid system based on these two technologies should have the flexibility to optimize production of one, two, or all three of the products depending upon market demand.

A flexible system should have a single reactor capable of maximizing the yield of any product, depending on the markets. Fixed-bed gasification is limited by heat and mass transfer for the endothermic steam gasification reaction for hydrogen and syngas production. An entrained-bed system presents difficulties in maintaining sufficient solids residence times without extensive recycle. A fluidized-bed system offers excellent heat and mass transfer and significant flexibility of operating conditions with uniform temperature and solids distributions. The smaller particles in a fluidized-bed system result in less diffusional resistance than in a fixed-bed system, more efficient waste heat recovery, and smaller pressure drops. Tests at the University of North Dakota Energy and Environmental Research Center (EERC) have demonstrated that coal devolatilization, gasification, and ash removal can be done within a single vessel using a fluidized-bed system.

The two most important considerations for producing hydrogen from coal in a single reactor are to maintain operating conditions that 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 product gas hydrogen content requires steam gasification at 700° to 800°C and atmospheric pressure. Low-rank coals are the preferred feedstock because of low mining cost and higher reactivity. This higher reactivity is caused by higher concentrations of active sites, higher porosity, and a more uniform dispersion of alkali impurities that act as inherent catalysts. Reactivity can also be increased by increasing the temperature within the range that maximizes hydrogen production and with the addition of a catalyst. Although reactivity increases with temperature and catalyst addition, the hydrogen content of the product gas was shown by previous work to be relatively constant with those changes (1). Catalysis of a bituminous coal char with loadings of alkali carbonates similar to those of the low-rank coals also increased reactivity. However, catalyzed bituminous coal char was found to be five to six times less reactive than similarly catalyzed lignites. Operating the gasifier at pressure, as recommended in the preliminary economic assessment by Black and Veatch Engineers-Architects, would change the product distribution.

A high-hydrogen gas, from 45% to 50%, has been produced at EERC on a pilot scale with low-rank coals. Although the production of high-hydrogen gas from a single reactor has been demonstrated, further processing of the gas is required to remove contaminants: fine particulates and sulfur compounds (H_2S and COS), as well as other product gas constituents. Classification as a contaminant depends on the end-use application of the product gas.

Solid products of the mild gasification process demonstrated at EERC have shown promise in areas not related to energy. One possible product is activated carbon, which is widely used in large quantities for removal of trace organics from secondary effluents. Sometimes more than 50% of the cost of wastewater treatment is attributed to the cost of makeup carbon. Activated carbon has also shown potential as a catalyst support (below 425°C).

Mild gasification produces condensables that may be directly fired or blended with petroleum-derived fuels or solid coal. These fuels have potential uses in gas turbines, aviation jet engines, diesel engines, and as chemical precursors. These do not match existing specifications for No. 2 diesel fuel, but research has demonstrated that off-specification fuels can perform adequately in diesel engines and turbines. These products have characteristics not available from petroleum. For example, the aromatic nature of coal makes it a source of high-density fuel. Incorporating a primary separation scheme with the quench step to selectively remove certain desired fractions of condensables may provide an economic advantage in their further upgrading for chemical production.

Coal gasification at mild conditions of 500° to 800°C and atmospheric pressure has the potential to produce hydrogen, syngas, methanol, and other products, as well as a variety of by-products, including condensable liquids and low volatile-content char. In the temperature range of 500° to 700°C, hydrogen production proceeds quite slowly, while coal liquids (petroleum substitutes) and char (coke and activated carbon) are the predominate products. Production of hydrogen becomes technically feasible in the range of 700° to 800°C, where cracking of hydrocarbons and gasification of char carbon occur at an appreciable rate. The different product slates determine the difference between mild gasification and hydrogen production.

2.0 GOALS AND OBJECTIVES

The objective of this research is to determine the optimum conditions for production of a gas stream enriched in hydrogen and the preferred conditions for production of by-products. Technology previously developed at EERC which involves catalytic steam gasification of coal will be utilized. Development of gas cleanup and separation process schemes will be necessary for utilization of hydrogen produced for methanol synthesis and fuel for a closely coupled fuel cell. To better understand the catalytic steam gasification process, bench-scale work will be done to determine the kinetics of catalysis, identification of components of pyrolysis and coal-steam reaction streams, and feed coal characterization.

3.0 ACCOMPLISHMENTS

3.1 Hydrogen-From-Coal CPU

The fluidized-bed gasifier continuous process unit (CPU) used for production of hydrogen from low-rank coals has been incorporated into the 100-lb/hr mild gasification process development unit (PDU). Refractory material

in the carbonizer and burner plenums has been cured. The CPU has been modified to allow continuous draining of the bed. To accommodate system changes, the gas quench train has been moved and expanded.

3.2 Char Characterization

3.2.1 Catalyst Evaluation

Limestone has been shown to be effective in catalyzing the steam gasification of low-rank coal (2). The catalytic effect of the calcium-rich mineral is not only noted with admixed limestone and coal feed, but also with raw coal to which no catalyst has been added. Limestone is present in the reactor as gasifier bed material. The mechanism that explains the means by which the coal char-steam reaction is promoted with catalyst is still not clear. The role of the calcium-associated anion, if any, in promoting the reaction is unknown and is part of this study. Four calcium compounds are being tested as part of this work. Natural limestone, primarily CaCO_3 , was selected for the base case on the basis of results observed in the CPU. Calcium oxide, calcined calcium carbonate that reacts with water to give Ca(OH)_2 , was the second catalyst selected. Calcium sulfate, refractory at the conditions of the tests, was the third catalytic agent chosen. Calcium acetate, initially water soluble (thus facilitating its dispersion) and decomposing during heat-up, was the fourth catalyst to be tested.

Increased reaction rate, however, is not the only consideration in the study of catalyzed reactions. Product quality and rate of production may also be affected by the added catalyst. Previous tests indicated that catalyst addition with a low-rank coal had the effect on liquid quality of altering proportions of liquid components such as benzene, phenol, catechol, and related compounds, and required further investigation (3).

Coals from three ranks: lignite, subbituminous, and bituminous, were used in the study of the catalyzed gasification kinetics of the coal char-steam reaction. Data from the study of catalytic gasification of Wyodak subbituminous and Velva lignite coal chars were reported in the July-September and October-December 1989 Hydrogen Production Quarterlies, respectively. The data from a similar study involving a bituminous coal char are reported below. Indiana bituminous coal from the Chinook mine was the bituminous coal selected for study under these catalytic conditions. The proximate analyses of the three test coals are shown in Table 1.

TGA-MS INTERFACE

Several samples of coal and coal-catalyst mixtures were heated in the TGA, and the products were "sipped" and analyzed by the MS. About one part in 101 of the sample of volatilized material collected by the interface was introduced into the MS. Low voltage current (10 eV) was used to ionize the particles, resulting in a spectrum that showed primarily molecular ions. Benzene, phenols, catechols, and small polynuclear aromatics predominated in the low-rank coals.

TABLE 1
PROXIMATE ANALYSES OF VELVA, WYODAK, AND INDIANA COALS

	<u>Velva</u>	<u>Wyodak</u>	<u>Indiana</u>
Proximate Analysis, wt%			
Moisture	36.30	32.91	13.50
Volatile Matter, mf	47.36	44.74	41.25
Fixed Carbon, mf	45.70	46.21	46.31
Ash, mf	6.94	9.05	12.09
Ultimate Analysis, mf, wt%			
Hydrogen	4.31	4.89	5.16
Carbon	65.49	66.09	67.99
Nitrogen	0.97	0.99	1.32
Sulfur	0.22	0.39	4.86
Oxygen (Diff.)	22.06	18.57	8.58

CATALYST STUDIES

Calcium Catalysis

The studies of calcium catalysis as a function of anion effects on coal char gasification continued this quarter by focusing on the catalyzed reactions of Indiana bituminous coal char. The reactions of the uncatalyzed and catalyzed Indiana char with steam were carried out in the usual manner (2) and the data were reduced. Table 2 shows catalysts, reaction temperatures, reactivities (k), energies of activation (E_a), and pre-exponential factors (A) for the reactions. E_a and A are calculated from the plot of $\ln k$ vs $1/T$ according to the Arrhenius relationship:

$$k = Ae^{-E_a/RT}$$

The reaction order for the uncatalyzed char-steam reaction at 1023K, calculated using the differential method (plot of $\log (dC/dt)$ vs. $\log C$), was determined to be second. Thus the reactivities shown in Table 2 were calculated according to the differential equation:

$$\frac{dx}{dt} = k(a-x)^2$$

which, upon integration, gives the form:

$$k = \frac{1}{t} \frac{x}{a(a-x)}$$

where k = specific rate constant, x is the carbon gasified, a is the beginning carbon concentration, and t is the time in hours.

