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**LOW-RANK COAL RESEARCH UNDER THE UND/DOE
COOPERATIVE AGREEMENT**

Quarterly Technical Progress Report for the Period April—June 1983

By
George A. Wiltsee, Jr.

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By
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Energy Research Center
Grand Forks, North Dakota

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QUARTERLY TECHNICAL PROGRESS REPORT
FOR THE PERIOD
APRIL 1983-JUNE 1983

George A. Wiltsee, Jr.

University of North Dakota
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Prepared for the
U.S. Department of Energy
Office of Fossil Energy
Under Cooperative Agreement DE-FC01-83FE60181

PREFACE

This is the first Quarterly Technical Progress Report produced under the UND/DOE Cooperative Agreement for Low-Rank Coal Research. On April 11, 1983 the former Grand Forks Energy Technology Center of DOE became the University of North Dakota Energy Research Center. The funding provided under the Cooperative Agreement was sufficient to maintain the continuity of the research program at the Center; so that, except for minor changes in task objectives or schedules, the program in the First Annual Research Plan for the Cooperative Agreement is a direct continuation of the on-site work that was ongoing under the Center's FY 1983 approved PTPA's.

The transfer of the Center and its employees from Federal to University status was relatively trouble-free. However, it did involve a great deal of extra work for several months before and after the event. It also involved the establishment of a new organizational structure which created new responsibilities for many employees. As a result, it was decided not to write the normal quarterly report for the period January-March 1983; the extra effort required would have been too great. Instead, it was decided to incorporate into this quarterly report all significant accomplishments and findings from the work done at the Center during its last quarter as a Federal institution. Thus, the work reported in this volume actually represents the period January through June, 1983.

HIGHLIGHTS

Gasification Wastewater Treatment & Reuse

- Two of the most successful gasifier runs, with durations of 169 and 118 hours of slagging operation, were concluded voluntarily when all of the lignite on site was consumed. Enough wastewater, nominally 23,000 gal, was generated from these tests to support a 50-day test in the cooling tower simulation unit.
- Wastewater was processed by solvent extraction and steam stripping to concentrations of about 150 mg/l phenol and 600 mg/l ammonia (the reported design values for the Great Plains Gasification Associates (GPGA) plant). Significant differences were noted in the UNDERC stripped gas liquor (SGL) analysis as compared to reported GPGA data. After accounting for phenol contributions, the bulk of the COD in UNDERC SGL is from methanol and hydantoin, with the hydantoin accounting for about 70% of the COD, whereas fatty acids are reported to comprise most of the COD in GPGA SGL.
- A new analytical GC method using on-column injection, a highly polar bonded phase fused silica capillary column and multi-level calibration with standards was developed for rapid analysis of hydantoin and phenols in water.
- The first 50-day cooling tower test assessing the use of SGL as makeup at 10 cycles of concentration was completed. Preliminary conclusions are as follows:
 - Hydantoin, which are not removed by solvent extraction with di-isopropylether, are not stripped or biodegraded in the cooling tower either; rather, they cycle up to roughly ten times the input concentration.
 - SGL at 10 cycles of concentration supports biological activity and leads to severe biofouling in process equipment including PVC cooling tower packing, and to high corrosion rates on carbon steel surfaces.
 - A significant amount of phenol in the SGL is stripped in the cooling tower and exhausted to the atmosphere.
- Hydantoin can be extracted from wastewater using N-butyl alcohol as a solvent. However, since the alcohol has considerable solubility in water, it remains to be seen if the solvent losses are commensurate with the benefits obtained by replacing the non-biodegradable hydantoin with degradable alcohol.

Fine Coal Cleaning

- Construction of the coal cleaning laboratory has been completed. Grinding, sizing, and preliminary analyses have been completed on the first 24 coal samples to be studied as part of the PETC study on the washability of 156 samples of western coals.

Coal-Water Slurry Preparation

- Batch autoclave studies with several North Dakota lignites have shown that moisture reduction via hot-water drying is a function of time, particle size, and temperature, with over 85 pct moisture reduction at 340°C. For particle sizes less than 350 μ in diameter, a 5-minute residence time at temperatures up to 340°C removes all the moisture possible at a given temperature. Significant decarboxylation as determined by acid group titration and increased heating value does not occur below temperatures of about 260°C.
- Moisture readsorption tendencies were determined for several of the dried lignites by equilibrating a filtered sample in a 100 pct relative humidity chamber at ambient temperature. Readsorption decreased with increasing drying temperature going to 28 pct moisture when dried at 200°C to 10 pct moisture for lignite dried at 340°C. These compare with undried lignite which equilibrated at 35 pct moisture.
- Detailed flow diagrams were prepared for the 5 major processing areas of the coal-water slurry (CWS) hot-water drying (HWD) PDU defining necessary instrumentation and piping details. The bulk of the pressure vessels, instrumentation, piping, fittings, pumps, valves, and even the structural steel and overhead crane to be used in the CWS HSD PDU have been salvaged and refurbished from Project Lignite at UND, thus minimizing capital costs. Construction of the PDU will begin immediately upon completion of the building to house the activity.

Coal Liquefaction

- Batch autoclave tests have been performed simulating the first stage of a staged liquefaction process for low-rank coals. Low-temperature tests, at 380°C, with 20 minutes at temperature were used to determine yields as a function of CO concentration in the reductant. While good yields were obtained when at least 25 pct of the reductant was CO, excellent conversion (55 pct maf coal to soluble residue and 28 pct to distillate) was obtained with pure CO as the reductant. Also, since the gas yields were so low at 380°C, reductant consumption was also very low at about 2.5 pct.
- In another staged liquefaction test, a very low sulfur subbituminous coal from Alberta was liquefied using staged catalysts as well as staged heating. The test was also different in that a tar sand bitumen was used as vehicle solvent. The first stage reaction was performed as a once-through test in the CPU using synthesis gas at ~2800 psi and 380°C using H_2S and K_2CO_3 as catalyst. The second

stage reactions were performed in a hot-charge autoclave without mineral separation at a series of temperatures from 415° to 440°C with pure H₂ at ~2800 psig using H₂S and K₂MoO₄ as catalysts. While there are far too many variables to interpret the results, this test based on recommendations from the Alberta Research Council, showed the tremendous potential of staged heating and a bitumen solvent, when the yields are examined. This test gave a high yield of total liquid product, over 78 pct based on the maf coal charged, which was of high quality as evidenced by the fact that over 88 pct of the liquid was distillable. Thus it becomes possible to convert one of the poorest coals, in terms of liquefaction yields, and solvent, in terms of alkane content, by a combination of catalysts and staged heating into predominately liquid products.

SO_x/NO_x Control

- NO_x reduction using throwaway catalysts was tested using a bench scale reactor. Early results indicate lignite ash containing iron oxide does provide significant reduction of NO_x in conjunction with NH₃ injection.
- Testing of lignite fly ash for NO_x reduction in the pilot scale facility equipped with a high temperature baghouse yielded reduction of up to 29 pct. Values were increased if fly was pulverized. Injection temperatures from 1000-1800°F had little effect on reduction of NO_x observed.

Particulate Characterization

- Detailed characterization of particulates generated by pulverized-coal combustion of Beulah lignite has been completed. Information generated included particle size distribution and particle composition as a function of size.
- Data generated indicates an increase in the concentration of sodium and sulfur with decreasing particle size. This result appears to support a vaporization-condensation mechanism of particulate formation.

Waste Characterization

- Manuscripts were prepared for publication on previous laboratory studies showing that the leaching of chemical species from alkali FGD sludge appears to be a function of both the physical and chemical properties of the sludge material. The leach mechanism appears to be solubilization of the chemical pollutants from the sludge solid to the aqueous medium. Generally, the leach profile demonstrates a stable or decreasing leach rate.

Combustion Research and Ash Fouling

- Construction of the bench scale combustion device was completed. Following the addition of a fluidized-bed coal feeder (early in the next quarter), this device will allow photographs and surface temperature determinations to be made for single coal particles in combustion-like environments.

Fluidized Bed Combustion

- A 480-hour run on the 2.25 sq. ft. AFBC using a high sodium Beulah lignite successfully completed using a gabbro (plagioclase-feldspar) bed. Bed agglomeration has occurred in previous tests at similar conditions using high sodium coals and silica sand bed material, usually after less than 200 hours of operation.
- Bed agglomeration using a silica sand bed and high-sodium lignite was prevented when the sodium concentration in the coal was reduced by only 10% using ion-exchange. Sodium levels in the bed were higher than has been previously observed except in cases where bed agglomeration had occurred. The run lasted 480 hours.

Ash and Slag Characterization

- A method is under development for the rapid low-temperature ashing of low-rank coal samples in an oxygen plasma. The treatment of the sample with ammonium acetate prior to ashing removes cations associated with the carboxylic acid groups of the organic structure, and results in a significant decrease in the time required to obtain complete ashing.
- A predictive equation has been developed to calculate low-rank coal ash slag viscosity at a given temperature from the slag composition. The equation was originally developed in France to calculate viscosities of metallurgical slags. The most notable modification made to adapt the equation to low-rank coal ash slags was to subdivide the slags into categories on the basis of silica content, then developing specific regression equations for each category.

Organic Structure

- A solution of cadmium oxide in ethylenediamine and water was used to extract cellulose from lignites. Subsequent hydrolysis of the cellulose produces a mixture of sugars, which can be esterified and analyzed by gas chromatography. The initial results indicate that the amount of cellulose in lignite is very low, probably less than 0.01%.
- The determination of methoxy ether groups is being used as an approach to determining the amount of residual lignin in lignite. The coal is oxidized, the resulting methyl esters hydrolyzed to

methanol, and the methanol analyzed by gas chromatography. Results on the lignite studied so far indicate that the lignin content is about 5%.

Distribution of Inorganics

- An in-house sample bank has been established for the collection, storage, and characterization of low-rank coal samples, which would be available to all Coal Science projects, or to other laboratory projects within the Center. So far eight North Dakota lignites and two Montana subbituminous coals have been collected, and are in various stages of characterization.

Physical Properties and Moisture

- A unique experimental method has been developed for measurement of free-sliding shear strength of lignite at particle sizes up to 0.75 inch, which are larger by a factor of 20-25 than the particle sizes able to be accommodated in traditional procedures. The shear strength of loosely compacted lignite was found to decrease with decreasing particle size in the range of 0.75 to 0.065 inch particles.
- Small-angle x-ray scattering measurements of pore size have shown that changes in the micropore structure occur upon heating above 225°C, possibly as a result of escape of volatile matter such as CO₂. Above 300°C the surface area of the micropores continues to increase but the size of the pores remains nearly constant.

Supercritical Solvent Extraction

- A semicontinuous apparatus for supercritical solvent extraction of low-rank coals was constructed and placed in operation. So far, runs have been made using toluene, benzene, and water as supercritical solvents.

Pyrolysis and Devolatilization

- Preliminary experiments on pyrolysis of lignite samples using a small tubular reactor in a tube furnace has shown that heating to maximum temperatures of 800°C at rates of about 0.5°C/sec virtually totally destroys the aliphatic character. The percent of the original amounts of hydrogen, nitrogen, oxygen, and sulfur still remaining in the char agrees reasonable well with literature compilations of data on coal pyrolysis and hydropyrolysis.

TABLE OF CONTENTS

	<u>Page</u>
1.0 GASIFICATION WASTEWATER TREATMENT AND REUSE	1-1
1.1 Goals and Objectives	1-1
1.2 Accomplishments	1-2
1.2.1 Pilot Plant Operations	1-2
1.2.1.1 Gasification	1-2
1.2.1.2 Solvent Extraction-NH ₃ Stripping Train	1-2
1.2.1.3 Cooling Tower - Phase I Test.....	1-7
1.2.1.3.1.1 Cooling Tower	1-7
1.2.1.3.1.2 Test Heat Exchangers	1-9
1.2.1.3.1.3 Dynamic Deposit Monitors	1-9
1.2.1.3.1.4 Trim Heat Exchanger	1-9
1.2.1.3.2 Preliminary Cooling Tower Test Results	1-10
1.2.1.3.2.1 System Control	1-10
1.2.1.3.2.2 Blowdown Quality	1-13
1.2.1.3.2.3 Heat Transfer Evaluation	1-13
1.2.1.3.2.4 Corrosion	1-20
1.2.1.3.2.5 Biological Monitoring	1-20
1.2.1.3.2.6 Atmospheric Emissions	1-22
1.2.1.3.2.7 Cooling Tower Conditions After Testing	1-23
1.2.1.4 Activated Sludge	1-25
1.2.2 Analytical	1-28
1.2.2.1 Methods Development	1-28
1.2.2.1.1 Phenols and Hydantoins by Capillary GC	1-28
1.2.2.1.2 Ion Chromatography	1-28
1.2.2.1.3 Deposits in the Cooling Tower	1-28
1.2.2.1.4 A Colorimetric Determination of Hydantoins	1-28
1.2.2.1.5 Investigation of Solvent Extraction of Hydantoins ...	1-29
1.3 References	1-29
 2.0 HYDROGEN PRODUCTION FROM LOW-RANK COALS	 2-1
 3.0 FINE COAL CLEANING	 3-1
3.1 Goals and Objectives	3-1
3.1.1 Uniform Data Base on Fine Coal Cleaning of Western Coals	3-1
3.1.2 Advanced Cleaning of Western Coals	3-3
3.2 Accomplishments	3-3
3.2.1 Centrifugal Float-sink Studies	3-3

TABLE OF CONTENTS--Continued

	<u>Page</u>
4.0 COAL-WATER SLURRY PREPARATION	4-1
4.1 Goals and Objectives	4-1
4.2 Accomplishments	4-2
4.2.1 Autoclave Tests	4-2
4.2.2 Design of the Continuous Hot-Water Coal Drying Process Development Unit	4-3
4.2.2.1 Area 01--Slurry Preparation and Pumping	4-5
4.2.2.2 Area 02--Slurry Heating and Coal Drying	4-5
4.2.2.3 Area 03--Slurry Recovery and Separation	4-6
4.2.2.4 Area 04--Water Recovery and Slurry Concentration	4-6
4.2.2.5 Area 05--Product Storage	4-7
4.2.3 Coal-Water Slurry Preparation Facility-- Building Construction	4-7
4.2.4 Coal-Water Slurry Pilot Plant Construction Activities	4-7
4.2.5 Coal-Water Slurry Pilot Plant Design Studies	4-8
5.0 LOW-RANK COAL LIQUEFACTION	5-1
5.1 Goals and Objectives	5-1
5.2 Accomplishments	5-2
5.2.1 Catalytic Liquefaction of Low-Rank Coals	5-2
5.2.2 Low-Temperature Liquefaction	5-4
5.2.3 Staged Liquefaction of Highvale Subbituminous Coal	5-7
5.2.4 Characterization of Reactor Solids	5-12
5.2.5 Liquefaction Mechanisms and Kinetics	5-14
5.2.5.1 Autoclave Test Conditions and Net Yields	5-14
5.2.5.2 Characterization of Autoclave Products and Discussion of Results	5-15
5.2.5.2.1 Addition of H-Donor	5-15
5.2.5.2.2 Processing with Labelled Gases, $^2\text{H}_2/\text{CO}$	5-17
5.2.5.2.3 Processing with Labelled Gases, $\text{H}_2/^{13}\text{CO}$ (99+ pct)....	5-21
5.2.5.3 Conclusions	5-21
5.2.6 Solvent Effects	5-24
5.2.6.1 Analyses of Products	5-25
5.3 References	5-36