TABLE 2

REACTIVITIES, ARRHENIUS ENERGIES OF ACTIVATION, AND PREEXPONENTIAL COEFFICIENTS FOR RAW AND CALCIUM-CATALYZED INDIANA STEAM GASIFICATION

Temp, K	Reactivity, k				
	Raw Coal	CaSO ₄	Ca(Ac) ₂	Limestone	CaO
973	0.18	0.17	0.36	0.18	0.21
1023	0.16	0.32	0.66	0.48	0.58
1073	0.31	1.17	1.53	1.17	1.26
E _a *	11.01	39.76	29.91	38.80	37.26
A, hr ⁻¹	4.70E1	1.29E8	1.80E6	9.35E7	4.94E7

*kcal/mole

Table 2 shows that calcium sulfate, limestone, and calcium oxide were ineffective as catalysts on the Indiana char-steam reaction at 973K. The effective catalysis of this char-steam reaction occurs at a temperature >973K (700°C) for the three mentioned catalysts. The calcium sulfate doubled the rate over that of the raw coal, whereas the limestone tripled the rate, and the calcium oxide nearly quadrupled it at 1023K. A fourfold increase was noted for all three at 1073K.

The calcium acetate, however, catalyzes the reaction over the entire temperature range. The reactivity is increased from two to five times, respectively, over that of the uncatalyzed reaction from the lower temperature to the higher temperature. In the temperature range 1023-1073K, the latter catalyst increases the reactivity by factors of four and five, as compared with the increase of two and four times for the calcium sulfate and limestone catalyzed reactions.

Trona-Taconite Catalysis

Gasification tests were carried out on trona-taconite catalyzed Velva and Wyodak char-steam reactions. Again the reaction order was determined by the differential method (Fig. 1). The reaction was first order at 1023K. The results of this suite of experiments are shown in Table 3.

Gasification tests were also carried out on trona-taconite catalyzed Velva char-steam reactions. Again the reaction order with respect to carbon was determined by the differential method (Fig. 1). The specific rate constants are shown for one-half, first, and second order along with the corresponding correlation coefficient for Log (-dC/dt) vs. Log C for each at all three temperatures. The results of this suite of experiments are shown in

temperatures. The results of this suite of experiments are shown in Table 4. Although the correlations are quite good for each of the orders, a comparison of r^2 clearly indicates that the reaction is not second order. One-half order correlations are slightly better than first order correlations, indicating that the best estimate of order for trona-taconite (20 wt% trona sintered with 80 wt% taconite) catalyzed steam gasification of Velva lignite char is one-half order with respect to carbon.

Surface Analysis

Wyodak subbituminous coal containing each of the four calcium compounds and carbonized at 1023K showed uniform dispersion of the calcium in only the char containing the calcium acetate. The calcium map of the surface of a char particle showed the calcium from calcium acetate to be dispersed uniformly over the entire surface. The other three calcium additives lacked uniform dispersion and were seen as discrete particles on the surface. The char containing the calcium acetate additive also showed signs of softening on the surface, whereas the others did not. This is another indication of the fluid disposition of the calcium acetate additive at elevated temperatures which contributes to the higher reactivity of the char in which it was present.

Figure 1. Trona-taconite catalyzed Velva lignite char-steam reaction at 1023K.

TABLE 3

REACTIVITIES, ARRHENIUS ENERGY OF ACTIVATION, AND PREEXPONENTIAL
COEFFICIENT FOR TRONA-TACONITE CATALYZED WYODAK STEAM GASIFICATION

Temp, K	k, hr ⁻¹
973	1.00
1023	3.33
1073	7.65
E _a , kcal/mole	42.09
A, hr ⁻¹	3.00E9

TABLE 4

RATE CONSTANTS, CORRELATION COEFFICIENTS FOR DIFFERENTIAL PLOTS
TO DETERMINE REACTION ORDER, ARRHENIUS ENERGY OF ACTIVATION,
AND PREEXPONENTIAL COEFFICIENT FOR TRONA-TACONITE
CATALYZED VELVA CHAR STEAM GASIFICATION

Temp, K	1/2 Order		1st Order		2nd Order	
	k*	r ² **	k	r ²	k	r ²
973	3.13	1.000	3.56	0.999	4.67	0.990
1023	7.22	0.998	8.46	0.994	11.84	0.972
1073	13.63	1.000	16.15	0.997	23.13	0.979
E _a , kcal/mole	30.56	0.999	31.42	0.997	33.25	0.996
A, hr ⁻¹	2.34E7		4.16E7		1.41E8	

*k = Reactivity (rate constants)

**r² = Correlation Coefficient

X-ray diffraction (XRD) of the trona-taconite catalyst was carried out on a ground (-60 mesh) sample. Spectra showed presence of quartz (SiO_2) as the major phase and magnetite (Fe_3O_4) as the only minor phase. No other crystalline minerals were detected. This was somewhat surprising in that no sodium-containing mineral was found, even though there had been 20 wt% trona mixed with the taconite prior to heating to 800°C under argon to react the two minerals. SEM photos are shown in Figure 2. Some evidence of sodium carbonate (trona) fluxing is seen, yet on microprobe analysis, sodium was not detected.

Active Sites

Surface sites on Velva lignite and Wyodak subbituminous coals active toward CO_2 were measured on the TGA according to a method previously described (3). Similar effects as shown by parallel slopes in Figure 3 were shown for the coals with the CaSO_4 additive. However, there was significant difference between the chars in the presence of limestone (Fig. 4) and the calcined form of limestone, calcium oxide (Fig. 5). Figure 6 shows the relative numbers of carbon/active sites for the two coals with the three catalysts at each of the three temperatures.

3.3 Production of Activated Carbon from Coal

The manufacture of activated carbon (AC) from lignite has been the subject of at least eight different research studies at EERC since the early 1930s (4-11). A review of this work was performed. Most of the earlier work focused on the activation parameters such as temperature, residence time, particle size, and steam rate. Some of the work used a rabble type furnace for activation while others used a fluidized-bed. Some of the later work recognized the importance of conditions under which the precursor is charred in determining the activity of the final product. Virtually all of the studies used lignite-based, commercially produced AC in decolorizing tests as a basis for determining the quality of the AC produced in the studies.

A review of recent marketing surveys has also been done (12,13,14). These studies indicate double digit growth in the AC market for at least the next three years. The main areas of growth are water purification, gas adsorption, and gold recovery. It appears from the literature that a lignite-based AC would be well-suited for these purposes (4-11). Due to relatively low feedstock costs and relatively high transportation costs, a plant located in the Midwest might be competitive in the midwestern, western, and central states as well as in Canada.

A review is also being done on current state-of-the-art technologies in characterization of AC. Sufficient activity in patents granted indicates interest in a further understanding of adsorption phenomena, surface chemistry, and pore size distribution determination techniques.

a

b

Figure 2. SEM photographs of sintered 20% trona:80% taconite.
(a) Mag. = 500x (b) Backscatter, Mag. = 500x.

Figure 3. Log (carbon/active sites) vs. Temperature for Velva lignite and Wyodak subbituminous chars prepared at 973, 1023, and 1073K (700, 750, and 800°C).

Figure 4. Log (carbon/active sites) vs. Temperature, deg K, for Velva lignite and Wyodak subbituminous coal chars prepared at 973, 1023, and 1073K (700, 750, and 800°C).

Figure 5. Log (carbon/active sites) vs. Temperature, deg K, for Velva lignite and Wyodak subbituminous coal chars prepared at 973, 1023, and 1073K (700, 750 and 800°C).

Figure 6. Carbon/active sites for Velva lignite and Wyodak subbituminous chars prepared from 10% calcium additive-raw coal mixture at 700, 750, and 800°C.

3.4 Primary Separation of Liquid By-Products

3.4.1. Literature Survey

Coal liquids are complex mixtures of water, phenolics, aromatics, nitrogen bases, sulfur-containing compounds, and fine particulates. The present state of coal liquid upgrading technology involves condensing these complex mixtures and reprocessing to upgrade. This literature search is the first step in a long-term development process to extend and improve on current coal liquid upgrading technology, such as that represented by the Great Plains Gasification Plant (GPGP) and various vendor-offered processes. The GPGP will soon begin upgrading the crude phenol stream to cresylic acids. This stream, in addition to the rectisol naphtha and tar oil streams, was previously burned in the plant's boilers and superheaters to produce steam. The HRI Dynaphen Process, an extension of Hydrocarbon Research, Inc.'s commercially proven hydrodealkylation (HDA) technology, can be used to upgrade coal liquids to benzene and phenol.