TABLE OF CONTENTS--Continued

	<u>Page</u>
6.0 COMBINED FLUE GAS CLEANUP/SIMULTANEOUS SO _x -NO _x CONTROL	6-1
6.1 Goals and Objectives	6-1
6.2 Accomplishments	6-2
6.2.1 Literature Search	6-2
6.2.2 Packed Bed Reactor Evaluation of Throw-Away NO _x Reduction Agents	6-3
6.2.3 Evaluation of Throwaway NO _x Reduction Reagents in the 130-scfm ^x PDU	6-5
6.2.4 Development of Continuous Bench-Scale Pressure Hydrator	6-10
6.2.5 Acquisition and Installation of Selective Catalytic Reduction (SCR) System	6-11
6.2.6 Evaluation of Operability and NO _x Reduction Capabilities of SCR System	6-12
7.0 PARTICULATE CONTROL AND HYDROCARBONS AND TRACE ELEMENT EMISSIONS FROM LOW-RANK COALS	7-1
7.1 Goals and Objectives	7-1
7.2 Accomplishments	7-2
7.2.1 Characterization of Beulah, ND Lignite	7-2
7.2.1.1 Background	7-2
7.2.1.2 The Particulate Test Combustor (PTC), Combustion Conditions, and Ash Sampling	7-3
7.2.1.3 Beulah Coal Analysis	7-3
7.2.1.4 Beulah Fly Ash Sampling	7-6
7.2.1.5 Particle Size Distribution	7-6
7.2.1.6 Bulk Ash Analyses and Analyses of Fractionated Ash	7-8
7.2.1.7 Scanning Electron Microscopy (SEM)	7-9
7.2.1.8 Auger-ESCA Observations	7-18
7.2.1.9 Conclusions	7-18
7.2.2 Publications and Presentations	7-18
7.3 References	7-19

TABLE OF CONTENTS--Continued

	<u>Page</u>
8.0 WASTE CHARACTERIZATION	8-1
8.1 Goals and Objectives	8-1
8.2 Accomplishments	8-1
8.2.1 Reports on Previous Investigations of FGD Wastes	8-1
8.2.1.1 Description of Pilot-Scale Wet Scrubber	8-2
8.2.1.2 Experimental Methods	8-3
8.2.1.3 Results	8-4
8.2.2 Laboratory Studies on Deleterious Elements in Waste Materials	8-9
9.0 COMBUSTION RESEARCH AND ASH FOULING	9-1
9.1 Goals and Objectives	9-1
9.2 Accomplishments	9-2
9.2.1 Construction of Bench-Scale Combustor	9-2
9.2.2 Gas Mixing System	9-2
9.2.3 Gas Heating System	9-3
9.2.4 Coal Feed System	9-6
9.2.5 Reaction Chamber	9-6
9.2.6 Photographic System	9-6
9.2.7 Optical Pyrometer	9-8
9.2.8 Computer System	9-9
9.2.9 Future Plans	9-10
9.2.10 Topical Report on Ash Fouling in Low-Rank Coal Combustion	9-12
9.2.11 Examination of Alkali Species in Low-Rank Coal Combustion Systems	9-12
9.2.12 Combustion Testing of Selected Low-Rank Coals	9-12
9.3 References	9-13
10.0 FLUIDIZED-BED COMBUSTION OF LOW-RANK COALS	10-1
10.1 Goals and Objectives	10-1
10.2 Accomplishments	10-1
10.2.1 Pilot-Scale Testing to Examine Bed Agglomeration	10-2
10.2.2 Lignite Symposium Paper	10-5
10.2.3 Heat Transfer	10-7
10.2.4 2.25-Ft ² AFBC Modifications	10-7
10.2.5 Topical Report	10-7
11.0 COAL/WATER SLURRY COMBUSTION	11-1

TABLE OF CONTENTS--Continued

	<u>Page</u>
12.0 ASH AND SLAG CHARACTERIZATION	12-1
12.1 Goals and Objectives	12-1
12.2 Accomplishments	12-2
12.2.1 Ashing of Low-Rank Coals	12-2
12.2.1.1 Background	12-2
12.2.1.2 Operating Conditions	12-2
12.2.1.3 Pre-treatment of Samples	12-3
12.2.1.4 Preliminary Results of Trial Ashing	12-3
12.2.1.5 ASTM and High Temperature Ashing	12-4
12.2.2 Slag Viscosity	12-4
12.2.2.1 Background	12-4
12.2.2.2 Viscosity Measurements	12-4
12.2.2.3 Correlation with Composition	12-8
12.2.3 Slag-Refractory Interactions in Gasification	12-11
12.3 References	12-11
13.0 ORGANIC STRUCTURE	13-1
13.1 Goals and Objectives	13-1
13.1.1 Cellulose	13-1
13.2 Accomplishments	13-2
13.2.1 Cellulose Extraction And Analytical Methods	13-2
13.2.2 Gas Chromatographic Methods For Carbohydrate Analysis	13-2
13.2.2.1 Results of Extraction and Analysis	13-3
13.2.2.2 Conclusions of Extraction and Analysis	13-3
13.2.2.3 Future Experiments with Carbohydrates	13-3
13.2.3 Lignin	13-3
13.2.4 Methoxy Determination	13-4
13.2.4.1 Results of Methoxy Determinations	13-4
13.2.4.2 Conclusions of Methoxy Determinations	13-5
13.2.4.3 Future Experiments of Methoxy Determination	13-5
13.3 References	13-5
14.0 DISTRIBUTION OF INORGANICS	14-1
14.1 Goals and Objectives	14-1
14.2 Accomplishments	14-1
14.2.1 Collection and Storage of Low-Rank Coals	14-1
14.2.2 Chemical Fractionation	14-2
14.2.3 Carboxylic Acid Group Determination	14-4
14.2.4 Mineral Analysis by Scanning Electron Microscopy	14-4
14.2.5 Lithotypes	14-5
14.2.6 Pressure Differential Scanning Calorimetry (PDSC)	14-5
14.3 References	14-6

TABLE OF CONTENTS--Continued

	<u>Page</u>
15.0 PHYSICAL PROPERTIES AND MOISTURE	15-1
15.1 Goals and Objectives	15-1
15.2 Accomplishments	15-2
15.2.1 Shear Strength	15-2
15.2.2 Permeability	15-2
15.2.3 Mechanical and Thermal Friability	15-3
15.2.4 Pore Size Distribution	15-3
16.0 SUPERCRITICAL SOLVENT EXTRACTION	16-1
16.1 Goals and Objectives	16-1
16.2 Accomplishments	16-2
16.3 References	16-6
17.0 PYROLYSIS AND DEVOLATILIZATION	17-1
17.1 Goals and Objectives	17-1
17.2 Accomplishments	17-1
17.2.1 Review of Pyrolysis in Slagging Gasification	17-1
17.2.2 Small Scale Pyrolysis Experiments	17-3
17.2.2.1 Thermogravimetric Analysis	17-3
17.2.2.2 Tube Furnace Experiments	17-4
17.2.3 Large Sample Thermogravimetric Unit	17-6

1. - GASIFICATION WASTEWATER TREATMENT AND REUSE

Project No.: 7102, 7103

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1.1 GOALS AND OBJECTIVES

The principal goal of the University of North Dakota Energy Research Center (UNDERC) wastewater treatment program is to develop public data on environmentally acceptable means of treatment, either for reuse or disposal, of wastewater derived from slagging fixed-bed gasification (SFBG) of lignite. All wastewater treatment and reuse unit operations at UNDERC are designed to yield scaleable data and are operated on a real gasification effluent. To the degree that SFBG wastewater is representative of commercial fixed-bed gasification, an immediate goal is to assess the consequences, both process and environmental, for the use of solvent-extracted and ammonia stripped wastewater (stripped gas liquor--SGL) as makeup to a cooling tower. To the extent that problems are expected with the use of SGL as cooling tower makeup, another objective is to test alternative treatments that may be necessary if disposal is used rather than zero discharge. The long-range goal is to develop and validate a working model for wastewater treatment design ultimately capable of using as input basic coal characterization data.

To accomplish these objectives, the four major activities in the gasification wastewater treatment and reuse program during the first year of the cooperative agreement are;

1. Phase I cooling tower assessment using stripped gas liquor as makeup, to determine environmental parameters and process fouling rates in cooling tower circuit. Wastewater will be prepared by tar/oil/water separation, filtration, solvent extraction, and ammonia stripping.

2. Phase II cooling tower assessment using SGL treated by single-stage activated sludge processing followed by carbon adsorption as makeup.
3. Characterization of the organic contaminants in lignite-derived wastewater, before and after each stage of treatment. Emphasis will be placed on the mechanism and kinetics for hydantoin formation and on methods development as needs arrive in characterizing the different process streams.
4. Development and validation of working models for solvent extraction, steam stripping, inorganic fouling of cooling tower, and organics in cooling tower.

1.2 ACCOMPLISHMENTS

1.2.1 Pilot Plant Operations

To prepare wastewater for the cooling tower tests, wastewater must first be produced in the UNDERC slagging fixed-bed gasifier (SFBG) and then processed through a solvent extraction-ammonia stripping train. For the Phase I cooling tower test, the effluent from the ammonia stripping column, stripped gas liquor (SGL), was fed directly to the cooling tower. For the Phase II cooling tower test, the SGL will be processed through an activated sludge reactor and carbon adsorption columns before it is fed to the cooling tower. A summary of these operations follows.

1.2.1.1 Gasification

Four gasifier runs (See Tables 1-1 and 1-2) using Indian Head lignite were performed during the period covered by this report. Two of these runs, UND-2 and UND-4, were the longest (169 hrs) and third longest (118 hrs) in gasifier history. Both were concluded by voluntary shutdowns when the onsite supply of lignite was exhausted. A total of 23,000 gallons of wastewater was collected and stored during these runs.

Two runs during the reporting period were not successful. In UND-3, a leak in the water-cooled hearth plate resulted in slag plugging the taphole. In UND-5, refractory ran into the taphole and froze. In attempting to melt the material from the taphole with the backup taphole burner, a hole was burned in the water cooled hearth plate. Both runs ended with no production of wastewater for later cooling tower tests.

1.2.1.2 Solvent Extraction-NH₃ Stripping Train

The solvent extraction-ammonia stripping train operation during this reporting period consisted of four runs, each of one week duration. These runs were designated numbers 11 through 14. During these runs, the objective was to produce wastewater with phenol and ammonia concentrations similar to Great Plains Gasification Associates (GPGA's) expected concentrations of phenol (148 mg/L) (1) and NH₃ (593 mg/L) (1). Table 1-3 shows the results for the four runs.

TABLE 1-1
SUMMARY OF PROCESS PERFORMANCE

Run Number:	UND:	2	3	4	5
Date:	Start:	01/11/83	05/09/83	05/23/83	11/17/81
	End:	01/18/83	05/10/83	05/28/83	11/17/81
FEEDSTOCK, HOURS OF SLAGGING:					
Indian Head Lignite		168.8	11.1	118.4	0.0
CONTROLLED VARIABLES:					
Pressure, psig		300	300	300	300
O ₂ feed rate, scfh		6500	6500	6500	6500
O ₂ /steam mole ratio		0.9	0.9	0.9	0.9
DESIGN CHANGES:					
Hearth plate number		23	24	24	24
Water-cooled stirrer		No	No	No	No
Vert. Dist., tuyeres to taphole, inch		3 5/8	3 5/8	3 5/8	3 5/8
PRIMARY TAPHOLE BURNERS:					
Conventional/External/Adjustable		No	No	No	No
Integral ring		Yes	Yes	Yes	Yes
SLAGGING SECTION RELINED		No	No	No	No
RESPONSE VARIABLES:					
Coal feed, lb/hr		2071.8	No Material Balance!	2043.6	No Material Balance!
Fuel rate, maf, lb/hr		1238.1		1256.8	
Product gas, scf/lb of Coal-IGF		16.60		15.78	
O ₂ Use, scf/lb of coal		3.15		3.26	
Steam use, lb/lb of coal		.17		.17	
Heating value of gas, Btu/scf		328.8		324.4	
Average offtake gas temp., °F		320.7		326.7	
REASONS FOR SHUTDOWN:					
Voluntary (test completed)		Yes		Yes	
Loss of slag flow		--	--	--	--
Bridging in fuel bed		--	--	--	--
Malfunction of auxiliary equipment		--	Yes	--	Yes
Taphole burner malfunction		--	--	--	--

*Laboratory analysis not completed; see later reports.

TABLE 1-2
SUMMARY SHEET

	UND -2	UND-4
1. Run Number		
2. Total Slagging, hrs	168.83	118.35
3. Data Period, hrs	163.27	75.23
4. Oxygen/Steam Mole Ratio	0.90	0.92
5. Operating Pressure, psig	300.0	300.0
6. Oxygen Rate, cu ft/hr	6,517.9	6,663.0
7. Steam Rate, lb/hr	341.9	343.1
8. Fuel Rate, lb/hr	2,071.8	2,043.6
9. Fuel Rate, lb maf/hr	1,238.1	1,256.8
10. Fixed Carbon Rate, lb/hr	677.5	674.4
11. Flux Rate, lb/hr	0.0	0.0
12. Flux Ratio, lb flux/lb fuel ash	0.00	0.00
13. Inert Gas Free Product Gas Rate, cu ft/hr	34,390.	32,256.
14. Inert Gas Free Drawdown Gas Rate, cu ft/hr	0.	0.
15. Total Gas, Inert Gas Free, cu ft/hr	34,390.	32,256.
16. Slag Recovered, lb/hr	92.4	90.7
17. <u>Oxygen Consumption, Inert Gas Free Basis:</u>		
Per 1,000 cu ft Product Gas, cu ft	189.53	206.57
Per 1,000 cu ft CO+H ₂ , cu ft	220.36	241.59
Per lb Fuel, cu ft	3.15	3.26
Per lb maf Fuel, cu ft	5.26	5.30
18. <u>Steam Consumption, Inert Gas Free Basis:</u>		
Per 1,000 cu ft Product Gas, lb	9.94	10.64
Per 1,000 cu ft CO+H ₂ , lb	11.56	12.44
Per lb Fuel, lb	0.17	0.17
Per lb maf Fuel, lb	0.28	0.27
19. IGF Gas Production, cu ft/lb fuel	16.60	15.78
20. IGF Gas Production, cu ft/lb maf fuel	27.78	25.66
21. Cold Gas Efficiency, %	80.1	75.6
22. Operational Efficiency, %	86.1	82.2
23. IGF CO + H ₂ Production, cu ft/lb maf fuel	23.89	21.94
24. Average Offtake Temperature, °F	320.7	326.7
25. Gas Liquor Production, lb/hr	689.7	755.0

TABLE 1-3
RESULTS OF SOLVENT EXTRACTION AND
STEAM STRIPPING

Run No.	Water Processed Gallons	Total Phenol Exit Treatment Train Average mg/l	Total NH ₃ Exit Treatment Train Average mg/l
11	4300	123	547
12	4500	198	572
13	4600	180	652
14	3100	160	629

During runs 11 and 12, samples of the liquor before solvent extraction (S-2), between solvent extraction - NH₃ stripping (S-7), and after NH₃ stripping (S-10) were taken daily and analyzed. These results were averaged and the average analyses are presented in Table 1-4. The S-2 sample represents wastewater produced in the UNDERC slagging fixed-bed gasifier after gravity separation of tars and oils and rough filtration. The S-7 sample has been further processed through solvent extraction and a nitrogen stripping step to remove carryover solvent. The S-10 sample has been free - NH₃ stripped and is representative of the SGL fed to the cooling tower.

No major problems were encountered in preparing wastewater for the phase I cooling tower test with phenol and NH₃ concentrations similar to those expected by GPGA.

UNDERC analysis of SGL points to marked differences in the organic contaminants in SFBG wastewater versus design analysis for Great Plains (1). A typical analysis of the stripped gas liquor is compared with the analysis of SGL anticipated as feed to the cooling tower by GPGA in Table 1-5.

TABLE 1-4
WASTEWATER ANALYSIS

	S-2	S-7	S-10
Methanol	1450	1440	230
Ethanol	5	5	0
Acetone	40	50	10
2-Propanol	0	50	0
Acetonitrile	420	370	2
DIPE	0	3410	0
1-Propanol	1	5	0
Propionitrile	85	38	0
Phenol	4560	210	160
O-Cresol	650	0	0
P-Cresol	880	3	0
M-Cresol	950	3	0
Dimethyl Hydantoin	2280	2340	2140
Ethyl-methyl Hydantoin	510	520	490
Acetic Acid	16	11	0
Propionic Acid	8	3	0
Butyric Acid	2	--	0
pH	8.3	8.5	8.9
Alkalinity	23200	23100	1500
NH ₃	7890	7980	565
Resistivity	33	34	386
Sulfide	370	300	8
Cyanide	75	63	39
Thiocyanate	230	200	210
COD	27900	16200	5700

These numbers are averages of eight daily, steady state samples between 02/08/83 and 2/18/83.

TABLE 1-5
COMPARISON OF STRIPPED GAS LIQUOR (mg/l)

	GPGA	UNDERC
Methanol	--	230
Fatty Acids	1600	0
Phenol	150	160
Hydantoins	--	2630
NH ₃	500	565
COD	2880	5700

The reported analysis of SGL for the GPGA were generated at SASOL in 1974 from operation on 12,000 tons of North Dakota lignite that was shipped to South Africa (1). The major differences are the lack of fatty acids, the presence of significant amounts of hydantoin, and higher COD in the UNDERC wastewaters. Possible reasons for these differences could include vastly improved analytical techniques since 1974, the sampling location at SASOL, effluent from a dry-ash gasifier may be different than from a slagger, or that significant differences exist in Lurgi's proprietary gas quenching and tar separation steps as compared to those being used at UNDERC.

Differences in the gas quenching and tar separation steps could have a marked affect on final effluent analysis, since data indicate that hydantoin is not primary devolatilization products, but rather are produced during quenching and tar separation from the reaction of ketones, cyanides, ammonia, and carbon dioxide via reaction [1-1].

[1-1]

1.2.1.3 Cooling Tower - Phase I Test

1.2.1.3.1 Test Equipment Description

Construction of the cooling tower test loop was completed in February. Shakedown testing was performed and resulted in several minor modifications, including the installation of an additional drift eliminator. The configuration of the test equipment as assembled for Phase I testing is described in Figure 1-1.

1.2.1.3.1.1 Cooling Tower

The test cooling tower is a packaged Baltimore Air Coil Company, Model VXT-20WC with a forced draft fan which operates in a counterflow configuration. All wetted parts of the cooling tower are constructed of 304 stainless steel. Air/water are contacted in a corrugated packing constructed of molded PVC sheets. The cooling tower was larger than required for the test program and, as a result, a baffle was installed, dividing the tower into two compartments. Only one compartment is required to provide the desired liquid-to-gas ratio for the cooling tower tests. The overall dimensions of the tower are 3 x 3 x 6.5 ft. The sectional area of the compartment used in the test is approximately 5 ft².

FIGURE 1-1. The UNDERC cooling tower test equipment.

The cooling tower was installed indoors with inlet and exhaust air ducts open to the outside. A steam heat exchanger was installed in the inlet air duct and is designed to automatically control the inlet air temperature at a predetermined value (70°F). The forced draft fan is also equipped with dampers, which are controlled by a temperature sensor in the cooling tower sump, to control air flow through the tower. Air flow is controlled to maintain a constant cooling water sump temperature at 82°F. Access ports were installed in the exhaust duct to allow for measurement of exhaust air flow rates and sampling of the drift and evaporate leaving the tower.

1.2.1.3.1.2 Test Heat Exchangers

Cooling water leaving the cooling tower is pumped through two single-pass test heat exchangers. One heat exchanger (HE-2) is equipped with four carbon steel tubes 3/8 inch O.D. (0.305 inch I.D.) by 3 feet long. Two tubes are being operated at a cooling water velocity of 3 ft/sec and the remaining two tubes at 5 ft/sec. Each tube has its own flow controller, cooling water inlet and outlet thermistors for temperature monitoring, and differential pressure taps. The shell side of the heat exchanger is a closed cycle circulating water system containing a heating element and thermostat designed to maintain the shell side water temperature at 120°F and a tube wall temperature of approximately 100°F, with a heat flux of 8000 Btu/hr-ft².

Another heat exchanger (HE-1) is operated in parallel with HE-2 and contain two 304 and two 316 3/8 inch O.D. by 3-foot long, stainless steel tubes. One tube of each material is operated at a cooling water velocity of 3 ft/sec and the other at 5 ft/sec. These tubes are instrumented and the shell side water system of HE-1 is set up in the same as the shell side of HE-2. The shell side water temperature in HE-1 is maintained at 190°F in order to provide a tube wall temperature of $\approx 140^\circ\text{F}$, with a heat flux of $\approx 20,000$ Btu/hr-ft².

1.2.1.3.1.3 Dynamic Deposit Monitors

In addition to the test heat exchangers, two Calgon Dynamic Deposit Monitors (DDM) are operated in parallel with the test heat exchangers. A DDM consists of a two-inch clear plastic tube with a heating element (1/2 inch diameter) located in the center. The heating element contains a thermocouple for measurement of skin temperature. As fouling occurs, the skin temperature of the heating element increases to maintain the same heat flux into the cooling water. The change in this temperature can be correlated to determine the rate of degradation of the performance of heat transfer equipment. Cooling water flow through these DDMs in a series arrangement at a rate of 1.25 gpm, giving a linear velocity of 0.83 ft/sec across the heating element. The skin temperature of DDM-1 was set initially at 100°F and DDM-2 was set initially at 150°F.

1.2.1.3.1.4 Trim Heat Exchanger

The full cooling water flow passes through the heat transfer equipment. However, the temperature of the recombined cooling water stream is only raised to about 92°F after the test heat exchangers and DDMs. In order to maintain a cooling tower inlet water temperature of 120°F, the cooling water is passed through a trim heat exchanger. Low-pressure steam (20 psig) is used on the shell side to maintain a tube wall temperature of approximately 160°F.

Equipment design and operating conditions are summarized in Table 1-6.

1.2.1.3.2 Preliminary Cooling Tower Test Results

The Phase I cooling tower assessment using stripped gas liquor (SGL) started March 31, 1981. Blowdown was established 5 days later after ten cycles of concentration were reached. The fouling/corrosion test equipment (DDMs, HEs, coupons, corrosometers, corrators) was brought on line at this point and was not exposed to the recirculating water during cycle-up. The tower was seeded on day eight with activated sludge that had been acclimated to full strength SGL as well as an extract from the local soil.

A major air sampling campaign was performed by researchers from Argonne National Lab (ANL) after the system had been running for 14 days. Additional campaigns were performed by UNDERC researchers at days 25, 29, and 37. The sampling program is described in detail in a later section.

The Phase I cooling tower test was completed May 26, 1983, after 51 days of operation at ten cycles of concentration.

1.2.1.3.2.1 System Control

During startup, severe foaming was encountered. Foaming was controlled by adding approximately 5 ml of a commercial, glycol-based antifoaming agent every two hours. Unfortunately, the glycol-based agent used a light petroleum distillate as a solvent, which interfered with GC analyses for polar volatile species expected from bio-oxidation of organics. A silicon-based antifoaming agent from Calgon (CL-37), which has no GC interferences, replaced the glycol-based antifoaming agent starting May 2, 1983, and this was in turn replaced with Union Carbide #3882 on May 9, 1983. Both of the latter antifoam agents are silicone based, and were added at the rate of approximately 2.5 ml per hour to control foaming.

Cycles of concentration generally ranged from 8X to 10X (based on C1⁻ measurements) as shown in Figure 1-2.

Good control of the cycles of concentration was made possible by the relatively short system turnover time (≈ 11 hours) and preheating of inlet air, thereby reducing the variability of the evaporation rates.

TABLE 1-6

UNDERC COOLING TOWER TEST LOOP
EQUIPMENT DESIGN/OPERATING CONDITIONS

Cooling Tower

Makeup Rate (SGL)	0.26 gpm (24 hour average)
Condensate Feed Rate	0.023 gpm
Recirculation Rate	8.2 gpm
Blowdown Drift Rate	0.028 gpm
Air Flow Rate	820 acfm*
Inlet H ₂ O Temperature	120°F
Outlet H ₂ O Temperature	82°F
Cycles of Concentration	10 (24 hour average)

Heat Exchanger 1 (HE-1)

Tube Type	Tubes 1 and 3 - 304 L stainless Tubes 2 and 4 - 316 stainless
Velocity	Tubes 1 and 2 - 3 ft/sec Tubes 3 and 4 - 5 ft/sec
Heat Flux	20,000 Btu/ft ² hr
Skin Temperature	140°F
Shell Side Water Temperature	190°F

Heat Exchanger 2 (HE-2)

Tube Type	Carbon Steel
Velocity - Tubes 1 and 3	3 ft/sec
Velocity - Tubes 2 and 4	5 ft/sec
Heat Flux	8,000 Btu/ft ² hr
Skin Temperature	100°F
Shell Side Water Temperature	120°F

Dynamic Deposit Meters:DDM-1

Flow Rate	1.25 gpm
Velocity	0.83 ft/sec
Skin Temperature (Initial)	100°F
Heat Flux	3000 Btu/ft ² hr

DDM-2

Flow Rate	1.25 gpm
Velocity	0.83 ft/sec
Skin Temperature (Initial)	150°F
Heat Flux	6000 Btu/ft ² hr

Trim Heat Exchanger

Tube Type	316 stainless
Velocity	1.01 ft/sec
Shell Side Temperature	20 psig steam - 225°F
Skin Temperature	160°F
Outlet Water Temperature	120°F

TABLE 1-6 (Continued)

UNDERC COOLING TOWER TEST LOOP
EQUIPMENT DESIGN/OPERATING CONDITIONS

Special Test Equipment

Rohrbach Corrotrator/Probes
Rohrbach Corrosometer/Probes
Dissolved Oxygen Monitor
pH Monitor
Coupons (Concrete, Carbon Steel, 304 and
315 Stainless Steel)

* This is an average rate. Day to day values vary with inlet humidity and temperature.

CYCLES OF CONCENTRATION

CORRECTED FOR POLISHED WATER

FIGURE 1-2. Cycles of concentration as a function of time.

1.2.1.3.2.2 Blowdown Quality

Table 1-7 presents average chemical composition data for the cooling tower makeup and blowdown, after the system had stabilized at ≈ 10 cycles of concentration. The pH of the makeup averaged 9.1, with the pH of the blowdown being slightly lower at 8.0. The blowdown pH was steady throughout the run, ranging from 7.9 to 8.1.

All major species (>1 ppm basin concentration) were analyzed. The metal ions present in the system all cycled up to concentrations approaching a 10X increase, indicating that up to the time of sampling there had been no significant precipitation of any of the cations. The cycles as figured from the Na analysis correlated very well with that indicated from the C1 analysis (8.9 versus 8.8, respectively).

The average ammonia in the makeup was 570 mg/L and was increased by about 2.1X to 1200 mg/L in the blowdown. Based on these numbers, over 75 percent of the ammonia fed to the tower was "free" ammonia which could be stripped during steam stripping with a higher steam-to-wastewater ratio.

The phenol level in the blowdown was 154 ppm, with a corresponding makeup feed concentration of 145 ppm. The total cresol level was lower in the blowdown than in the makeup. A portion of the phenols and cresols in the makeup was undoubtedly consumed by the biological activity in the tower, but the potential for stripping portions of these organics also existed. The analysis of exhaust samples collected by ANL during the run indicated a substantial amount of phenol had been stripped in the tower.

The level of hydantoin present is of special interest when examining the blowdown quality. The level of hydantoin present in the makeup, averaging ≈ 2200 mg/L, were increased to ≈ 18200 mg/L in the blowdown (8.3 cycles). This indicated that the hydantoin were not appreciably stripped off with the more volatile portions, nor were they significantly degraded by biological activity, resulting in a very high concentration in the blowdown.

About 60 pct of the BOD from the makeup was consumed in the tower, with the makeup concentrations of 1550 ppm being cycled up ~ 4 X or 5800 ppm. TOC in the makeup averaged 2550 ppm and was cycled up 6.9X to 17,500 ppm. Of the volatile organic compounds, methanol is the only one detected in any appreciable quantity. It runs ~ 230 ppm in the makeup and is consumed and stripped to less than 50 ppm in the blowdown.

1.2.1.3.2.3 Heat Transfer Evaluation

The effect of using SGL on heat transfer surfaces is being evaluated by several different methods, the two major being Dynamic Deposit Monitors (DDM) supplied by Calgon Corporation, and Test Heat Exchangers. Data from the DDMs indicate that at low velocities, the use of SGL as makeup water will have a severe effect on heat transfer (see Figure 1-3). In DDM-1, which was operated at an initial skin temperature of 100°F, a 44 pct reduction in heat transfer was noted, with the heat transfer coefficient decreasing from about 130 to 70 Btu/hr-ft²-°F. In DDM-2, operated with an initial skin temperature of 150°F, the heat transfer loss was 31 percent, with the heat transfer coefficient decreasing from about 130 to 90 Btu/hr-ft²-°F.

TABLE 1-7
COOLING TOWER ANALYTICAL RESULTS

	Makeup	Blowdown
pH	9.1	8.0
Conductivity	2700	8100
Alkalinity (CaCO ₃)	1500	2600
Ammonia	570	1200
Phosphorous	0.4	3.0
Nitrates	<1	<1
Sulfate	16	150
Chloride	25	220
Cyanide	31	275
Thiocyanate	200	1720
Calcium	2.6	27.2
Sodium	170	1510
Silica	4.4	25.5
Magnesium	2.1	15.5
Iron	14.5	128
Copper	0.1	1.5
Manganese	0.1	0.7
Aluminum	0.3	2.0
Zinc	0.3	7.7
Arsenic	0.3	2.4
Boron	1.4	10.2
Chromium	<0.1	0.3
Lead	<0.1	0.1
Total Suspended Solids	40	890
Total Volatile Suspended Solids	20	720
Total Dissolved Solids	3,500	30,000
Total Volatile Dissolved Solids	2,900	23,000
BODs	1,550	5,800
TOC	2,550	17,500
COD	6,520	46,800
Dissolved Oxygen	0.5	6.5
Phenol	145	154
o-cresol	10	0
p-m-cresol	20	20
5-5-dimethyl hydantoin	1,700	14,400
5-ethyl-5-methyl hydantoin	500	3,800
Acetone	0	0
Acetonitrile	0	0
Propionitrile	0	0
Methanol	230	40
Ethanol	0	0
2-propanol	0	0
Diisopropyl ether	0	0
Density	1.0	1.0
Surface Tension	65	56

All units mg/l, with these exceptions

Conductivity	-- mmhos/cm
Density	-- g/ml
Surface Tension	-- dynes/cm

FIGURE 1-3. Heat transfer results from dynamic deposit monitors.