Numerous low severity pyrolysis processes have been economically unsuccessful in the past because it was assumed that the coal tar liquids could be sold for an attractive profit to pay for the operation of the plant. This was never realized in practice. Therefore, the success of a mild gasification process will depend on obtaining a premium value for the char. However, the economic viability of the mild gasification process will be enhanced by the production of high end-value liquid products requiring minimal upgrading. A reduction in the complexity and cost of liquid upgrading may be

accomplished by incorporating a primary separation step with the primary condensation. In addition, it may be possible to adjust the product slate (e.g., by catalytically hydrotreating the pyrolysate in the vapor phase utilizing the hydrogen in the product gas) to reduce downstream processing and meet changes in market demand.

A complete and consistent set of physical property data for the liquids from mild gasification is not available in the literature. Mild gasification refers to coal pyrolysis at temperatures less than 800°C (1472°F) and pressures less than 10 atm. The Morgantown Energy Technology Center (METC) has contracted with an independent laboratory with expertise in assaying petroleum products to establish standard and consistent data for one mild gasification liquid. These data are necessary to: (1) make comparisons between liquids produced in various mild gasification processes and petroleum and other liquid fuels, (2) evaluate the potential markets and upgrading techniques required for mild gasification liquids, and (3) generate and validate models for evaluating various upgrading alternatives and predicting fuel performance characteristics based on physical and chemical properties. Data from early research are of limited use, since they were not obtained using standard techniques and thus are not presented on a consistent basis. Therefore, it was decided as a first step to focus the literature search on coal pyrolysis liquids from more recent investigations.

Appendix A contains additional data on the liquids from the Char Oil Energy Development (COED) process. These data are included because the EERC mild gasification process is a simplification and improvement of the COED process. Appendix B contains additional references on the products from the low-temperature pyrolysis of coal.

CHARACTERISTICS OF PYROLYSIS LIQUIDS

The following analyses are commonly used to characterize mild gasification liquids:

- elemental analysis for carbon, hydrogen, nitrogen, sulfur, and oxygen;
- water content;
- specific gravity;
- viscosity;
- heating value;
- atmospheric and vacuum distillation (ASTM D-86 and D-1160, respectively) and/or simulated distillation using gas chromatography (ASTM D-2887);
- aliphatics/aromatics ratio.

In addition to distillation and viscosity data, flash point, cloud point, water and sediment percent by volume, carbon residue, percent ash, percent sulfur, copper strip corrosion, and cetane number are commonly used to determine whether a liquid meets fuel specifications. Mass spectrometry, gas chromatography, and ¹³C nuclear magnetic resonance are used to determine the compounds present in a particular mild gasification liquid fraction.

The quality and quantity of mild gasification liquids depend on coal type and process conditions. For example, high volatile bituminous coals give the highest liquid yields, while low-rank coals give much lower yields. The

former tend to yield higher molecular weight species desired as pitch for anode production, and the latter yield lower molecular weight species with high phenolic content suitable as chemical intermediates (13). Temperature, pressure, reactor configuration, heating rate, and reaction atmosphere all affect the yield and composition of the liquid by-products.

Under rapid heating conditions in a fluidized-bed reactor, yields of heavier polynuclear aromatic hydrocarbons are greater than in a fixed-bed slow heating rate reactor. In a fixed-bed reactor, free radicals produced during pyrolysis may be hydrogenated in situ by donatable hydrogen. This increases the quality of the liquids (as defined by the H/C atomic ratio), but results in a lower yield. Additional cracking of the primary products often occurs in the fixed bed, producing lower molecular weight liquids. The higher H/C ratio of the fixed-bed liquids is due to the presence of a larger amount of hydro-aromatic and naphthenic compounds and fewer polycyclic aromatic compounds. In this case, the pyrolysis products tend to bear little resemblance to the structures present in the parent coal (14).

The COED Process (Char Oil Energy Development)

The COED Process was developed from May 1965 to June 1975 under a series of contracts between FMC and the United States Government. The goal of the project was the development of an economic process for converting coal to gas, liquid, and solid products with a higher value than the coal itself. Coals ranging in rank from lignite to high volatile A-bituminous were processed in the COED pilot plant.

The COED pilot plant consisted of a coal preparation system for pulverizing and partially drying coal, a staged fluidized-bed pyrolysis process operating at near atmospheric pressure, a pressurized, rotary-drum precoat filter for removing solids from the pyrolysis oil, a fixed-bed catalytic hydrotreater, and oil recovery and hydrogen by-product gas handling facilities. Figure 7 is a flow diagram of the COED process. A four-stage process was used to overcome the agglomerating tendencies of the coal feed. Lignite and subbituminous coals could be processed in two stages, while bituminous coals required three or more stages. Typical operating temperatures for the four stages were 550, 850, 1050, and 1550°F, respectively. Originally the product recovery system consisted of a two-stage direct water quench, followed by one stage of indirect cooling. Late in 1972, an oil absorption tower was installed in parallel with the original aqueous quench system, so that either recovery method could be used. The purpose of installing the oil absorption tower was to recover product liquids in separate boiling ranges. Properties of the product liquids from bituminous coal runs with the oil scrubber (D-300) on-line are given in Table 5. Additional data for the COED process are given in Appendix A. Since the EERC mild gasification PDU is a simplification and improvement of the COED process, these data should prove valuable.

GREAT PLAINS GASIFICATION PLANT (GPGP)

The tar oil, crude phenol, and rectisol naphtha streams are the liquid by-product streams produced from the gasification of Beulah-Zap lignite at the GPGP. All three streams have been used to fire the plant's boilers and superheaters to produce steam. Plans are currently underway to upgrade the

4 OF 4

TABLE 5

PROPERTIES OF OIL DERIVED FROM UTAH KING COAL COED RUN PDU-168B

Molecular Weight	<u>D-300 Bottoms</u>		<u>D-300 Top</u>		<u>Decanter</u>	
	390		280		240	
	<u>°F</u>	<u>Density g/cc</u>	<u>°F</u>	<u>Density g/cc</u>	<u>°F</u>	<u>Density g/cc</u>
	356	0.89	189	0.97	140	0.86
	410	0.88	223	0.97	203	0.95
	428	0.82	298	1.03	219	0.96
	446	0.87			347	0.77
	464	0.92				

Distillation at 10 mm Hg, converted to atmospheric pressure using the "Esso Charts."

	<u>D-300 Bottoms</u>		<u>D-300 Top</u>		<u>Decanter</u>	
	<u>10 mm(F)</u>	<u>760 mm(F)</u>	<u>10 mm(F)</u>	<u>760 mm(F)</u>	<u>10 mm(F)</u>	<u>760 mm(F)</u>
	<u>300°</u>	<u>550°</u>	<u>236°</u>	<u>472°</u>	<u>160°</u>	<u>378°</u>
IBP	330	586	250	489	180	403
1 ml	352	612	272	516	194	420
2	390	658	290	538	200	428
5	444	721	320	574	228	462
10	540	832	390	658	280	526
20	544*	836*				
23	436	712	330	586		
30	470	751	380	646		
40	504	791	434	709		
50	530	820	470	751		
60	560	855	510	797		
70	642*	947*				
78		566	861			
80		578	875*			
90						

	<u>D-300 Bottom</u>		<u>D-300 Top</u>		<u>Decanter</u>	
	<u>Temp. °F</u>	<u>Viscosity, Centistokes</u>	<u>Temp. °F</u>	<u>Viscosity, Centistokes</u>	<u>Temp. °F</u>	<u>Viscosity, Centistokes</u>
	410	**	200	33.0	200	10.0
			220	25.0	220	6.5
			240	17.0	240	4.5
			260	11.0	260	3.5
			280	8.0	280	2.5
			300	6.0	300	2.0
			320	4.0	320	2.0
			340	3.0	340	1.5
			360	2.5	360	1.0
			380	1.5		

* Cracked

** D-300 bottom oil too stiff at 400°F for viscosity determination.

TABLE 6
TYPICAL ASTM-D86 DISTILLATION DATA FOR GPGP LIQUID BY-PRODUCTS

	<u>Rectisol Naphtha</u>	<u>Crude Phenol</u>	<u>Tar Oil</u>
Specific Gravity	0.825	1.072	1.014
Volume Percent Distilled	Temperature, °F		
	IBP = 100	210	210
10%	120	365	250
20%	140	380	360
30%	160	385	400
50%	180	395	440
70%	195	425	520
80%	215	470	640
90%	230	525	690
EP	270	570

Figure 8. TOSCOAL process.