After being removed from service, the DDMs were dismantled and examined. The inlet headers into the DDMs were heavily fouled. The fouling in these headers is believed to have caused the flow reduction noted. The heating surfaces of the DDMs were coated with a black material, which was mostly biological in nature. The organic portion of the deposit was characterized as consisting primarily of 5,5-dimethyl hydantoin.

Data from the Test Heat Exchangers also indicates that scaling and/or fouling of the heat transfer surfaces is occurring primarily in the exchangers with carbon-steel metallurgy.

Pressure drop versus time is plotted in Figure 1-4 for HE-1 with SS metallurgy. The pressure drops for tubes 1, 2, and 3 showed little change throughout the test, and small decreases (<10 percent) were noted in the heat transfer coefficients for these tubes.

The pressure drop from tube 4 increased from an initial value of 12 inches of water to over 100 inches of water. After the run when the tube was removed, deposits on the inside of the tube were such that one could not see light through the tube. After two weeks of air drying, the deposit has dehydrated and exists as a thin layer of material on the tube surface, suggesting that the deposits found in the tube were largely biological.

Data from HE-2, carbon-steel metallurgy, are presented in Figures 1-5, 1-6, and 1-7. Figure 1-5 is a plot of pressure drop versus time for tubes 1 and 3 (velocity = 3 ft/sec). The pressure drop increased continually for the entire test, to above 100 inches of water for tube 1 and 50 inches of water for tube 3, from an initial pressure drop of 10 inches of water. The heat

FIGURE 1-4. Pressure drops across stainless steel high temperature heat exchange No. 1.

FIGURE 1-5. Pressure drops for low velocity carbon steel tubes in heat exchanger No. 2.

FIGURE 1-6. Heat transfer for low velocity carbon steel tubes in heat exchanger No. 2.

FIGURE 1-7. Pressure drops for high velocity tubes in heat exchanger No. 2.

transfer coefficient for these two tubes is plotted as a function of time in Figure 1-6. In tube 1, the coefficient decreased 56 pct during the test, from 240 to 105 Btu/hr-ft²-°F. A decrease of 17 pct, from 240 to 200 Btu/hr-ft²-°F was noted for tube 3.

Pressure drops for tubes 2 and 4 are presented in Figure 1-7. In both tubes, the pressure drop increased at an initial rate of approximately 5 inches of water per day indicating a relatively high initial rate of fouling. Both tubes were removed and inspected on day twelve. Deposits on the inside of the tubes formed a rough surface having the appearance of many miniature stalactites protruding from the tube surface. This tube roughness apparently caused the dramatic pressure drop increase noted across the tubes as there did not appear to be any appreciable decrease in the tube cross sectional area. The heat transfer coefficient did not vary to any significant degree during this time, indicating that the overall thickness of the scaling probably was insufficient to greatly affect the rate of heat transfer.

At this time, tube 2 was replaced with a clean carbon steel tube and tube 4 with a 304 stainless steel tube. Replacing these tubes afforded the opportunity to determine if the pressure drop increases noted were a function of initial startup of the system and/or tube metallurgy. Changes in the pressure drop for the new tubes were also noted, the carbon steel tube from 20 to 80 inches of water and from 20 to 50 inches of water for the stainless steel tube. These data indicate that the rapid initial increase in pressure drop may have been partially due to the chemical conditions during start-up, but that a marked increase in pressure drop can be expected for the carbon steel tubes in the system over a period of time.

The heat transfer coefficient for the carbon steel tube (tube 2) decreased from about 240 to 200 Btu/hr-ft²-°F, or a 30 pct reduction in heat transfer. No significant change was noted in the heat transfer coefficient for the stainless steel tube.

All of the heat exchanger tubes used during this test have been sectioned and examined using the scanning electron microscope (SEM). Pictures taken at 100X show the surface pitting that has taken place during the run. Prints 1 and 2 show the outer and inner surfaces of tube 3 taken from HE-2. The pits noted on this tube are typical for all carbon steel tubes used during the Phase I test. These pits varied in depth ranging from 2.5 to 6 mils for 50 days of operation. No significant pitting was noted on the stainless steel tubes, as shown in print 3, a representative picture of the stainless steel tubes used for the test.

A preliminary analysis of deposits on the tube surface has been performed. SEM data on the tube deposits indicates iron obviously, and sulfur is the primary contaminant. Silica, phosphorous, potassium, and calcium were identified as minor components. X-ray diffraction indicated that the material was mostly amorphous. The only identifiable crystalline material was iron oxide hydroxide - FeO(OH) - (Goethite). The elements present in the region of corrosion are not uncommon considering the nature of the wastewater. The oxidation state of the sulfur is not known at this time; therefore, whether biological activity is associated with its presence is also unknown.

PRINT 1. HE-2 Tube-3, O.D., 100X
Pits typical (carbon steel)

PRINT 2. HE-2, Tube-3, I.D., 100X
Pits typical - 6 mils deep (carbon steel)

PRINT 3. HE-1, Tube-1, 100X
Pits typical (stainless steel)

The tendency to form inorganic scale on heat transfer surfaces will be evaluated using a computerized cooling tower simulation model developed by Radian, and these predictions will be verified and correlated with the test data. This will prove a valuable tool in understanding the nature and mechanism of the fouling that can be expected when using SGL as process water. In addition, data will be obtained on the effects of organics on scale formation in the system so that the cooling tower simulation model can be modified to include their effects.

1.2.1.3.2.4 Corrosion

The corrosive effects of using SGL as a cooling tower feed have been examined using coupons, Rohrbach corrator probes, Rohrbach corrosometer probes, as well as the metallurgical examination of the heat exchanger tubes described above. The Rohrbach corrator probe measures the potential for a system to corrode, by measuring the electrical resistance of the probe-fluid interface when a voltage is applied across two metal electrodes. The Rohrbach corrosometer gives a direct measure of the corrosion rate by measuring the change in the electrical resistance of a metal specimen as it corrodes, converting it from a very conductive metal to a poor conducting metal oxide.

The corrosion data presented in Table 1-8 show a higher corrosion rate for carbon steel than generally accepted for most commercial processes. The corrosion rates for carbon steel varied from 7-23 mpy for the various locations as measured by the corrator and corrosometer probes. The corrosion rate in the cooling tower basin was also assessed using a carbon steel coupon as 10.9 mpy. This correlated well with the basin corrosion rates noted by the corrator and corrosometer probes, (C1), 11.3 and 12.0 mpy, respectively.

Current assessment of corrosion data indicates that the corrosion of stainless steel will be low under the process conditions tested - 0.02 mpy as measured by coupons in the basin and from 0.02 - 0.8 mpy as measured by the corrosometer and corrator probes.

Concrete coupons taken from the same pour as the cooling tower basin at the Great Plains Gasification Plant in Beulah, North Dakota, were placed in the basin of the UNDERC cooling tower during Phase I testing. Heavy deposits were noted on the concrete coupons after the tests. These deposits were determined to be primarily biological in nature. The concrete specimen was broken and examined. The outer surface of the concrete (1/16-inch deep) which was discolored, was soft and friable. The inner areas appeared to be unaffected. Further analyses are being performed to determine the nature of the degradation of the outer surface of the concrete.

A concrete specimen was also placed above the spray header and below the demisters. There was no noticeable deterioration of the concrete as noticed with the basin sample, however, the rock aggregates show evidence of erosion or dissolution. These aggregates are apparently limestone and are possibly attacked by weak carbonic acid being formed in the exhaust stream.

1.2.1.3.2.5 Biological Monitoring

In order to separate biological fouling from chemical/physical fouling, a biological monitoring program was established. This monitoring involved

TABLE 1-8
CORROSION RATES AS MEASURED BY THE
CORRATOR AND CORROSOMETER PROBES

Position No.	Probe Location & Metallurgy	Velocity (ft/sec)	Temp., °F	Reading (mpy)	
				Corrator	Corrosometer
C- 1	Cooling Tower Basin Carbon Steel	-	82	11	12
C- 2	Dynamic Deposit Monitor Carbon Steel	1.9	82	8	21
C- 3	Tube 4 Outlet (HE-1) Carbon Steel	0.43	95	7	11
C- 4	Tube 3 Outlet (HE-1) 340 L Stainless	0.43	95	0.05	0.2
C- 5	Cooling Tower Inlet Carbon Steel	1.9	120	23	13
C- 6	Cooling Tower Inlet 304 L Stainless	1.9	120	0.7	0.1
C- 7	Tube 3 Outlet (HE-2) Carbon Steel	0.25	90	ND	19
C- 8	Tube 4 Outlet (HE-2) 304 Stainless	0.43	90	ND	0.1
C-9	Tube 3 Outlet (HE-2) 304 Stainless	0.25	90	ND	0.1
C-10	Tube 4 Outlet (HE-2) 304 L Stainless	0.43	90	ND	0.1

ND = Not Determined

sampling thrice-weekly for total bacterial counts for suspended growth according to Standard Methods (APHA, 1975) (3) and examination of metal and concrete coupons placed in various locations throughout the tower for attached growth. In addition, predominate microbes were identified to the species level.

Results of the total counts for suspended growth can be seen on Table 1-9. Lower counts in the Basin compared to the inlet were probably due to settling out of the microbes.

TABLE 1-9
TOTAL HETEROTROPHIC AEROBIC COUNT
(ML⁻¹)

Date	Cooling Tower Inlet	Cooling Tower Basin
04-04-83	4.0×10^4	4.0×10^4
04-12-83	2.9×10^5	3.7×10^5
04-13-83	3.4×10^5	3.8×10^5
04-18-83	1.4×10^6	1.4×10^6
04-20-83	1.0×10^6	8.3×10^5
04-22-83	1.2×10^6	5.4×10^5
04-25-83	1.3×10^6	9.2×10^5
04-27-83	3.2×10^6	1.4×10^6
04-29-83	1.6×10^6	1.1×10^6
05-02-83	2.4×10^6	2.0×10^6
05-04-83	3.7×10^6	3.9×10^6
05-06-83	3.4×10^6	1.8×10^6
05-09-83	3.3×10^6	2.4×10^6
05-11-83	3.7×10^6	4.6×10^6
05-13-83	1.7×10^6	1.9×10^6
05-16-83	7.3×10^6	6.8×10^6
05-19-83	15.0×10^6	11.0×10^6
05-20-83	9.4×10^6	7.7×10^6
05-23-83	4.0×10^6	4.9×10^6
05-24-83	5.7×10^6	3.6×10^6
05-25-83	4.1×10^6	3.6×10^6
05-26-83	4.4×10^6	3.2×10^6

Pseudomonas aeruginosa is the predominant microbe isolated from both attached and suspended growth. This is consistent with what other investigators have found in similar wastewater (4). Additional microbes identified thus far include *Pseudomonas stutzeri* and CDC Group V E-1. Yeast, filamentous fungi, as well as some Gram positive bacilli, have been isolated, but not yet identified.

1.2.1.3.2.6 Atmospheric Emissions

An intensive sampling campaign was carried out to evaluate the atmospheric emissions from the cooling tower. Argonne National Laboratory provided sampling equipment, procedures, and personnel to sample the cooling tower exhaust system. Sampling performed to date includes three isokinetic

samples drawn from the cooling tower exhaust stream through a six-stage multicyclone and an XAD-2 resin trap. The multicyclone fractionates any aerosol (drift) by particle size and collects sufficient volume for further chemical characterization. The XAD-2 resin trap is used to separate/concentrate organics from the gas stream.

High-volume air samples were taken up and downwind of the exhaust stream. Air samples will be used to determine particulate and volatile organic concentrations in the exhaust stream. Several water sensitive paper samples were taken to determine the relative drift rate and size fractionation. The principle of this method is that paper sensitive to water droplets is exposed to the gas stream for a short time period. Water striking the paper leaves a stain which is related to the droplet size.

Preliminary results from sensitive paper and isokinetic drift sampling gave a drift rate of 3.0×10^{-4} gpm drift/gpm recirculation or about 0.03 pct. This compared well with the 3.6×10^{-4} gpm/gpm calculated via material balances. Data from the isokinetic sampler, the multicyclone, and XAD resin filters indicate that a significant amount of phenols were emitted into the atmosphere. The average phenol concentration measured during testing were $8000 \mu\text{g}/\text{m}^3$ exhaust air (2.2 ppm). Cresols were measured in the exhaust stream at concentrations of $760 \mu\text{g}/\text{m}^3$ (0.19 ppm). No hydantoins were detected in these samples.

1.2.1.3.2.7 Cooling Tower Conditions After Testing

Upon shutdown of the cooling tower, the side panel was removed to allow inspection of the internals. A dark-colored material was found deposited to every sheet of packing in the tower (see Print 4). Preliminary analysis indicate the deposit is a combination of attached biological growth (~70 pct) and organics (~30 pct).

Print 5 shows the condition of the corrator probes after the run. The carbon steel probes are coated with corrosion products and organic material, while the stainless steel probes remained virtually unaffected.

A concrete coupon that was located above the basin water and below the packing is shown in place after the test in Print 6. In this print, degradation of several pieces of the aggregate in the concrete can be seen. Also in this print, the dark-colored deposits are evident on the bottom of the packing.

Print 7 shows fouling that has occurred in the process piping. This material is also biological/organic in nature.

Sludgy deposits were noted along the walls and bottom of the basin. Heavy deposition also occurred wherever instrumentation was mounted in the basin.

Demisters were removed after the run. Deposits were evident on the bottom demister, but fouling was not severe on these surfaces. Some material had accumulated on the woven mesh type demister, resulting in the potential for blockage of the pores in the demister pad.

Print 4. Cooling tower packing after run.

Print 5. Corrator probes after run.

Print 6. Concrete coupon after run.

Print 7. Process piping after run.

1.2.1.4 Activated Sludge

The Phase II cooling tower assessment will involve the operation of a cooling tower utilizing wastewater treated to a greater degree than Phase I. Treatment steps will include solvent extraction, ammonia stripping, activated sludge processing, and granular activated carbon adsorption.

Results of the Phase I cooling tower assessment indicated high corrosion rates associated with carbon steel heat exchanger tube surfaces, excessive foaming requiring addition of antifoam agents, organic fouling of cooling tower packing and all metal surfaces, chemical attack on concrete coupons, and significant stripping of phenol from the cooling tower into the atmosphere. Many of these problems can be eliminated by greater organic removal before the wastewater is used as makeup to the cooling tower. Activated sludge treatment of the wastewater will be used to reduce the organic loading and will essentially remove the BOD content of the wastewater. Removal of phenol in this treatment step will also eliminate stripping of this material from the cooling tower into the atmosphere which could be a significant environmental problem. Hydantoin, a class of cyclic organic compounds which are not readily removed from wastewater by chemical or biological processes, are the major organic constituent of the wastewater after the activated sludge treatment. Beside being present in the drift from the cooling tower these compounds may contribute to the organic fouling of heat exchanger surfaces. Granular activated carbon adsorption will be used to remove these compounds and hopefully produce a satisfactory makeup to the cooling tower.