After leaving the pyrolysis drum at a temperature of 800-1000°F, the char product falls through a trommel screen, is cooled, and sent to storage. The cooled ceramic balls pass over the trommel screen to a separate container and are returned to the ball heater by an elevator. The pyrolysis vapors are condensed and fractionated. The uncondensed gas, with a heating value of 500-1000 Btu/lb, may be used as a fuel for the ball heater. Properties of the product oil from TOSCOAL pilot plant runs with Wyodak subbituminous coal are given in Table 7.

LIQUID BY-PRODUCT MARKETS

Diesel Fuels and Fuel Additives

ASTM diesel fuel specifications are given in Table 8, along with specifications for a new diesel fuel which has been proposed by the Association of American Railroads (AAR) (17). The proposed new fuel, with a wider range of distillation temperature and viscosity and a lower minimum cetane rating than existing diesel fuels, may make it possible to economically blend mild gasification liquids with petroleum-derived fuels. It may be possible to use the fraction distillable below 700°F as blending stock, which accounts for over 90% of the total liquid.

Regulations modifying existing gasoline and diesel fuel compositions will be necessary to improve air quality and limit human exposure to critical hydrocarbons. Highly polluted areas such as Los Angeles may be required to use alternative fuels. Several Colorado cities, including Denver, require oxygenates in gasoline during the winter to reduce carbon monoxide emissions. Targets may include additional controls on gasoline volatility, limits on the amount of benzene in gasoline, and restrictions on undesirable hydrocarbons in both gasoline and diesel fuel. The concentration of aromatics in gasoline rose from 22% by volume in 1980 to the current level of 32 vol% in an effort to maintain octane quality in light of the phasedown of tetraethyl lead as an anti-knock agent (18). In addition to increasing the concentration of aromatics and isoparaffins, the lead phasedown has increased fuel volatility and decreased the concentration of low-octane normal paraffins. Restrictions may be imposed to limit the aromatics concentration to 25 to 30 vol%. In addition, benzene concentration may be limited to 0.5 to 1.0 vol% from the current level of 1-5 vol%.

Reduction of the aromatics in gasoline will be difficult to achieve, while maintaining fuel quality. Ethers are the only refinery component which can replace the octane quality lost when aromatics content is reduced. Methyl tertiary butyl ether (MTBE) is currently the most widely used additive to increase gasoline octane quality. It has been proposed that methyl aryl ethers produced from coal liquids would also be suitable as gasoline anti-knock additives. However, aryl ethers typically have higher boiling points and densities and lower octane blending values than alkyl ethers.

Military Jet Fuels

Jet fuels consist of four general types of hydrocarbons: paraffins, cycloparaffins or naphthenes, aromatics, and olefins. A typical fuel contains hundreds of different compounds. The proportions of hydrocarbon types are not

TABLE 7
PROPERTIES OF OIL FROM TOSCOAL PROCESS

Temperature	800°F	900°F	970°F
Run No.	C-8 ¹	C-2	C-3
Distillation, ²			
Vol% Recovered			
2.5	413°F	420°F	390°F
10	490	475	405
20	575	550	455
30	645	625	545
40	710	700	640
50	765	776	725
Viscosity, SUS ³			
180°F	122	123	128
210°F	63	66	69
API Gravity	7.9	4.5	1.9
Pour Point (°F)	90	100	95
Heating Value (But/lb)	16,590	16,217	15,964

¹ Feed coal differed from that used in Runs C-2 and C-3.

² Combination of True Boiling Point (TBP) and D-1160 distillations.

³ Saybolt Universal Seconds.

TABLE 8
ASTM DIESEL FUEL SPECIFICATIONS

	ASTM 1-D Highway Distillate	ATM 2-D Off-Highway Distillate	AAR Railroad	ASTM 4-D Marine Resid
Fuel Property				
Flash Point (°F), Min.	100	125	125	140
Cloud Point (°F), Max.	a	a	a	a
Water and Sediment (vol. %), Max.	0.05	0.05	0.05	0.05
Carbon Residue (% on 10% residuum), Max.	0.15	0.35	0.35	---
Ash (weight %), Max.	0.01	0.01	0.01	0.10
90% Distillation Temp. (°F)				
Minimum	---	540	---	---
Maximum	550	640	700	---
Saybolt Universal Viscosity at 100°F (sec)				
Minimum	---	32.6	29	45.0
Maximum	34.4	40.1	55	125.0
Sulfur (weight %), Max.	0.50	0.50	0.50	2.0
Copper Strip Corrosion, Max.	No. 3	No. 3	No. 3	---
Cetane Number, Min.	40	40	32	30

^a To be set by fuel purchaser.

directly controlled, although there are limitations on aromatics and olefins. Specifications for primary military jet fuels are given in Table 9. The navy fuel specification, JP-5, is identical to JP-8 except for a minimum flash point of 140°F for safety on aircraft carriers.

Coal liquids are unsuitable for use as jet fuels without hydroprocessing due to their high aromatics content, which causes smoking. Even a small percentage of naphthalenes causes problems. However, research with tar sand has shown that aromatic compounds can be converted to cycloparaffinic (naphthenic) compounds, which may be an excellent jet fuel.

The military (through various research contracts) has investigated the possibility of modifying jet fuel specifications to reduce fuel costs, while minimizing any effect on aircraft performance. This may be done by reducing the hydrogen requirement and increasing the aromatic content, thus reducing or eliminating the need for expensive hydrotreating of coal liquids. Allowing jet fuels to become more cyclic has the benefit of increasing the fuel density. Volumetric heating value increases with density, resulting in increased aircraft range and a lower freezing point. However, cyclic hydrocarbons have lower H/C ratios than their straight chain analogues, which results in increased flame radiation and soot formation. If the aromatics can be hydrogenated without cracking the naphthenic rings, coal/tar oil-derived liquids may be a preferred feedstock for the production of high density jet fuels.

Benzene and Phenol

Coke oven light oil was once an important source of benzene and BTX (benzene, toluene, xylene). However, the production of benzene from coke oven oil dropped precipitously between 1979 and 1982, from approximately 4% to less than 2% of total benzene production. The major sources of benzene and BTX are the catalytic reforming of petroleum naphtha, pyrolysis gasoline from the steam cracking of hydrocarbons to make ethylene and propylene, and hydrodealkylation of toluene. Other than gasoline, the largest markets for benzene and BTX are in the production of plastics and fibers. Major end uses for benzene include styrene for polystyrene production, cumene for phenol production, and cyclohexane for nylon production. Commercial grade benzene must have a minimum freezing point of 5.35°C, indicating a purity of 99.7%. Other specifications for commercial grades of benzene are given in Table 10 (15). Demand for benzene as an octane enhancer has increased due to the phaseout of leaded gasoline beginning in 1986. In addition, the demand for benzene as a feedstock for the manufacture of petrochemicals has soared. These factors combined to push the price of benzene to approximately \$1.50/gal in early 1987. The current selling price of benzene is \$1.45/gal (19).

Coal was once the dominant source of phenol and other precursors for the production of resins and plastics. The crude phenol from coke ovens and coal gasification plants contains tar acids, tar bases (pyridines, picolines), neutral oil, organic acids, and pitch. Crude phenol contains phenol, cresols, xylenols, ethylphenols, and, in some cases, catechols and resorcinol. Currently, approximately 90% of phenol is synthesized from cumene. In the cumene process, cumene (produced by alkylating benzene with isopropylene) is

TABLE 9
PRIMARY MILITARY FUEL SPECIFICATIONS

	JP-4 (Jet B) MIL-T-5624L	JP-8 (Jet A-1) MIL-T-83133A
Specific Gravity, 60°F	0.751-0.802	0.775-0.840
Gravity, API at 60°F	45-57	37-51
Distillation, Max. °F		
10% Recovered	---	---
20% Recovered	293	401
50% Recovered	374	---
90% Recovered	473	---
Final Boiling Point	518	572
Freezing Point, °F	-72 (-58)	-54
Viscosity,		
Centistokes at -40°F, Max.	---	8.0
Aromatics, Vol% Max.	25.0 (20.0)	25.0 (20.0)
Olefins, Vol% Max.	5.0	5.0
Sulfur, Wt% Max.	0.40 (0.30)	0.40 (0.30)
Net Heat of Combustion,		
Btu/lb, Min.	18,400	18,400
Hydrogen Content, Wt%, Min.	13.6	13.6
Thermal Stability, JFTOT		
Pressure Drop, mm Hg, Max.	25	25
Heater Deposit, Max.	3	3
Flash Point, °F, Min.	---	---
Vapor Pressure, Reid, psi	2-3	---