The objective of this portion of the Phase II studies is to use activated sludge treatment and granular carbon adsorption on pretreated (extracted and stripped) wastewater to prepare a satisfactory feed to the cooling tower. The two major goals of this work will be to:

1. Optimize the activated sludge process for BOD removal with "reasonable" hydraulic detention times (<2 days).
2. Demonstrate hydantoin (COD) removal with granular activated carbon adsorption.

A flow diagram showing the test equipment is presented in Figure 1-8.

Fabrication of all equipment needed for continuous activated sludge processing has been completed. Installation of the unit is continuing and should be completed in July 1983. The equipment to be used for carbon adsorption was obtained on loan from Calgon Corporation and will also be installed during July. Startup of the activated sludge granular activated carbon adsorption system is scheduled for July 25, 1983 with steady state processing of wastewater for the cooling tower to begin approximately 3 weeks later.

A series of both batch and continuous bench scale activated sludge acclimation tests were performed to obtain data for the design on the activated sludge system. An effective, acclimated microbial population for the treatment of SGL was successfully developed in all reactors. Phenol was completely removed and ammonia levels were reduced significantly in the reactors.

FIGURE 1-8. Flow schematic of activated sludge carbon adsorption process.

Batch methods produced a substantially higher cell concentration and subsequent higher ammonia substrate removal than continuous methods. Batch feed methods provided a temporary daily condition of excess substrate, spurring rapid cell synthesis. With the increased microbial population, no additional substrate was provided for 24 hours. The resulting cyclic low food to microorganism ratio resulted in increased competition, biological flocculation and better settling. Continuous methods, however, provided an environment in which the active microbial population utilized the influent substrate primarily for cell maintenance. No excess substrate was introduced to trigger rapid cell growth, but rather a continuous inflow of substrate satisfied the requirements of the population, producing a moderately active state of cell maintenance and limited synthesis. This conclusion regarding substrate utilization in batch and continuous methods is strengthened by settleability results. An average 7.9 ml/l settleability for continuous as compared to the average batch settleability of 37.2 ml/l indicates better biological flocculation occurring using batch methods.

Results arising from the temperature test variant were that warmer reactors operating at 29.4°C would produce a smaller population of microorganisms with a higher metabolism and subsequently a higher substrate removal efficiency than those operated at 22°C. Observation of test results indicates that reactors maintained at the elevated temperature did produce a 10 pct higher ammonia substrate removal efficiency of 44 pct. In addition, total suspended solids (TSS) results (Figure 1-9) imply that reactors at 29.4°C maintained a relatively smaller microbial population than lower temperature 22°C reactors.

FIGURE 1-9. Total suspended solids.

Substrate removal tests indicated an acclimated microbial population with almost complete removal of phenol. These analyses were initiated too late in the test to determine the minimum period necessary for acclimation to occur. The relatively low influent SGL concentrations used earlier in the test period allowed for the gradual adaptation of the microorganisms to their environment. All test results indicate a well acclimated and adapted microbial population was produced using the test methods and lead to the expectation that the pilot scale activated sludge system will work well with SGL as influent even at short hydraulic detention times.

1.2.2 Analytical

1.2.2.1 Methods Development

1.2.2.1.1 Phenols And Hydantoins By Capillary GC

An Analytical method for trace amounts of phenols and hydantoins in water was developed using direct, cool on-column injection, a highly polar bonded phase fused silica capillary column, and a multi-level calibration with standard mixtures. The method was published in Analytical Chemistry (5) and performed well on various wastewater samples from solvent extraction and ammonia stripping. When cooling tower blowdown samples were injected, numerous interfering peaks from the anti-foaming agent were encountered. The anti-foaming agents also tended to deactivate the capillary coatings of the GC columns, destroying their separation efficiency very rapidly. Several commercial anti-foaming agents were characterized by NMR and GC, and an antifoamer with less deactivation characteristics was chosen. Since column degradation and the lengthy (1 hr) analysis time continued to be problem areas, a procedure using non-polar capillary GC columns (SP-1000) and shorter temperature rise program (15 min) was developed and applied to cooling tower blowdown samples.

1.2.2.1.2 Ion Chromatography

Methods are in place for determination of five anions on a Dionex ion chromatograph, including chloride, nitrite, phosphate, sulfate and nitrate. An ion chromatograph procedure for thiocyanate is under development to replace the current spectrophotometric method.

1.2.2.1.3 Deposits In The Cooling Tower

Black deposits removed from various points in the cooling tower were extracted with methylene chloride after air drying. The air dried deposits were about 26 to 30 pct soluble organics, primarily 5,5-dimethyl hydantoin. The insoluble portion is presumed to be biological origin.

1.2.2.1.4 A Colorimetric Determination Of Hydantoins

A rapid colorimetric determination of hydantoin concentration which involved formation of a blue colored complex of cobalt (II) acetate and isopropyl amine with 5,5-dimethyl hydantoin (DMH) in methanol was developed from a linear plot of absorbance at 578 nm versus concentration of DMH over a range of 300 to 2000 ppm DMH. The major limitation of the method is the dark color of some of the water samples.

1.2.2.1.5 Investigation of Solvent Extraction of Hydantoins

An investigation was initiated to determine if hydantoins could be effectively removed from diisopropyl ether extracted and ammonia stripped water (S-10 samples) by solvent extraction. N-Butyl alcohol saturated with water was investigated and found to effectively recover 5,5-dimethyl hydantoin in multiple extractions. The average K_D was about 1.4 for several extractions using a separatory funnel, depending on the time allowed for equilibration, the extent to which n-butyl alcohol is saturated with water prior to extraction, and the concentration of various components in the original solution.

$$K_D = \frac{\text{n-butyl alcohol (sat. with H}_2\text{O)/100ml}}{\text{S-10 sample water/100ml}} = 1.43$$

N-Butyl alcohol also extracts phenols from water, which leads to the possibility that a simultaneous removal of phenols and hydantoins by solvent extraction of gasifier wastewater may be possible.

A 4 ft. x 1 in. countercurrent flow solvent extraction column is presently under construction to test this hypothesis. A drawback of this method is the partial solubility of n-butanol in water which leads to complications in solvent recovery.

Other extraction solvents for DMH removal have been investigated by Mohr and King of the Lawrence Berkeley Laboratory (6). Tributyl phosphate was reported to give excellent DMH removal with a K_D of 2.6. Drawbacks to its use are its density of 0.97 (very near to that of water), its high boiling point of 189°C at 20 mm (making hydantoin recovery difficult) and the fact that it is a skin irritant.

1.3 REFERENCES

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2. - HYDROGEN PRODUCTION FROM LOW-RANK COALS

(New Project; no work planned during this reporting period.)

3. - FINE COAL CLEANING

Project No.: 7104

B&R No.: AA052000

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3.1 GOALS AND OBJECTIVES

The goals for the Fine Coal Cleaning project are two-fold. The first concern is to build a uniform data base on fine coal cleaning of western coals by float-sink methods. The second goal is to investigate advanced coal cleaning methods for select low-rank coals.

3.1.1 Uniform Data Base on Fine Coal Cleaning of Western Coals

The Pittsburgh Energy Technology Center (PETC) will provide approximately 156 samples for centrifugal float-sink analysis. The tests diagrammed in Figure 3-1 will be done on -65, -200, -325 mesh splits of prepared coal at specific gravities of 1.3, 1.4, and 1.6. Washability studies on these coals in the conventional size range has been funded by other PETC projects.

The specific objectives of the float-sink studies scheduled to continue through 1985 are as follows:

1. Establish consistent comminution methods to provide usable size fractions for the float-sink studies.
2. Establish limits of applicability for float-sink methods used in this study with regard to particle size, while performing the float-sink cleaning studies. Identification of the smallest coal particle size that is amenable to wet gravity separation in float-sink tests performed at specific gravities of 1.30, 1.40, and 1.60.
3. Control moisture content and evaluate the impact of surface and bound moisture on the fine coal cleaning procedure used in this study. Determine the degree of segregation of inorganic constituents in finely ground samples of selected low-rank coals as a function of coal source, coal moisture (after conventional or steam drying), and size fraction.
4. Identify the separation of coal components in various size fractions of the comminuted samples.
5. Compile and reduce data leading to evaluation of the levels of physical removal of inorganics from the fine coals investigated (in conjunction with PETC).

FIGURE 3-1. - FINE SIZE CENTRIFUGAL FLOAT-SINK PROCEDURE

The objectives for the current quarter were to:

1. Start construction of laboratory facilities where float-sink specific gravity fluid could be used safely and other portions of the study could be performed. The laboratory construction is scheduled for mid-July completion.
2. Develop methods for performing the tests that lead to consistent results on screening and other tests where heavy media are not required.
3. Train laboratory personnel assigned to the project in analytical methods and in crushing, grinding, and sizing.
4. Start work on the sections of the test procedure where heavy media are not required on the first set of 24 samples which have been received from PETC.

3.1.2 Advanced Cleaning of Western Coals

The second goal of the project is to evaluate the potential for advanced fine coal cleaning methods on at least four select low-rank coals representative of different western coal regions and with a variety of rank, mineralogy, and other properties. Tentatively chosen were Indian Head lignite, San Juan subbituminous, a Texas lignite, and a Powder River Basin coal.

Potential advanced cleaning methods will be evaluated based on preliminary analytical data and fine coal float-sink studies. A paper will be prepared discussing these possible alternatives in November 1983. This will be used to plan the 1984 and 1985 test program.

Other aspects of this study include: 1) determination of moisture content, reduction, and readsorption during processing; and 2) observation of any extraction of coal components by water or heavy fluids, and other chemical changes induced in the organic or inorganic matter during cleaning.

This work is scheduled to begin after laboratory facilities are complete in about July 1983.

3.2 ACCOMPLISHMENTS

3.2.1 Centrifugal Float-sink Studies

Three Associated Western University supported people are assigned to the project, including a full-time post-masters appointment and two part-time undergraduate students, who have been trained in all the methods required for the project except for the centrifuge float-sink separation, which cannot be done until the laboratory is completed and the equipment installed. The air handling system for the laboratory is scheduled for completion in mid-July. The only analytical technique requiring development is for forms of sulfur, which has not been done previously at the Grand Forks laboratory. We expect to use a modified ASTM procedure using ICAP to determine the iron concentration. This will be done on large groups of samples for ease in running ICAP analysis.

The 24 PETC samples that have been received are listed in Table 3-1. They have been crushed to -65 mesh and split into the fractions required in the procedure shown in Figure 3-1. The samples were dry-screened twice and then split for the various tests. Unfortunately, the samples contained less material than specified for the tests, but it is hoped that by using smaller samples there will be sufficient material in the various size and float-sink fractions for all the analyses to be done. Wet sieve analysis was completed and the analytical work is in progress. The wet screening has been done without the use of a surfactant, and recovery ranges from 90 to 97 pct.

Work planned for the second quarter 1983 includes:

1. Completing the wet screen analytical measurements;
2. Establishing a pyritic sulfur determination; and
3. Starting heavy media separation studies.

TABLE 3-1
FINE COAL CLEANING SAMPLES

<u>GF Number</u>	<u>Location</u>	
83-1062	Paris Bed, Logan Co., AR	W-1
1063	Upper Hartshorne Bed, Lamar Co., AR	W-2
1064	Charleston Bed, Franklin Co., AR	W-3
83-1065	Lower McAlister Bed, Latimer Co., OK	W-4
1066	Upper McAlister Bed, Latimer Co., OK	W-5
1067	Croweburg Bed, Okmulgee Co., OK	W-6
1068	Croweburg Bed, Wagner Co., OK	W-7
1069	Croweburg Bed, Rogers Co., OK	W-8
1070	Secor Bed, Wagner Co., OK	W-9
83-1071	San Pedro Bed, Webb Co., TX	W-10
1072	Bull Creek Bed, Coleman Co., TX	W-11
1073	Thurber Bed, Erath Co., TX	W-12
83-1074	Dilco Bed, McKinley Co., NM	W-13
1075	PQ Dilco Bed, McKinley Co., NM	W-14
1076	Sundance Bed, McKinley Co., NM	W-15
1077	Dilco Bed M Seam, McKinley Co., NM	W-16
83-1078	Lignite Wilcox Fd., Titus Co., TX	W-17
1079	Lignite, Wilcox Bed, Titus Co., TX	W-18
83-1080	Rowe Coal Bed, Barton Co., MO	W-19
1081	Kniveton Bed, Barton Co., MO	W-20
1082	Fleming Seam, Veron Co., MO	W-21
1083	Fleming Seam, Veron Co., MO	W-22
1084	Mulberry Seam, Bates Co., MO	W-23
1085	Weir Seam, Henry Co., MO	W-24

4. - COAL-WATER SLURRY PREPARATION

Project No.: 7105

B&R Nos: AA0520000
AA2530000
AA3515050

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4.1 GOALS AND OBJECTIVES

The overall project objective is to develop methodology to prepare stable low-rank coal-water slurries with high enough solids and Btu contents to be economically utilized as replacement fuel for oil-fired combustors, feed to high pressure gasifiers, and/or transported by pipeline. The key to accomplishing this goal is the development of an economical coal drying procedure that gives a product which is resistant to moisture reabsorption. One of the most promising processes is hot-water drying of finely ground coal in slurry.

Hot-water drying is a process for removal of liquid water from high moisture coal by heating the coal-water slurry under pressure. The drying temperature may be sufficiently high so that some carboxylic groups in the coal decompose to form carbon dioxide. Dewatering is enhanced when the carbon dioxide formed in the pores of the coal forces the liquid out of the pores and into the carrier medium. Drying also occurs because of surface modification which reduces the ability of the coal to bind water. This is due to the replacement of the hydrophilic carboxyl groups on the surface of the coal by hydrocarbon groups which are hydrophobic. Energy requirements for drying can be minimized because vaporization of the water is not required, and feed/effluent heat exchange can be employed. Hot-water drying of low-rank coals produces a product that will reabsorb a minimum amount of water. Further, evidence exists that this process will reduce sodium and sulfur resulting in a higher quality fuel. Some of the more attractive features of this process include: high coal throughput; good heat recovery; and the potential to incorporate fine coal cleaning and coal beneficiation via

ion removal. An additional benefit may be that the water removed in drying may be used for slurring the solids, resulting in reduced surface or ground-water usage, which may be an important consideration in the western United States, where most of the low-rank coals occur, and where water is relatively scarce.

Specific objectives for the current budgetary year are: (a) perform autoclave tests on North Dakota lignite to produce data necessary for the successful design of a hot-water/coal drying process development unit (PDU) and perform autoclave tests on other coals to develop a low-rank coal hot-water drying data base, and (b) design and construct a hot-water/coal drying process development unit to prepare high solids-content low-rank coal-water slurries. The initial design will include steps for coal-water mixing, heating, drying and partial dewatering by flash evaporation.

Near-term objectives of the project for the period of April through June 1983 are:

1. Complete cursory autoclave tests on the hot-water drying of lignite and subbituminous coals.
2. Complete the initial PDU design along with the piping and instrumentation drawings.
3. Complete the structural and electrical design and the isometric piping drawings for the coal-water slurry process development unit.
4. Initiate construction of the coal-water slurry preparation building and salvage of the equipment from the UND - Project Lignite coal liquefaction pilot plant.
5. Initiate construction of the main work platform and the coal-water slurry mix tank support structure.

4.2 ACCOMPLISHMENTS

4.2.1 Autoclave Tests

Autoclave testing of hot-water drying was completed with several lignites and with some higher-rank coals. The experiments were designed as a cursory investigation of several processing parameters including temperature, time, and coal source. Some of these results were summarized in a paper entitled, "Steam/Hot-Water Drying of Lignite" by D.N. Baria, D.J. Maas, and L.E. Paulson, which was presented at the 1983 Lignite Symposium. Highlights of that paper included results which showed that moisture removal during hot-water drying of lignite was a function of the interior temperature of the particle which in turn was dependent on the residence time and the particle size. In hot-charge autoclave tests using Velva lignite, ground to less than 350 micron particle size, moisture reduction was complete in about 5 minutes. Shorter tests of 3 minutes showed only about half of the moisture reduction measured for the 5-minute test.

In addition to the effects of residence time, the consequences of drying temperature were also measured. For the hot-charge autoclave tests with Velva lignite dried in hot-water, the moisture reduction was found to increase in going from 200° to 340°C, with the moisture reduction at the highest temperature being about 85 pct. The temperature range where the greatest change in the drying rate was observed was between 240° and 320°C with the increase in rate probably due to a combination of decarboxylation and drying.

Product characterization of the hot-water dried coals focused primarily on moisture reabsorption tendencies, decarboxylation, and heating value, and inorganics removal. Moisture absorption tendencies of the dried lignite were determined by filtering a processed slurry sample and then equilibrating the filter cake in a 100-pct humidity chamber at room temperature. Results showed that the moisture content changes as a function of the number of days in the humidity chamber and reaches a constant value after about 8 days. From these studies it was observed that, for Velva and Indian Head lignites, the constant moisture content, following humidity equilibration, increased as the drying temperature decreased. For Velva lignite this equilibrated constant moisture varied from 10 pct when the lignite was dried at 340°C to 28 pct when the coal was dried at 200°C. Raw, untreated lignite equilibrated at 35 pct constant moisture after 8 days in the humidity chamber.

Results of carboxylic acid group determinations for the original coals and for the hot-water dried lignites showed the extent of decarboxylation to be strongly dependent on the drying temperature employed. It was noted that the greatest decrease in carboxylic acid groups occurred between the temperatures of 260° and 340°C. These results correlate well with the increased drying rates observed for the same temperature range. The gross heating value for the dried lignite, being closely tied to oxygen content, was observed to increase with increased drying temperature. For Velva lignite, the gross heating value on a moisture-free basis increased from about 10,800 for the untreated coal to about 12,700 following hot-water drying at 340°C.

Metal ion concentrations for the raw and dried lignite were measured by atomic absorption spectroscopy. Sodium removal increased with an increase in hot-water drying temperature. Eighty percent of the sodium was removed from the Velva lignite when it was dried at 340°C. Since part of the alkali cations in low-rank coals occur as salts of carboxylic acids, they are released from the coal structure and migrate through the pores into the carrier medium where they can be removed from the product by filtration. Additional elemental analysis of the dried lignite showed the hot-water drying process had little effect on the amount of calcium or sulfur removed.

4.2.2 Design of the Continuous Hot-Water Coal Drying Process Development Unit

Detailed flow diagrams were prepared for the five processing areas of the CWS drying pilot plant defining the instrumentation and giving some vessel and piping details.

Figure 4-1 is the overall flow sheet illustrating the main flow patterns and the general inter-relationship of the individual areas. The five unit operations are:

FIGURE 4-1. Simplified schematic of the hot-water/coal drying process development unit.

- Area 01 Slurry Preparation and Pumping
- Area 02 Slurry Heating and Coal Drying
- Area 03 Slurry Recovery and Separation
- Area 04 Water Recovery and Slurry Concentration
- Area 05 Product Storage

A description of each of these areas, as currently designed, is given below.

4.2.2.1 Area 01--Slurry Preparation and Pumping

This area includes the pulverized coal hopper, the pulverized coal feeder, the slurry mix tank, the slurry circulation pump, the high pressure slurry feed pumps, the water storage tanks and recirculating pump, and the water feed pump.

As designed, pulverized coal from a storage bin is gravity fed into the hopper of an Acrision volumetric feeder (P-1), from which it is augered into the slurry mix tank (M-1) at a constant volumetric flow rate equivalent to 100 pounds per hour. As coal is added to the slurry tank, recycle water is metered into the tank by a variable speed gear pump (P-5) whose speed is controlled by a flow controller working in conjunction with an in-line orifice flow transmitter.

A 4-stage, 3 blades per stage, impeller-type mixer is used to wet the incoming coal and to keep solids in suspension. For circulating the slurry around the mix tank loop a lobe pump (P-2) is used. This pump also feeds slurry through an offtake to the suction of the four high pressure reciprocating pumps (P-3A and B and P-4A and B) at about 30 psig. Sample connections in the circulating line are provided so that samples for density and rheological determinations can be obtained whenever desired.

The high-pressure reciprocating pumps are equipped with variable stroke drives, which can be adjusted to maintain constant inventory in the mix tank, thus forcing the slurry feed rate to the drying section of the plant to match the sum of the coal and water feed rates to the mix tank.

4.2.2.2 Area 02--Slurry Heating and Coal Drying

This section of the plant includes the steam preheaters, the electrically heated Dowtherm slurry heaters, and the coal drying reactors.

The coal-water slurry from the reciprocating pumps, now at about 2500 psig pressure, is first heated to about 150°C in a steam-heated exchanger (E-1 through E-4) and then enters a coil that is suspended in the slurry heater (E-5 and E-6) and which is heated by condensing Dowtherm vapor. Leaving the slurry heater at about 300-340°C, the slurry enters at the top of a down-flow coal drying reactor (R-1 through R-5) where it is held at temperature for about 10 minutes while still flowing on its way to the slurry recovery section of the plant. Evolved gases, mainly carbon dioxide, liberated during the drying process are siphoned off the top of the reactor and piped to the high pressure gas-liquid separator (S-1).

4.2.2.3 Area 03--Slurry Recovery and Separation

The coal-water slurry leaving the coal drying reactors is piped to a combination high pressure gas-liquid separator and level controller (S-1). This vessel is maintained at about 300°C and is mounted high enough that the coal drying reactors remain flooded. The vapor and non-condensable gases from the high pressure separator are cooled by a water-cooled exchanger (E-7) to 37°C or lower and then collected in a recycle condensate separator (S-2). The gaseous products from this separator consist primarily of carbon dioxide with lesser amounts of hydrogen and hydrogen sulfide. The gas is vented across a back-pressure control valve to a thermal oxidizer where it is incinerated. The liquid products from the recycle condensate separator (S-2) consist mainly of water. This stream is depressured and fed to the low-pressure (60 psig) flash separator (S-4).

The hot coal-water slurry from the high pressure separator (S-1) is depressured through two captive volume pressure letdown systems and enters an intermediate pressure (300 psig) flash separator (S-3) which is maintained at the same temperature as the high pressure separator (S-1). The overhead products from the intermediate pressure flash separator consist mainly of water vapor and some carbon dioxide. This stream is first passed through a pressure control valve and then cooled to 37°C or below by water coolers. The cold stream is piped to the low pressure flash separator (S-4) and combined with the liquid products from the recycle condensate separator (S-2). From the low-pressure flash separator (S-4) recycle water is returned to the water feed tank.

The slurry from the intermediate pressure flash separator (S-3) flows through a level control valve and is then piped to either the product storage tanks or the water recovery section of the plant.

4.2.2.4 Area 04--Water Recovery and Slurry Concentration

This area of the Process Development Unit includes a slurry heater, two slurry flash concentrators, a condensate receiver, a condensate return pump, and a vacuum system complete with refrigerated cold trap.

The hot coal-water slurry leaving the intermediate pressure flash separator (S-3) is further heated in slurry heater E-9. The flashing mixture from this preheater is piped to the slurry flash concentrator (F-1A or F-1B) where vapor is taken overhead. The slurry flash concentrators can be operated at atmospheric or sub-atmospheric pressure. The concentrated coal slurry is removed at the bottom through a two-valve captive volume system and temporarily stored in a 600 gallon tank (T-2) where it is constantly stirred and is allowed to cool. Periodically the finished coal-water slurry product is transferred to the larger 3000 gallon product slurry storage tanks (T-4 through T-6).

The overhead products from the slurry concentrator are passed through a water cooled condenser, E-10, where the temperature is reduced to below 37°C. The liquids are then collected in a condensate receiver (S-5) and subsequently pumped using a gear pump (P-8) to the water feed tank for recycle. Non-condensable gases are piped to the thermal oxidizer.

When the slurry concentrators are operating under vacuum, the pressure in the system is controlled using a pressure control valve which throttles the suction of the vacuum pump.

4.2.2.5 Area 05--Product Storage

This section of the coal water slurry preparation facility includes the storage tanks, tank agitators, and slurry transfer pumps.

Product slurry from either the intermediate pressure flash separator (S-3) or the slurry concentrators (F-1A or F-1B) is piped to storage in this area. The three storage tanks represent sufficient capacity for 360 hours of PDU operation. Each tank is agitated by an electrically-driven mixer and is mounted 14 feet above grade to facilitate off loading to a tank truck or other container. The tank drain system is set up for both dumping by gravity and by a pump.

4.2.3 Coal-Water Slurry Preparation Facility--Building Construction

When the hot-water coal drying project was initiated in October of 1982, the Grand Forks Energy Technology Center issued several construction contracts in support of the project. The first of these was to a local engineering firm to handle the design of a new building to house the equipment and to supervise the construction, while a number of other contracts were awarded to local building contractors for construction of the building and installation of utility services including water, sewer, steam and electricity.

Although none of this construction work is actually part of the coal water slurry project being performed by the UND Energy Research Center, the completion date for the building impacts on the milestones established for the project. Therefore the following is a brief status report on construction activities. The shell for the building has been erected and the roof installed. City utilities including water, sewer and natural gas have also been brought into the building. As of the end of June, however, installation of the electrical and steam services has not been completed and installation of the concrete floor, mezzanine support beams and access doors has not been initiated. At present it appears doubtful the building will be ready for occupation by the end of July which is the scheduled contract completion date.

4.2.4 Coal-Water Slurry Pilot Plant Construction Activities

One of the premises upon which construction of the hot-water/coal drying process development unit centers is the salvage and reuse of equipment and structural steel from the decommissioned UND Project Lignite coal liquefaction pilot plant. Since initiating work on the coal water slurry project, all of the Project Lignite process equipment has been recovered and moved on-site. Cleaning efforts are essentially complete and many of the pumps have been refurbished to nearly new condition. Salvage of structural steel is continuing by project personnel and construction of new work platforms and vessel mounting structures has begun. Of these, construction of the slurry tank and coal feeder support stand was completed, with the exception of the load cell platforms for the coal hopper. The slurry tank and coal feeder were mounted in the framework.

The process instrumentation recovered from Project Lignite was steam cleaned, sorted, and labeled to correspond with the instrument tag numbers for the new coal-water slurry preparation process development unit. Instrument shortages were defined, and procurement is proceeding. Salvaged process piping, fittings, and valves were disassembled to the basic components, and cleaning is continuing.

The electrical drawings and design of the overhead crane support structure were completed. The five isometric piping drawings for the PDU are nearly complete, and design work has started on the product storage tank mezzanine.

4.2.5 Coal-Water Slurry Pilot Plant Design Studies

A small continuous unit was constructed and operated to obtain design data relative to both overall and inside heat transfer coefficients when coal-water slurry is heated, while flowing through a tube, by a condensing heating medium such as steam or Dowtherm. Approximately 30 test conditions at various flow rates and coal loadings were investigated. On the average, the inside heat transfer coefficient for a coal-water slurry heated by condensing steam in stainless steel tubes appears to be about $1500 \text{ Btu/ft}^2\text{-hr-}^\circ\text{F}$.

Tests were run passing air countercurrent to down-flowing water in a vertical pipe to model the behavior of evolved gas in the PDU reactors. Evidence from these tests indicate that it is necessary to redesign the reactor piping for removal of evolved gas. Without this piping change liberated gases would accumulate in the reactor and purge out the slurry.

Two 5-gallon, highly concentrated coal-water slurries were blended and sent to separate companies of mixing equipment for testing of rheological properties for the design of the slurry storage tanks and agitator systems. Results of the tests and the recommendations from the mixing equipment manufacturers are not yet available but are anticipated early next quarter.

5. - LOW-RANK COAL LIQUEFACTION

Project No.: 7106

B&R No.: AA1515100
AA2515050
AA2530100

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5.1 GOALS AND OBJECTIVES

The overall goal of the Low-Rank Coal Liquefaction project is to continue developing the technical data base necessary to adapt direct liquefaction expressly for low-rank coals (LRC), including both lignites and subbituminous coals. The data base includes correlations of process yields with operating parameters and with process modifications, such as use of synthesis gas and catalysts, that effectively capitalize on unique properties of LRC. These properties include high moisture, high reactivity associated with oxygen functionality, and alkaline mineral matter.

During the term of the Cooperative Agreement, four major research areas are to be pursued. They are: a) catalytic liquefaction, with emphasis remaining on disposable catalysts, while focusing increased attention on understanding the effects of adding H_2S , particularly in the presence of iron-containing materials; b) staged liquefaction, with emphasis on a low-temperature first stage using CO as the feed gas where differences in coal rank will be most evident; c) mechanism/kinetic studies using labeled reactants and reductants, to determine the effects of CO reactions with coal and to elucidate the role of H_2 in LRC liquefaction; and d) determining the effects of solvent on LRC liquefaction (specifically, to evaluate if start-up solvent composition influences lined-out product) and continuing to characterize liquefaction products.

The work reported here includes activity and results obtained since January 1, 1983. Because the work planned and conducted under the Cooperative Agreement largely extended the FY 1983 activities for the Grand Forks Energy Technology Center (GFETC), there is no discontinuity in the research activities because of the transfer.

5.2 ACCOMPLISHMENTS

5.2.1 Catalytic Liquefaction of Low-Rank Coals

The initial phase of the catalyst screening program is underway. The minerals and pure chemicals that are being evaluated as potential catalysts are listed in Tables 5-1 and 5-2, respectively. The catalyst screening is being done using the multiple tubing bomb apparatus. Twelve tubing bombs can be run simultaneously at the same temperature and for the same time.

TABLE 5-1

MINERALS BEING TESTED AS LIQUEFACTION CATALYSTS

Acmite	Hematite
Actinolite	Ilmenite
Alunite	Limonite
Anhydrate	Magnesite
Anorthoclase	Magnetite
Anthophyllite	Manganite
Barite	Molybdenite
Bauxite	Pentlandite in Pyrrhotite
Bornite	Platinum Ore
Brucite	Pyrite
Cassiterite	Pyrolucite
Chalcocite	Pyrrhotite
Chalcopyrite	Siderite
Fayalite in Granite	Smithsonite
Franklinite	Sphalerite
Galena	Stibnite
Gibbsite	Zincite
Goethite	Fly Ash
Gypsum	

The reaction conditions are: 440°C, synthesis gas (i.e., equimolar mixture of hydrogen and carbon monoxide) having an initial pressure of 1000 psig at room temperature, Zap, North Dakota, lignite (from the Indian Head Mine), anthracene oil solvent (A04), and a 20-minute reaction time. Analyses of reaction products include determination of overall conversion (using THF solubility), distillates and soluble residuum yields, and carbon-to-hydrogen ratio. In order to reduce the analytical load created by screening the large number of potential catalysts, the product yields will be determined only if the overall conversion exceeds 60 pct of the MAF coal fed, and the C/H ratio will be measured only if the distillate yield is greater than when no additive is present.