TABLE 10
BENZENE SPECIFICATIONS

Specification	Refined Benzene-535 (ASTM D2359-69)	Refined Benzene-485 Nitration-Grade (ASTM D835-71)	Industrial-Grade Benzene (ASTM D836-71)
Specific Gravity	0.8820-0.8869	0.8820-0.8860	0.875-0.886
Color (ASTM D1209)	No darker than 20 max. on the platinum cobalt scale.		
Distillation Range	Not more than 1°C including 80.1°C	Not more than 1°C including 80.1°C	
Solidifying Point	5.35°C min.	4.85°C min.	
Acid Wash Color (ASTM D848)	No. 1 max.	No. 2 max.	
Acidity (ASTM D847)	Nil	No free acid	
Sulfur Compounds	Free of H ₂ S and SO ₂	Free of H ₂ S and SO ₂	
Thiophene	1 ppm max.		
Copper Corrosion (ASTM D849)	Copper strip shall not show discoloration.		
Nonaromatics (ASTM D2360)	0.15% max.		

oxidized with air to cumene hydroperoxide which is converted by aqueous acid to phenol and acetone. Phenols are produced in the catalytic cracking of petroleum. The effluent from the cracker is washed with sodium hydroxide, primarily to remove mercaptans and organic sulfur compounds, and phenols and cresols are simultaneously extracted as the sodium salts. The caustic waste can be processed to recover phenols, cresols, and xylenols. Most synthetic phenol is sold at a purity of over 99.5% to control the properties of subsequent synthesis products. Typical specifications for phenol are given in Table 11. The selling price of phenol rose from \$0.20/lb in 1986 to \$0.45/lb in early 1987, with the current selling price at \$0.41/lb (19).

The HRI Dynaphen process can be used to convert alkylphenols in coal liquids to benzene and phenol. A flow diagram of the Dynaphen process is shown in Figure 9. In the Dynaphen reactor, cresylic acids are dealkylated, and some dehydroxylation also occurs. Unconverted alkylphenols and toluene and xylene (the products of dehydroxylation) are recycled to the Dynaphen reactor, yielding benzene and phenol as the main products.

CONCLUSIONS

Coal liquids have potential uses as military jet fuels, octane enhancers, blending stock for diesel fuels, pitch binders for coke briquetting, and intermediates for the production of valuable chemicals such as phenol and benzene. The challenge is to reduce the number of upgrading steps required and to limit the consumption of hydrogen. Coal liquids are complex mixtures of hundreds of compounds, and their composition is dependent on the coal used and conditions of pyrolysis (including temperature, reaction atmosphere, and reactor configuration). Therefore, it will be necessary to establish a program of bench- and pilot-scale research to identify the optimum primary separation and upgrading steps required to produce a slate of liquid products from a specific mild gasification process capable of meeting changes in market demand.

3.4.2 Cryogenic Trap for CPU Product Sampling

Construction of the new insert for the cryogenic trap has been completed. The new design of the insert should significantly increase the time that the product gas is in contact with the wall of the trap that separates the gas from the cooling fluid. The expected decrease in condensable materials passing through the trap should help improve the material balance and protect downstream instruments.

3.4.3 Design of a Small Batch Gasifier

A laboratory-scale fluidized-bed reactor will be interfaced with a mass spectrometer to determine the effects of rapid heatup on the distribution of liquid products. The interface will allow identification of the major components of the pyrolysate directly as they are formed, without an intermediate condensation step. Information learned may make it possible to adjust the product slate (e.g. by catalytically hydrotreating the pyrolysate in the vapor phase, utilizing the hydrogen in the product gas) to reduce down-

TABLE 11
PHENOL SPECIFICATIONS

Property	Specification	Test Method
Appearance	Crystalline Solid	Visual
Color of Melt, APHA	10 max.	ASTM D-1686
Color of NaOH Solution	1.5 max.	ASTM D-1500
Freeze Point, °C	40.6 max.	ASTTTM D-1493
Turbidity of Melt, APHA	1 max.	HC 390A-80
Iron, ppm	0.5 max.	WT-2
Water, wt%	0.07 max.	ASTM D-1631
Nonvolatile Residue, wt%	0.05 max.	ASTM D-1353
Impurities by GC, ppm		
α-methyl styrene	100 max.	
2-methylbenzylfuran	25 max.	
di-methylbenzyl alcohol	100 max.	
acetophenone	5 max.

Figure 9. Dynaphen process.

stream processing and meet changes in market demand. A better developed design of the laboratory-scale reactor is illustrated in Figure 10.

Figure 10. Schematic of laboratory-scale reactor.

3.5 Gas Cleanup and Separation

3.5.1 Design of a Versatile Test Area in CPU

In the scenario where the CPU would be closely coupled to a fuel cell, there are significant constraints on the concentrations of contaminants that can be tolerated. Among these constraints is the requirement that the fuel gas to the fuel cell should contain no more than 10 ppm of particles greater than 1 micron in diameter to limit fouling. This would be most efficiently achieved by reducing particulate levels without cooling the product gas from the CPU.

Several particulate removal systems are in various stages of development. Depending on availability, ceramic candles, sintered metal, high-temperature fabric filters, and others will be tested. The Vortex Venturi described in the following section will be evaluated for its ability to remove fine particulates. To permit flexibility, a test area is being designed which should accommodate the filtration systems to be tested. Figure 11 is a schematic of the hot-gas cleanup test area.

Figure 11. Schematic of hot-gas cleanup test area.

In addition to operation of the CPU, the mild gasification PDU is planned to have a fairly intensive operation schedule. Product gas from the CPU functioning as the calciner will be available for testing of hot-gas cleanup devices also. Particulates produced by the calciner should be sufficiently similar to those produced by the CPU to permit shakedown and preliminary evaluation of the particulate removal systems.

3.5.2 Vortex Venturi for Gas Separation

This device is an ultrahigh G cyclone, originally developed with the intent of removing particulate from stack gases. The original research (20) demonstrated that 98.5% of particles having an average diameter of two microns were removed. Particles driven to the wall of a converging throat were captured and removed from the device in a film of water flowing down the throat. For a variety of reasons, the concept proved unfeasible as a stack gas scrubber and was abandoned, following granting of the patent, by its inventors and assignee.

Centrifugal forces in the converging throat were as high as 20,000 times the acceleration of gravity, comparable to those encountered in the gaseous diffusion process for uranium enrichment. The apparently laminar flow conditions in the throat, as indicated by the lack of reentrainment of water

film or particulates, suggest that significant gas separation may be possible. The ratio of molecular weights of CO_2 , CO , or CH_4 to H_2 is orders of magnitude greater than that of ^{235}U and ^{238}U isotopes in the form of UF_6 vapor. A further possibility, within the scope of this program, is to use the same principle for hot particulate removal, which may be substantially more effective than by conventional cyclones.

A test unit has been built and is now ready for characterization tests. This unit, shown schematically in Figure 12, is a simplified version of the device used by the original inventors (20) for laboratory confirmation of the claims subsequently cited in their patent. This experimental effort was assisted by W.B. Hauserman, presently Principal Investigator of this study. Presentation of further details of the device shown in Figure 9 and discussion of fundamental principles involved will be deferred pending a new invention disclosure which is in preparation. The disclosure will cover novel design features, not envisioned by the original inventors, that may justify a separate patent for a gas separation device and/or a hot, high-pressure particulate removal application, both beyond the scope of the original inventors.

Figure 12. Schematic of Vortex Venturi.

4.0 PRESENTATIONS AND PUBLICATIONS

An abstract of a paper entitled "Characterization of Gasification Coal Char" was submitted for presentation at the Pittsburgh Coal Conference in September, 1990. The manuscript is due by July 1.

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APPENDIX A
COED PILOT PLANT DATA

The data in this appendix are from COED report PCR-708. The COED pilot plant was also operated using lignite and subbituminous coals, however, no data on these runs were located. A water quench system was used in place of the oil scrubber for the majority of the runs, but no data on those runs were available. The EERC mild gasification PDU is a simplification and improvement on the COED process; therefore, it is expected that the liquids from the EERC PDU will possess qualities similar to those from the COED process.

COED Process (PCR-708)

ASTM Distillation Data for Oil from PDU Runs with Oil Scrubber, D-300

Run Number: PDU-163

Coal: Crown (Illinois #6)

Coal Type: ¹Bituminous

Time Period, hr: 49 to 57 0 to 57 49 to 57

	D-300 Bottom	D-300 Top ²	Decanter
Vol. % Distilled	Temp., (°F)	Temp., (°F)	Temp., (°F)
IBP	226	212	208
5	576	475	428
10	604	513	448
15	626	532	468
20	649	550	489
24	660		
25		568	513
30		586	540
35		601	561
40		615	586
45		628	608
50		640	626
55		651	642
60		662	662
65		673	673
70		684	687
72		684	
75			709

Temp., (°F)	Viscosity ³ , centistokes	Temp., (°F)	Viscosity ² , centistokes	Temp., (°F)	Viscosity, centistokes
205	31,800	---	---	230	21.0
260	30,600			241	15.3
302	490			300	6.6
338	104			348	3.9
374	34			388	1.9

¹ Time increment represented by sample. Zero time was the start of coal feeds to the second stage.

² No oil recovered from top section of D-300. Analysis represents material drained from column at end of run.

³ All viscosities determined by Bendix Ultra Viscometer (vibrating reed type).

Run Number: PDU-165

Coal: Peabody No. 10 (Illinois #6)

Coal Type: Bituminous

Time Period, hr: 32 to 40 0 to 40 32 to 40

	D-300 Bottom	D-300 Top ²	Decanter
<u>Vol. % Distilled</u>	<u>Temp., (°F)</u>	<u>Temp., (°F)</u>	<u>Temp., (°F)</u>
IBP	250	210	208
5	507	214	428
10	595	450	444
15	608	484	459
17	617		
20		507	473
25		529	493
30		549	520
35		567	545
40		581	565
45		595	581
50		608	592
55		622	601
60		626	609
61		626	
65			617
70			624
75			631
80			635

<u>Temp., (°F)</u>	<u>Viscosity³, centistokes</u>	<u>Temp., (°F)</u>	<u>Viscosity², centistokes</u>	<u>Temp., (°F)</u>	<u>Viscosity, centistokes</u>
310	11,000	200	105.0	200	70.0
315	6,000	220	45.0	220	35.0
320	3,500	240	23.0	240	16.0
330	1,750	260	12.0	260	9.5
340	850	280	7.5	280	6.0
350	400	300	5.5	300	4.0
		320	3.0	320	3.0
		340	2.0	340	2.0
		360	1.5	360	1.5

¹ Time increment represented by sample. Zero time was the start of coal feeds to the second stage.

² No oil recovered from top section of D-300. Analysis represents material drained from column at end of run.

³ All viscosities determined by Bendix Ultra Viscometer (vibrating reed type).

Run Number: PDU-167A
 Coal: Utah King
 Coal Type: Bituminous
 Time Period¹, hr:

	42 to 58	42 to 58	42 to 58
	D-300 Bottom	D-300 Top ²	Decanter
<u>Vol. % Distilled</u>	<u>Temp., (°F)</u>	<u>Temp., (°F)</u>	<u>Temp., (°F)</u>
IBP	246	298	208
5	561	450	441
10	603	482	473
15	617	509	505
20	626	536	540
21	626		
25		562	565
30		585	590
35		606	612
40		626	628
45		644	640
50		658	649
55		669	655
60		679	664
65		685	667
69			667
70		694	
75		702	
80		707	
85		718	
88		720	

<u>Temp., (°F)</u>	<u>Viscosity³, centistokes</u>	<u>Temp., (°F)</u>	<u>Viscosity², centistokes</u>	<u>Temp., (°F)</u>	<u>Viscosity, centistokes</u>
235	20,000	190	12.0	190	29.0
240	10,500	200	9.5	200	27.0
260	2,800	220	6.0	220	18.0
270	1,800	240	4.5	240	10.0
280	1,250	260	3.5	260	6.5
290	700	280	2.5	280	4.5
300	400	300	2.0	300	3.5
310	275	320	1.5	320	2.5
320	200	340	1.0	340	1.5
330	150	360	0.5-1.0	360	1.0
340	110				
350	80				
400	75				

¹ Time increment represented by sample. Zero time was the start of coal feeds to the second stage.

² No oil recovered from top section of D-300. Analysis represents material drained from column at end of run.

³ All viscosities determined by Bendix Ultra Viscometer (vibrating reed type).

Run Number: PDU-167B
 Coal: Utah King
 Coal Type: Bituminous
 Time Period¹, hr:

	29 to 37	29 to 37	29 to 37
	D-300 Bottom	D-300 Top	Decanter
Vol. % Distilled	Temp., (°F)	Temp., (°F)	Temp., (°F)
IBP	207	266	207
5	374	464	208
10	558	491	216
15	599	511	455
20	626	531	487
22	626		
25		550	512
30		568	555
35		585	581
40		599	608
45		612	621
50		624	637
55		635	646
60		642	655
65		648	660
70		653	664
75		637	666
80		658	
85		660	
89		664	

Temp., (°F)	Viscosity ³ , centistokes	Temp., (°F)	Viscosity ² , centistokes	Temp., (°F)	Viscosity, centistokes
280	35,000	190	15.0	200	50.0
290	15,600	200	11.5	220	26.0
300	6,000	220	7.5	240	14.5
310	2,800	240	5.0	260	9.0
320	1,800	260	3.5	280	6.0
330	1,100	280	2.5	300	4.0
340	650	300	2.0	320	3.0
350	340	320	1.5	340	2.0
380	100	340	1.0	360	1.5
400	45	360	0.5-1.0		

¹ Time increment represented by sample. Zero time was the start of coal feeds to the second stage.

² No oil recovered from top section of D-300. Analysis represents material drained from column at end of run.

³ All viscosities determined by Bendix Ultra Viscometer (vibrating reed type).

APPENDIX B
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6.2 Chemistry of Sulfur Removal in Mild Gas

SULFUR REMOVAL FROM COAL/MILD GASIFICATION CHAR

**Quarterly Technical Progress Report
for the Period January - March 1990**

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SULFUR REMOVAL FROM COAL/MILD GASIFICATION

1.0 INTRODUCTION

The objective of this research is to develop analytical methods for quantitating the sulfur forms in coal and char. Better analytical methods are needed to more accurately determine the chemistry of the sulfur contained in raw coal and char, in order that effective means for sulfur removal from coal--either during or before mild gasification char production--can be developed. A primary goal of this work is to develop techniques for directly quantitating the pyritic and organic sulfur in coal and chars. Direct measurement techniques are needed, because in the American Society for Testing and Materials (ASTM) method for determining sulfur forms in coal, pyritic sulfur content is calculated based on the amount of iron extracted from the coal using nitric acid, and organic sulfur content is calculated to be the difference between the sum of the pyritic and sulfatic sulfur contents and the total sulfur content. For coals with significant quantities of nitric acid-soluble iron in forms other than pyrite (such as pyrrhotite and iron oxides), the ASTM method may provide an inaccurate measurement of pyritic sulfur content, which would also result in an inaccurate measurement of organic sulfur content.

The research is divided into two tasks: analytical methods development and char characterization. The analytical methods developed will be used (in addition to ASTM methods) to quantitate sulfur in a series of chars produced in the 1-lb/hr continuous fluid-bed reactor (CFBR) at the University of North Dakota Energy and Environmental Research Center (EERC), as a means of evaluating in situ sulfur removal techniques for incorporation into the mild gasification process under development at EERC.

2.0 CHAR PRODUCTION

Analytical methods development will be based on studies of Indiana No. 3 coal and up to eight chars produced from the coal in the 1-lb/hr CFBR including:

1. High sulfur-content char--produced under mild conditions that remove very little sulfur.
2. Char that contains a significant quantity of elemental sulfur.
3. Low sulfur-content char--produced under conditions that significantly reduce total sulfur content.
4. Low pyritic sulfur-content char--produced at high temperature.
5. Char produced in the presence of tetralin.
6. Char produced under hydrogen.
7. Char produced in the presence of ionic calcium--probably dolomite (calcium-magnesium carbonate)--under nitrogen, and under a mixture of hydrogen and nitrogen.
8. Char produced under nitric oxide (NO).

To obtain Chars 1-4, a series of chars was produced in the CFBR under nitrogen, using varying temperatures and residence times. The chars were sent to AMAX for ASTM sulfur-forms and total sulfur analysis. Total sulfur analysis was also performed at EERC with a Leco sulfur analyzer. The results of the char sulfur analyses are shown in Table 1, along with sulfur analyses of the Indiana coal from which the chars were made. The actual feed coal for the CFBR was the -60 x +200-mesh coal. Removal of the -200-mesh material from the initial -60-mesh feed coal was necessitated after an unsuccessful attempt to feed the -60-mesh coal; the reactor had to be shut down because of a feed-auger plug caused by coal fines. No problems were encountered during feeding of the -60 x +200-mesh coal.