Table 5-3 lists the materials that have been tested in the tubing bomb apparatus. Analyses of the products are not complete, so no data are presented.

TABLE 5-2

PURE CHEMICALS BEING TESTED AS LIQUEFACTION CATALYSTS

Ammonium Formate	Phenol
Ammonium Hydroxide	Potassium Bisulfate
Ammonium Iron (II) Sulfate Hexahydrate	Potassium Hydroxide
Ammonium Iron (III) Sulfate Dodecahydrate	Potassium Molybdate (VI) Pentahydrat.
Ammonium Molybdate (VI) Tetrahydrate	Potassium Sulfate
Ammonium Sulfate	Quinoline
Benzyl Disulfide	Resorcinol
Catechol	Resorcinol Sulfide
Cobalt Molybdate	Sodium Bisulfide
o-Cresol	Sodium Carbonate
m-Cresol	Sodium Hydroxide
p-Cresol	Sodium Sulfate
Dibenzylamine	Sodium Sulfite
1,5-Dihydroxy Naphthalene	Sulfur
1,8-Dihydroxygan Thraquinone	1,2,3,4-Tetrahydroquinoline
Ferrocene	p-Thiocresol
Formanilide	4,4'-Thiodiphenol
Formic Acid	2-Thiohydantoin
Iron (III) Nitrate Nonahydrate	Thiolacetic Acid
Iron (III) Oxide	Tin (VI) Oxide
Iron (II) Sulfate Heptahydrate	Zinc Acetate Dihydrate
Lithium Hydroxide Monohydrate	Zinc Oxide
Methylamine	Zinc Sulfate Heptahydrate
Molybdenum Trioxide	

TABLE 5-3
ADDITIVES TESTED AS LIQUEFACTION CATALYSTS

Fe ₃ O ₄ (Magnetite)	Micaceous Hematite
K ₂ CO ₃	Fayalite in Granite
Na ₂ CO ₃ (Sodium Carbonate)	Bornite
Fly Ash (325 Mesh)	Zinc Sulfate Heptahydrate
FeS ₂ (Pyrite)	Ammonium Sulfate (NH ₄) ₂ SO ₄
K ₂ MoO ₄ ·5H ₂ O (Potassium Molybdate)	Resorcinol C ₆ H ₄ -1,3-(OH) ₂
(C ₆ H ₅ CH ₂) ₂ S ₂ (Benzyl Disulfide)	(CH ₃ CO ₂) ₂ 3n·2H ₂ O Zinc Acetate Dihydrate
K ₂ SO ₄ (Potassium Sulfate)	2-Thiohydantoin
Dihydroxyanthraquinone	5[C ₆ H ₃ -1,3-(OH) ₂] ₂ Resorcinol Sulfide
HCONHC ₆ H ₅ (Formanilide)	Sphalerite
Na ₂ S ₂ O ₄ (Sodium Hydrosulfite)	Manganite
Dibenzothiophene	Smithsonite
NaHCO ₃	Pyrite
ZnO (Zinc Oxide)	Pyrrhotite
NaOH (Sodium Hydroxide)	Gypsum
Sulfur	Potassium Hydroxide (KOH)
Cobalt Molybdate	Formamide (HCONH ₂)
SnO ₂ (Tin (IV) Oxide)	Dibenzylamine (C ₆ H ₅ CH ₂) ₂ NH
Fe ₂ O ₃ (Iron (III) Oxide)	Ammonium Molybdate Tetrahydrate
Ca ₂ S (Chalcocite)	Molybdenum (VI) Oxide
Barite	Thiolacetic Acid (CH ₃ COSH)
Anthophyllite	Magnetite
Stibnite (Sb ₂ S ₃)	Brucite
Chalcopyrite	Platinum Ore
Ilmenite	Pentlandite in Pyrrhotite
Siderite	Molybdenite
Limonite	Alunite
Magnesite	

5.2.2 Low-Temperature Liquefaction

A series of hot-charge autoclave experiments to study low temperature liquefaction of lignite using pure carbon monoxide as feed gas was completed. Reaction temperature was varied from 320° C to 400° C. The reaction time was 60 minutes, anthracene oil (A04) was the solvent, and Zap lignite (from the Indian Head mine) was the feed coal. The solvent-to-MAF coal ratio was maintained at two for all of the runs.

Table 5-4 summarizes the conversion and yield data, while Figure 5-1 shows the same data graphically. The overall conversion and yields generally increase with increasing temperature, but there is relatively little increase with temperature above about 365° C.

TABLE 5-4
LOW-TEMPERATURE LIQUEFACTION USING CO

Run No.	N131	N124	N128	N123	N134
Coal	Zap	Zap	Zap	Zap	Zap
Solvent	AO4	AO4	AO4	AO4	AO4
Additive	None	None	None	None	None
Run Time, min	60	60	60	60	60
Average Temp.	320	345	363	375	400
Max Press, psig	2980	3250	3300	3550	3450
% H ₂ Feed Gas	.0	.0	.0	.0	.0
Moisture (GMS)	100.6	99.4	97.7	99.9	99.1
Net Yields (Wt. % maf Coal Charged)					
CO	- 5.2	-22.6	-45.6	-11.2	-47.2
H ₂	.3	.4	.6	1.1	1.3
CO ₂	58.7	59.6	69.8	57.4	95.5
C ₁ - C ₃	.0	.2	.1	.5	1.3
H ₂ S, NH ₃	.2	.1	.2	.2	.7
H ₂ O	-13.9	-16.5	-17.4	-21.2	-23.0
Gas + H ₂ O	40.1	21.3	7.7	26.7	28.7
Light Oil	3.5	3.4	- .4	.3	- .1
Mid. Oil	-38.7	-18.6	-22.4	.9	- 2.5
Heavy Oil	30.6	27.3	33.3	14.7	17.7
C ₄ + Dist.	- 4.5	12.1	10.6	16.0	15.1
Sol. Residuum	11.8	36.3	61.8	42.6	45.4
IOM	52.6	30.3	20.0	14.7	10.9
Solent Rec.	91.7	100.0	101.0	103.5	103.2
H ₂ Equiv Consumption	.1	1.2	2.6	- .2	2.0
IOM/Gram Ash	8.1	8.1	8.1	8.1	8.1
Conversion	47.4	69.7	80.0	85.3	89.1
Material Balance Closure	91.6	97.2	97.6	95.6	94.8

FIGURE 5-1. Low-temperature liquefaction with CO.

For comparison, data at 460°C are shown in Figure 5-1, both using syngas (equimolar mixture of carbon monoxide and hydrogen) and pure hydrogen. It should be noted the reaction time was 20 minutes at this higher temperature. In any case, it can be seen that the overall conversion of maf coal is higher at the lower temperatures. On the other hand, the distillate yield is greater at 460° C, while the yield of soluble residuum is much reduced compared with the yields at 80° to 100° lower temperature in the presence of CO. In addition, the hydrocarbon gas yield is higher at 460° C as compared with the gas yields at the lower reaction temperatures. This is all consistent with the hypotheses that at higher liquefaction temperatures the solvent degrades to hydrocarbon gases, and the reactive species formed in the reaction mixture recombine to form refractive materials that are not soluble in THF. At the lower temperatures there are somewhat lower yields of distillate and hydrocarbon gas, but the overall conversion is relatively higher because of the increased yield of THF-soluble, but nondistillable, product (i.e. soluble residuum). These data suggest that a low-temperature pretreatment in the presence of CO may enhance the overall liquefaction of low rank coals; more severe conditions may upgrade the soluble residuum fraction to distillate.

Preliminary time-sample data for these same runs indicate that the conversion of the coal to products may be nearly complete within the first 6 to 10 minutes of reaction. These data are not complete and will be reported later.

Table 5-5 shows results obtained when the fraction of hydrogen in the feed gas was increased while maintaining reaction temperature constant at about 380°C. All other reaction conditions remained the same as in the previously discussed set of experiments. The data indicate that at the relatively low temperature of 380°C pure CO as the feed gas gives the highest overall conversion and the greatest yields of both total distillate and soluble residuum. The conversion ranged from 75 pct of the maf coal fed for 75 pct hydrogen in the feed gas to nearly 88 pct when pure carbon monoxide was used. The distillate yield ranged from 7 pct of the MAF coal fed to 28 pct, and the soluble residuum yield ranged from 43 pct to 55 pct; in each case, the greater yield was in the presence of pure CO, while the lowest yield was at the highest fraction of hydrogen in the feed gas. It should be mentioned that the distribution between the distillate fractions may show some variation, but the total distillate (indicated as C4 + distillate) is a reliable figure. Figure 5-2 shows the product distribution for the same set of runs. The total liquid yield for the 100-pct CO run was much higher than for any other mixture and, in fact, was even as high as the total conversion in other runs. Reducing gas consumption, calculated as hydrogen equivalent, is greatest for the pure CO case, and decreases with increasing fraction of hydrogen in the feed gas.

5.2.3 Staged Liquefaction of Highvale Subbituminous Coal

A series of experiments using both the continuous process unit (CPU) in once-through operation and the hot-charge batch autoclave equipment were performed to evaluate the liquefaction response of Highvale subbituminous (Canadian) coal slurried in tar sands bitumen. The "as-received" coal was pulverized to -60 mesh, and slurried with tar sands bitumen and K_2CO_3 , the catalyst. The feed slurry was 29.7 pct by weight coal, 69.28 pct by weight bitumen, with the balance being K_2CO_3 . The slurry was heated to 50°C, pumped to system pressure, and then mixed with H_2S and water. The mixture was then preheated to 250°C before feeding it to the vertical tubular reactor. The reducing gas, an equimolar mixture of carbon monoxide and hydrogen was preheated to 360°C before it was fed to the reactor. The slurry flow rate was 3800 grams per hour; this gave the nominal 20-30 minute residence time. The reactor temperature was maintained in the 370°C to 380°C range.

The three-phase product from the reactor passed through a high-pressure, and then a low-pressure separator to remove gases, light oils, and water. The bottoms product from the operation was used as the feed for the second-stage experiments in the hot-charge autoclave. Two run series were completed; in one series the temperature was varied from 415°C to 440°C, and in the other series the catalyst was changed. The nominal run conditions were 20 minute reaction time, pure hydrogen feed gas, and maximum reaction pressure from 2600 psig to nearly 2800 psig.

The series of second stage runs was to be completed over a 2- to 3-month period. Potassium molybdate (K_2MoO_4) and hydrogen sulfide (H_2S) were added as catalysts at levels of one pct of the maf coal as fed to the CPU and 3 mole pct of the hydrogen fed, respectively. To determine if there were any effects of time between the first and second stages, two duplicate runs were made. One run (N119) was made within hours of the first stage, and the second run (N142) was made at the time the second stage runs were completed, three months later. Table 5-6 is a summary of these two runs.

TABLE 5-5

LOW TEMPERATURE LIQUEFACTION USING H₂/CO MIXTURES

Run No.	N160	N159	N157	N158
Coal	Zap	Zap	Zap	Zap
Solvent	AO4	AO4	AO4	AO4
Additive	None	None	None	None
Run Time, min.	60	60	60	60
Average Temp.	380	383	380	383
Max Press, psig	3490	3550	3500	3580
% H ₂ Feed Gas	.0	24.9	50.2	75.1
Moisture (GMS)	99.3	100.1	97.6	105.2
Net Yields (Wt.% maf Coal Charged)				
CO	- 46.5	- 29.2	- 22.3	- 9.8
H ₂	.8	.8	.7	1.0
CO ₂	67.8	64.3	57.2	39.1
C ₁ - C ₃	.6	.7	.7	.7
H ₂ S, NH ₃	.7	.3	.2	.5
H ₂ O	- 18.3	- 19.0	- 8.7	- 5.5
Gas + H ₂ O	5.2	18.0	27.7	26.0
Light Oil	1.5	4.1	- 3.2	1.4
Mid. Oil	24.9	4.9	26.6	21.1
Heavy Oil	1.4	9.9	- 15.2	- 15.6
C ₄ + Dist.	27.8	18.9	8.2	6.9
Sol. Residuum	54.6	42.6	46.2	42.5
IOM	12.5	20.5	17.9	24.7
Solvent Rec.	108.8	103.1	99.8	98.4
H ₂ Equiv. Consumption	2.5	1.3	.9	- .2
IOM/Gram Ash	8.1	8.1	8.1	8.1
Conversion	87.5	79.5	82.1	75.3
Material Balance Closure	95.3	93.9	97.4	95.8

FIGURE 5-2

PRODUCT YIELDS FOR ZAP COAL IN AO4 SOLVENT AT 380°C
FOR VARYING FEED GAS COMPOSITIONS

Wt % maf	H ₂ -pct in feed gas			
	.0	24.9	50.2	75.1
80	CCCCC		CCCCC	
	CCCCC		CCCCC	
	CCCCC		CCCCC	
	BBBBB		CCCCC	
70	BBBBB		CCCCC	
	BBBBB	CCCCC	CCCCC	
	BBBBB	CCCCC	CCCCC	CCCCC
	BBBBB	CCCCC	CCCCC	CCCCC
60	BBBBB	CCCCC	CCCCC	CCCCC
	BBBBB	CCCCC	CCCCC	CCCCC
	BBBBB	CCCCC	CCCCC	CCCCC
	BBBBB	CCCCC	CCCCC	CCCCC
50	BBBBB	CCCCC	CCCCC	CCCCC
	BBBBB	BBBBB	CCCCC	CCCCC
	BBBBB	BBBBB	CCCCC	CCCCC
	BBBBB	BBBBB	BBBBB	CCCCC
40	AAAAA	BBBBB	BBBBB	CCCCC
	AAAAA	BBBBB	BBBBB	CCCCC
	AAAAA	BBBBB	BBBBB	CCCCC
	AAAAA	BBBBB	BBBBB	BBBBB
30	AAAAA	BBBBB	AAAAA	BBBBB
	AAAAA	BBBBB	AAAAA	BBBBB
	AAAAA	AAAAA	AAAAA	AAAAA
	AAAAA	AAAAA	AAAAA	AAAAA
20	AAAAA	AAAAA	AAAAA	AAAAA
	AAAAA	AAAAA	AAAAA	AAAAA
	AAAAA	AAAAA	AAAAA	AAAAA
	AAAAA	AAAAA	AAAAA	AAAAA
10	AAAAA	AAAAA	AAAAA	AAAAA
	AAAAA	AAAAA	AAAAA	AAAAA
	AAAAA	AAAAA	AAAAA	AAAAA
	AAAAA	AAAAA	AAAAA	AAAAA

Symbol Fraction: A - A = SOL-RES; B - B = C4-DIST C - C = GAS-H₂O

TABLE 5-6
COMPARISON OF DUPLICATE SECOND STAGE RUNS

Run No.	N119	N142
Coal	ALB2	ALB2
Solvent	Bitumen	Bitumen
Additive	K2MoO4/H ₂ S	K2MoO4/H ₂ S
Run Time, min	20	20
Average Temp.	440	440
Max. Press., psig	2450	2740
% H ₂ Feed Gas	99.0	99.5
Moisture (GMS)	1.8	4.3
Net Yields (Wt.% MAF Coal Charged)		
CO	.1	1.4
H ₂	- 3.2	- 2.9
CO ₂	1.5	1.7
C ₁ - C ₃	4.9	6.7
H ₂ S, NH ₃	2.6	2.2
H ₂ O	5.6	7.2
Gas + H ₂ O	11.5	16.3
Light Oil	21.6	21.4
Mid. Oil	- 55.2	- 31.8
Heavy Oil	103.1	64.3
C ₄ + Dist.	69.5	53.9
Sol. Residuum	9.3	20.5
IOM	9.7	9.4
Solvent Rec.	73.2	67.6
H ₂ Equiv. Consumption	1.2	2.5
IOM/Gram Ash	4.9	4.9
Conversion	90.3	90.6
Material Balance Closure	103.1	97.8

Conversion is the same for both runs. The yields of total liquid were comparable for both runs although somewhat higher for the early run (78.8 pct for the N119 and 74.4 pct for N142). However, there appears to be a shift in the product distribution as shown by both the distillate and soluble residuum yields. In the early run more distillate was produced, 69.5 pct compared to 53.9 pct and less soluble residuum, 9.3 pct compared to 20.5 pct. Gas production was also lower in the early run, 4.9 pct compared to 6.7 pct. Based on these yield data, it appears that the first-stage products degraded slightly during the three-month interval between the first and second stages, but not enough to cause concern about the results obtained.