TABLE 1
CFBR CHARS FOR ANALYTICAL METHODS DEVELOPMENT

	wt% Sulfur (moisture-free)				
	Total Sulfur		Sulfur Forms (AMAX)		
	EERC	AMAX	Pyr.	SO ₄	Org.
Indiana No. 3 Coal					
1/4 x 0	4.09	4.89	0.48	1.31	3.11
-60 mesh	5.43	6.45	3.47	0.37	2.60
-60 x +100 mesh	5.09	5.65	2.78	0.26	2.61
-100 x +230 mesh	5.63	6.14	3.13	0.31	2.71
-230 mesh	6.76	7.06	4.33	0.47	2.26
-60 x +200 mesh (CFBR Feed Coal)	4.90	NA ¹	NA	NA	NA
Chars					
Temp °F (°C), Residence Time					
1) 660° (350°), 25 min	5.13	5.62	2.45	-0.29	2.88
2) 660° (350°), 2 hr	5.07	5.72	2.57	0.09	3.06
3) 750° (400°), 25 min	4.97	5.00	2.13	0.16	2.72
4) 750° (400°), 2 hr	4.86	5.02	2.11	0.11	2.80
5) 840° (450°), 25 min	4.75	5.03	2.16	0.15	2.72
6) 840° (450°), 2 hr	4.87	4.96	2.06	0.14	2.75
7) 930° (500°), 25 min	4.59	4.83	1.84	0.12	2.87
8) 1290° (700°), 25 min	3.82	4.25	0.54	0.06	3.65
9) 1290° (700°), 2 hr	4.07	NA	NA	NA	NA
10) 1470° (800°), 6-hr ²	NA	1.25	0.04	0.04	1.17

¹ Not analyzed.

² Char 10 was made in the 30-lb/hr gasifier normally used for catalytic gasification.

All chars were produced under nitrogen with no steam, using staged heating, which works as follows: Coal is reacted at 660°F (350°C) to yield char, which is then reacted at 750°F (400°C) to yield char, which is then reacted at 840°F (450°C), etc. Since char is lost during processing at each temperature, enough coal must be reacted at 660°F (350°C) to ensure the recovery of 1290°F (700°C) char in a quantity sufficient for analysis.

Based on the analytical results, the chars representative of the sulfur-form and content requirements that define Chars 1-4 were selected for study in the development of sulfur analysis techniques. Char 1 was chosen as the high-sulfur content char, and Char 10 was chosen as both the low-sulfur content and the low pyritic sulfur content char. Char 8 was substituted for Char 10 in two of the analytical studies (Supercritical Carbon Dioxide Extraction and Perchloroethylene Soxhlet Extraction), since at the time of the studies, Char 10 was unavailable. Based on screening tests to determine elemental sulfur levels, the raw coal was chosen to represent the char containing a significant quantity of elemental sulfur (0.1%), because all of the chars analyzed displayed extremely low elemental sulfur contents (about 0.003%). Char 5 was also selected for analysis, since its 840°F (450°C) reaction temperature falls within the temperature range of observed agglomeration effects.

3.0 SUPERCRITICAL CARBON DIOXIDE EXTRACTION

Selected 400-mg (approximately) coal and char samples were extracted sequentially with about 1.2 mL/min of supercritical CO₂ (400 atm of pressure) at 131°F (55°C) for 10 minutes, then at 840°F (450°C) for an additional 25 minutes (about 15 minutes of this time was required for heating to 840°F). The extracts were designated as the Low-Temperature Extract (collected over the first 10 minutes of extraction) and the High-Temperature Extract (collected over the remaining 25 minutes), respectively. The extracts were collected by bubbling the extracting CO₂ fluid through a vial containing benzene. Benzothiazole was then added as an internal standard, and the extracts were analyzed using gas chromatography/mass spectrometry (GC/MS) and GC/atomic emission detection (GC/AED). The recently acquired atomic emission detector can monitor individual compounds (as they elute from a GC column) for the presence of sulfur, carbon, hydrogen, nitrogen, and oxygen. Most importantly for this work, the AE detector can simultaneously monitor for the presence of carbon, nitrogen, and sulfur. The atomic emission data can be stored and used to quantitate (by weight percent) the amount of sulfur, nitrogen, and carbon in an extract, or in a specified simulated distillate fraction of the extract. This allows plotting a simulated distillation curve showing the weight percent of sulfur distilling over a specified temperature range.

Before analyzing the supercritical fluid extracts, the ability of the AE detector to accurately quantitate organic sulfur on a weight-percent basis (regardless of how the sulfur was bound) was tested by analyzing 13 quantitative standards including alkylthiophenes, thiazole, thiocresol, mono- and di-sulfides, alkylthiols, and dibenzothiophene. On the basis of these analyses, it was determined that the GC/AED response per unit sulfur was the same (with a relative standard deviation of plus or minus 10%), regardless of

how the sulfur was bound. Thus, an average response factor can be used to quantitate the organic sulfur in each extract based on GC/AED analysis. The calibration for elemental sulfur (S_8) was not as successful; however, this is thought to be a chromatographic rather than an AED problem. The amounts of elemental and organic sulfur extracted from the coal and four chars are shown in Table 2, as micrograms of sulfur extracted per 400 milligrams of sample. Extractions were performed on three samples of -60-mesh Indiana No. 3 coal and two samples of each char.

With the exception of elemental sulfur, no sulfur species, and only traces of other organics, were found in the low-temperature extracts. The elemental sulfur was found primarily as S_8 , with lesser amounts as S_6 . None of the low-temperature extracts of the chars contained detectable amounts of any kind of sulfur. Approximately 150 significant sulfur organics were extracted from the chars (except the 1290°F (700°C) char) at 840°F (450°C). GC/MS analysis showed phenol- and catechol-related organics as major non-sulfur-containing species and alkyl thiophenes and alkyl benzothiophenes as the major sulfur-containing species (see Figures 1 and 2).

Table 3 shows the sulfur contents (determined using a Leco sulfur analyzer) of the coal and chars before and after extraction. The higher sulfur content of the extracted coal (compared to the unextracted coal) is due

TABLE 2
SUPERCRITICALLY EXTRACTED SULFUR

Sample		(μg S/400 mg SAMPLE)					
		Extracted S 131°F (55°C)			Extracted S 840°F (450°C)		
		Test 1	Test 2	Test 3	Test 1	Test 2	Test 3
Indiana Coal		176	212	168	173	185	178
Char Temp °F (°C)	Residence Time						
660° (350°)	25 min	ND ¹	ND	NP ²	215	207	NP
840° (450°)	25 min	ND	ND	NP	39	37	NP
1290° (700°)	25 min	ND	ND	NP	<1	<1	NP
660° (350°)	2 hr	ND	ND	NP	179	212	NP
750° (400°)	25 min	ND	ND	NP	117	126	NP

¹ Not detected (Detection limit was <1 μg S/sample).

² Not performed.

Figure 1. AED sulfur chromatogram showing sulfur-containing species extracted at 840°F (450°C) from 660°F (350°C) char using supercritical carbon dioxide. The vertical scale is the relative emission intensity at 181 nm.

Figure 2. AED carbon chromatogram showing carbon- (as well as sulfur-) containing species extracted at 840°F (450°C) from 660°F (350°C) char, using supercritical carbon dioxide. Sulfur-containing species are detected when the AED monitors for carbon, since these species also contain carbon. The vertical scale is the relative emission intensity at 193 nm.

TABLE 3
SULFUR CONTENT OF SUPERCRITICAL CARBON DIOXIDE EXTRACTS¹

		Sulfur Content (wt%)			
		Unextracted Samples	Extracted Samples (Duplicate Tests)		
Indiana Coal, MF		5.43	5.36	5.88	5.75
Char					
Temp °F (°C)	Residence Time				
660° (350°)	25 min	5.13	4.26	4.79	NP ²
660° (350°)	2 hr	5.07	4.30	3.91	NP
750° (400°)	25 min	4.97	4.00	4.40	NP
840° (450°)	25 min	4.75	4.25	4.17	NP
1290° (700°)	25 min	3.82	3.85	3.74	NP

¹ Extraction at 131°F (55°C) for 10 min, then at 840°F (450°C) for 25 min.

² Not performed.

to the extraction of a significant amount of non-sulfur-containing organic material in addition to organic sulfur compounds. In order to compare the sulfur contents of the raw and extracted coal on an equal basis, the initial weight of coal can be adjusted by subtracting the weight of these other extractable organics, which results in a coal sulfur content, on an organic extract-free basis, of 6.53%. Similar calculations can be performed with the char sulfur data, to show effective sulfur content reductions of about 1.5 percentage points for all of the chars except the 1290°F (700°C) char. The data for this char indicate that treatment at 1290°F (700°C) causes organic sulfur to be virtually inaccessible to the supercritical carbon dioxide.

The data in Table 3 shows that supercritical carbon dioxide extraction can lower measured sulfur content in chars by as much as 20%. This result could have significance if it could be proven that all or most of the sulfur extracted from the chars was organic. However, quantitation of the sulfur in the extracts using GC/MS and GC/AED did not yield sulfur extract weights equal to those calculated based on the Leco sulfur analyses of the chars before and after extraction. In most cases, GC quantitation accounted for only about 20% of the sulfur calculated to have been extracted. Possible explanations for this include:

1. A significant portion of the sulfur removed from the coal and chars is extracted as, or reacts during or after extraction to form S₂, which, because of its high volatility, would be difficult to detect using the chromatographic techniques employed for this work.

2. A significant portion of the extracted sulfur is contained in gaseous molecules that are insoluble, or only marginally soluble, in the benzene used to trap the extracted sulfur compounds. However, such molecules would escape into the atmosphere and probably emit unpleasant odors--and none were noticed.
3. A significant portion of the extracted sulfur is contained in molecules too large (and/or nonvolatile) to elute through the GC column.

The lack of quantitative agreement between the total sulfur analyses performed with the Leco and the analyses performed using GC will be further investigated.

4.0 SOXHLET PERCHLOROETHYLENE EXTRACTION

A sample of -60 x +200-mesh Indiana No. 3 coal and four chars made from the coal were Soxhlet-extracted for 5 hours using perchloroethylene at 250°F (121°C). All of the chars were made in the 1-lb/hr CFBR; three were made under nitrogen, and one was made under a mixture of hydrogen and nitrogen, in the presence of dolomite (dolomite was added to 930°F (500°C) char in an amount equal to 20 wt% of the char). The results of the extractions are shown in Table 4.

In Table 4, the column labeled "Total Wt% Extracted" refers to the percentage of the sample extracted, which includes both sulfur-containing and non-sulfur-containing species. The weight of this extracted material was

TABLE 4
PERCHLOROETHYLENE EXTRACTIONS

	<u>Total Wt%</u> <u>Extracted</u>	<u>Wt% Sulfur</u>			<u>% Sulfur</u> <u>Removed</u>
		<u>Before Ex. (MOF¹)</u>			
		<u>Before Ex.</u>	<u>After Ex.</u>	<u>After Ex.</u>	
-60 x +200-mesh Indiana	17.93	4.82	5.87	4.46	24.02
660°F (350°C) Char	14.15	5.65	6.58	4.43	32.67
840°F (450°C) Char	17.13	4.62	5.57	4.10	26.39
1290°F (700°C) Char	0	3.74	3.74	3.69	1.30
1290°F (700°C) Char	0	4.28	4.28	3.61	15.65
(with dolomite)					

¹ Moisture- and oil-free--sulfur contents in this column were calculated based on the weight of coal remaining after subtracting the weight of the material extracted with perchloroethylene.

subtracted from the total weight of each sample to calculate its moisture- and oil-free (MOF) sulfur content before extraction. The percentage of sulfur extracted was then obtained by comparing the MOF before-extraction sulfur content with the after-extraction sulfur content.

Comparison of the perchloroethylene extraction results with the results of the supercritical carbon dioxide extractions shows that both solvents removed similar amounts of sulfur from the coal and chars. Also, the two extraction techniques gave almost identical sulfur-content reductions when performed on identical char samples, and neither solvent extracted a significant quantity of sulfur from the 1290°F (700°C) char. These observations suggest that the same sulfur species are extracted by the two techniques; however, this has not been substantiated by rigorous analysis.

5.0 OTHER ORGANIC SULFUR ANALYSES

Three other methods are being studied for organic sulfur quantitation; two are described in this section. The first involves reacting coal or char with t-butylhypochlorite to selectively oxidize organic sulfur species to sulfoxides, which can then be quantitated using infra-red (IR) spectroscopy. The success of the method is dependent on whether the hypochlorite reacts with all of the organic sulfur species in the coal or char and whether undesirable interference effects can be subtracted from the IR spectra.

A second, related organic sulfur quantitation method also involves the above mentioned oxidation to yield sulfoxides, which are then reacted with an alcohol (trimethylbicycloheptanol). When the alcohol reacts with the coal- or char-bound sulfoxides, it is converted to a ketone (trimethylbicycloheptone). The ketone is then quantitated using gas chromatography (GC) to provide a measurement of organic sulfur content (the moles of ketone detected equal the moles of organic sulfur oxidized). Like the first method, the accuracy of this method is limited by the extent of the oxidation reaction, but, unlike the first method, this is the only limiting factor, since the GC analysis needs no development.

6.0 INORGANIC ANALYSES

X-ray fluorescence (XRF) analysis is normally performed on the ash of a coal to determine the coal's mineral content, but the technique can also be applied (with varying degrees of accuracy) to raw coal. The quantitative accuracy of the technique when applied to coal usually depends primarily on the coal's carbon content: the higher the carbon content, the less accurate the analysis. According to XRF analysis of -60-mesh Indiana No. 3 coal, the moisture-free (MF) sulfur content of the coal is 3.5%. Leco sulfur analysis puts the coal's MF sulfur content at 5.1%, and XRF analysis of the ash of the coal gives an MF coal sulfur content of 4.1%.

An attempt was made to determine total sulfur and pyritic sulfur content of the Indiana coal using computer-controlled scanning electron microscopy (CCSEM). The results obtained were unsatisfactory, and the analysis will be

performed again using a new coal sample. An inherent problem with using CCSEM to determine sulfur content in coal is that quantitation (with the instrumentation and software presently employed at EERC) is ordinarily based on energy dispersive spectra (EDS) emitted from analyzed particles. EDS for an analyzed particle can vary in intensity depending on the matrix surrounding the particle and the composition of any particles in close proximity. These interferences can result in significant quantitation errors. However, accurate sulfur quantitation may be possible using wavelength dispersive spectra SEM (WDS-SEM), since WDS are not subject to as severe a variation in intensity as EDS.

The third method being studied for sulfur quantitation involves performing three sequential WDS-SEM scans across a specific area of the sample--which has been mounted in a epoxy plug, cross-sectioned, and polished. When the plug is cross-sectioned, particles contained in the plug are also cross-sectioned. This random slicing of particles theoretically allows SEM, which is a surface analysis technique, to be used for bulk analysis. However, since SEM is a surface analysis technique, the described method will need to be validated by other more widely accepted bulk quantitative analyses. The first SEM scan monitors for sulfur, the second for iron, and the third for calcium. Each scan traverses a straight line between identical starting and ending locations on the sample plug. The three scans are "superimposed" on each other to determine the occurrence of pyrite, calcium sulfate, and organic sulfur, using the following rationale: The simultaneous detection of iron and sulfur is indicative of pyrite, the simultaneous detection of calcium and sulfur is indicative of calcium sulfate, and the detection of sulfur without the simultaneous detection of either iron or calcium is indicative of organic sulfur. The successful development of this method would provide a means of directly quantitating the pyritic and organic sulfur contents in coal.

Low-temperature ashes were prepared from samples of -60 x +200-mesh Indiana No. 3 coal and the chars selected for analysis. The low-temperature ashing procedure is used to minimize the occurrence of thermally driven mineral transformations and sulfur vaporization. The effect of low-temperature ashing can be seen in Table 5, which is a comparison of selected elemental concentrations in oxygen-free low- and high-temperature ashes made from Indiana No. 3 coal, as determined using XRF analysis. The low-temperature ashes will be analyzed using XRD, XRF, and SEMPC. CCSEM analysis will also be performed on the coal and chars. The analyses will be compared, with each other and with results of other analytical techniques, to ascertain the fate of sulfur species during mild gasification.

TABLE 5
COMPARISON OF LOW- AND HIGH-TEMPERATURE ASHES (XRF)

	<u>-60-mesh Indiana No. 3 Low-temp ash</u>	<u>-60 x +200-mesh Indiana No. 3 High-temp ash</u>
Silicon	25.7 wt%	35.8 wt%
Aluminum	13.5	19.3
Iron	28.1	33.4
Calcium	5.9	4.1
Magnesium	1.0	1.1
Potassium	1.0	2.5
Sulfur	22.3	2.5
Other	2.5	1.3

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