Table 5-7 shows the results of varying the second stage temperature. The data show that when second-stage temperature increased from 415°C to

TABLE 5-7

LIQUEFACTION OF HIGHVALE COAL WITH VARYING SECOND STAGE TEMPERATURE

Run No.	N150	N149	N138	N145	N148	N142
Coal	ALB2	ALB2	ALB2	ALB2	ALB2	ALB2
Solvent	Bitumen	Bitumen	Bitumen	Bitumen	Bitumen	Bitumen
Additive	K2MoO ₄ /H ₂ S	K2MoO ₄ /H ₂ S	K2MoO ₄ /H ₂ S	K2MoO ₄ /H ₂ S	K2MoO ₄ /H ₂ S	K2MoO ₄ /H ₂ S
Run Time, min	20	20	20	20	20	20
Average Temp.	413	419	425	430	435	440
Max. Press., psig	2660	2680	2620	2695	2660	2740
% H ₂ Feed Gas	99.5	94.7	99.5	99.5	99.5	99.5
Moisture (GMS)	4.4	4.4	4.1	4.3	4.3	4.3
<u>Net Yields</u>						
<u>Wt. % maf Coal Charged:</u>						
CO	.4	.7	.7	.7	.4	.5
H ₂	-1.5	-1.1	-2.3	-2.3	-2.8	-2.9
CO ₂	1.4	1.1	1.5	1.1	1.0	1.7
C ₁ - C ₃	1.6	2.5	3.4	3.2	5.4	6.7
H ₂ S, NH ₃	2.2	1.8	2.0	3.0	4.0	2.2
H ₂ O	5.0	1.6	2.4	4.2	3.9	7.3
Gas + H ₂ O	9.1	6.7	7.7	10.0	11.9	15.4
Light Oil	5.2	16.1	24.5	16.0	18.8	21.4
Mid. Oil	-45.6	-42.3	-26.3	-37.9	-73.8	-31.5
Heavy Oil	73.6	73.1	29.3	71.1	109.9	64.4
C ₄ + Dist.	33.3	46.9	27.5	49.2	50.0	54.3
Sol. Residuum	36.4	29.3	44.6	29.5	24.1	20.8
IOM	21.2	17.0	20.1	11.3	14.0	9.4
Solvent Rec.	66.0	66.9	56.9	67.8	68.9	67.7
H ₂ Equiv. Consumption	1.3	.9	1.9	2.0	2.4	2.5
IOM/Gram Ash	4.9	4.9	4.9	4.9	4.9	4.9
Conversion	78.8	83.0	79.9	88.7	86.0	90.6
Material Balance Closure	97.6	98.9	101.2	99.6	94.4	97.5

440°C, the yields of hydrocarbon gases increased from 1.6 wt pct of the maf coal fed to 6.7 pct; the distillate yield increased from 33 pct to 54 pct; the overall conversion of maf coal fed increased from 79 pct to 91 pct; and the reducing gas consumption, as hydrogen equivalent, increased from 1.3 wt pct of the maf coal fed to 2.5 pct. The overall conversion and product yields are solely attributed to the coal, but the bitumen "solvent" is about 44 wt pct soluble residuum (i.e. THF-soluble but nondistillable) and 56 wt pct middle oil. Thus, we see a consumption of middle oil, while there are net makes of light oil, heavy oil and soluble residuum together with relatively high conversion of the feed coal. The solvent is likely converted to light oil and gases, while the coal is probably converted largely to soluble residuum and heavy distillate. However, there must also be some retrograde behavior in which the solvent cracks and repolymerizes to form heavier constituents, that are either in the heavy oil or soluble residuum fractions. As the temperature increased, the yield of soluble residuum decreased indicating either greater conversion of the coal to distillate or less "retrograde" behavior; that, together with, the increased overall coal conversion and the increased consumption of reducing gas, indicates hydrotreating of the coal and/or of the soluble residuum fraction.

Table 5-8 shows the results when using various catalysts in the second stage while keeping the temperature constant at about 420°C. The highest conversions were in the runs in which potassium molybdate was present either with or without added H₂S. The highest distillate yield was realized when no catalyst was present in the second stage; the overall conversion, based on maf coal fed, was also the lowest in that instance suggesting that most of the distillate from the non catalyzed run resulted from the upgrading of the heavy portion of the solvent. The effects of adding H₂S as a catalyst, either by itself or in the presence of K₂M₁₀O₄, are not definitive though it does not enhance overall conversion.

5.2.4 Characterization of Reactor Solids

Reactor solids and blowdown samples from several CPU runs made in 1981 and 1982 were analyzed, and the results of the study were reported in a paper entitled "Characterization of Reactor Solids from the Liquefaction of Select Low-Rank Coals". The paper was presented at the 75th Annual Meeting of the North Dakota Academy of Science (1983).

Samples chosen for analyses were from CPU runs made using lignites from both North Dakota (Beulah-3) and Texas (Big Brown-2). The objectives of the study were to: 1) megascopically describe the reactor coke solids; 2) microscopically analyze and photograph reactor solids; 3) identify and compare minerals in the feed coal with minerals in the reactor solids; and 4) study the pyrite-pyrrhotite transformation inherent in coal liquefaction and its dependence on process parameters.

Minerals found in the original coals included quartz, pyrite, calcite, kaolinitic clays, gypsum, and trace quantities of feldspars. With the exception of gypsum and pyrite, all of the minerals were also present in the reactor cokes. All of the pyrite was reduced to pyrrhotite. Results also showed that adding H₂S during the runs did not decrease the fraction of iron in the reactor solids.

TABLE 5-8

LIQUEFACTION OF COAL WITH DIFFERENT CATALYSTS IN SECOND STAGE

Run No.	N149	N155	N156	N151
Coal	ALB2	ALB2	ALB2	ALB2
Solvent	Bitumen	Bitumen	Bitumen	Bitumen
Additive	K ₂ MoO ₄ /H ₂ S	K ₂ MoO ₄	H ₂ S	None
Run Time, min	20	20	20	20
Average Temp.	419	422	413	420
Max. Press., psig	2680	2625	2620	2770
% H ₂ Feed Gas	94.7	100.0	99.5	100.0
Moisture (GMS)	4.4	4.5	4.3	4.3
<u>Net Yields (Wt.% maf Coal Charged):</u>				
CO	.7	1.0	.2	.2
H ₂	-1.1	-1.6	-.7	-.0
CO ₂	1.1	.8	1.5	1.9
C ₁ - C ₃	2.5	2.8	2.4	2.6
H ₂ S, NH ₃	1.8	2.2	2.3	3.1
H ₂ O	1.6	.9	4.0	5.7
Gas + H ₂ O	6.7	6.1	9.7	13.4
Light Oil	16.1	14.4	20.9	16.6
Mid. Oil	-42.3	-56.2	-70.0	-41.2
Heavy Oil	73.1	77.7	82.7	75.6
C ₄ + Dist.	46.9	35.9	33.7	50.9
Sol. Residuum	29.3	43.7	22.0	3.8
IOM	17.0	14.2	34.6	31.8
Solvent Rec.	66.9	63.6	60.4	68.2
H ₂ Equiv. Consumption	.9	1.4	.6	.0
IOM/Gram Ash	4.9	4.9	4.9	4.9
Conversion	83.0	85.8	65.4	68.2
Material Balance Closure	98.9	91.8	98.7	98.7

5.2.5 Liquefaction Mechanisms and Kinetics

Preliminary experiments were carried out to determine the applicability of the methods chosen. The objectives for these preliminary tests were to:

1. Compare liquefaction products from identical autoclave tests with and without the addition of small amounts of H-donor by natural abundance 30.7 MHz ^2H NMR.
2. Compare the products formed when labelled syngas was used with identical tests using unlabelled syngas. Two experiments were performed with deuterium labeled gas (50/50 $^2\text{H}_2/\text{CO}$) plus one with carbon-13 labeled gas (50/50 $\text{H}_2/^{13}\text{CO}$).

5.2.5.1 Autoclave Test Conditions and Net Yields

The tests were carried out in a one-liter hot-charge autoclave with Big Brown (BB2) Texas lignite (65 g); solvent designated 66PBD (120 g) (prepared by distilling the end-of-run product-slurry from CPU Run 66 in which BB2 lignite was liquefied), and synthesis gas, an equimolar mixture of CO and H_2 (45 g). The runs are summarized in Table 5-9.

TABLE 5-9
AUTOCLAVE CONDITIONS AND NET YIELDS

Run No.	L003	L004	L005	L008
Coal	BB2	BB2	BB2	BB2
Solvent	66 PBD	66 PBD	66 PBD	66 PBD
Additive, wt % of solvent	None	0.27	0.20	None
Res. Time, min	20	20	20	20
Aver. Temp., °C	447	447	443	
Max. Temp., °C	450	449	455	
Max. Press., psig	3700	3650	3400	
<u>Misc. Net Yields,</u>				
<u>Wt % mat Coal:</u>				
Dist. Oil	4.01	12.08	2.18	
Solid Resid.	51.49	47.60	47.70	
Total THF Solubles	55.49	59.68	49.88	
Unconv. Coal	27.57	30.02	32.68	
Water	1.76	4.07	4.30	
Gas	15.16	6.23	13.14	
Conversion, %	72.41	69.98	67.32	
Solvent Recovery, Wt %	89.65	91.74	91.11	
Mat. Balance Closure, Wt %	92.77	92.77	90.82	

The products were separated into a water layer, an ASTM D-1160 distillate and vacuum bottoms and a small quantity of light oil collected in a cold trap. A gas sample was also collected.

5.2.5.2 Characterization of Autoclave Products and Discussion of Results

It has been suggested that ^2H NMR observations of deuterium enrichments and observation of deuterium NMR distributions are useful tools to investigate liquefaction reactions (1-5), though particular areas remain unexplored. Natural abundance ^2H NMR sensitive enough to be used to examine small fractions separated from products has recently become available using superconducting magnets operating in the Fourier transform (FT) mode. (The natural abundance of deuterium is only 0.015 pct of all hydrogen found.) Since it cannot be assumed that any starting solvent is at thermal isotopic equilibrium if it has a processing or preparative history that could include hydrogen transfer steps, it is essential that each experiment carried out have a baseline or control experiment. These experiments can now be successfully monitored by natural abundance ^2H NMR spectroscopy.

Many studies have been designed that obscure solvent and gas effects by employing a very active H-donor as the solvent. Deuterotetralin is often chosen. While these studies are useful, they have not addressed the questions that arise when "real" processing conditions are used. We have attempted to address both the interactions of the gas with the solvent and the H-donor activity of the solvent separately in a preliminary way.

5.2.5.2.1 Addition of H-Donor

Autoclave test No.'s L003 and L004 are identical except that a small amount of an H-donor (1,2,3,4-tetrahydrophenanthrene) was added to test L004 (Table 5-10). Comparing products of the two runs by 200 MHz ^1H NMR, 50 MHz ^{13}C NMR and fractionation by a simple silica gel column chromatographic technique showed no differences in the products. Table 5-10 compares the integrated proton, ^1H , areas for the three regions of the spectrum, aromatic and phenolic (9-6 ppm), alpha and beta (5.1-1.8 ppm) and other (1.8-0.1 ppm) with those of deuterium, ^2H , spectra. These divisions of the spectrum were selected because they are points where natural valleys occur in both the ^1H and ^2H spectra. The ^1H spectra are essentially the same for both tests, L003 and L004. Ratios of the areas were determined ($^2\text{H}/^1\text{H}$) for the three regions; Table 5-11 shows comparisons in hydrogen and deuterium distributions. Table 5-12 shows ratios of the integrated areas for the two autoclave runs, L003 and L004. All of the ^1H L004/L003 ratios are approximately 1; however, the $\alpha + \beta$ ^2H ratio for L004/L003 is 1.25 and the ratio for the ^2H "other" region is 0.61. A large change in the natural abundance ^2H distribution, when the only difference between the two tests is a very small amount of added H-donor indicates that there is a much larger number of hydrogen transfer reactions occurring in L004. For each hydrogen transfer there is a small deuterium isotope effect which, when taken cumulatively, results in the changed ^2H NMR distribution. The results indicate the most active positions are the alpha and beta positions with the "other" aliphatic positions the least active. These hydrogen shuttling reactions are likely very important in the liquefaction process.

TABLE 5-10
ADDITION OF H-DONOR TO LIQUEFACTION
AUTOCLAVE REACTIONS

Autoclave Run No.	<u>Solvent</u> <u>66 PBD</u>		<u>L003</u>	<u>L004</u>
<u>Additive, THPhen:</u>				
Wt %, maf coal	--		0.0	0.50
Wt % of solvent	--		0.0	0.27
<u>Natural Abundance</u> <u>NMR, Integrated Area, %:</u>				
Aromatic and phenolic (9-6 ppm)	¹ H	32.2	34.3	37.7
	² H	37.9	39.7	45.9
Alpha and Beta (5.1-1.8 ppm)	¹ H	32.6	32.0	31.4
	² H	34.7	28.6	35.7
Other (1.8-0.1 ppm)	¹ H	35.2	33.7	30.9
	² H	27.2	31.6	19.4

TABLE 5-11
¹H NMR DISTRIBUTIONS COMPARED WITH
²H NMR DISTRIBUTIONS

Relative Area Distribution Ratios, ² H/ ¹ H:	Solvent PBD	L003	L004
$(^{2}\text{H}_X/^{2}\text{H}_T/^{1}\text{H}_X/^{1}\text{H}_T)$			
Aromatic	1.18	1.16	1.22
Alpha and Beta	1.06	0.89	1.14
Other	0.77	0.94	0.63

TABLE 5-12
COMPARISON OF INTEGRATED ^1H AND ^2H NMR AREAS -
ADDITION OF H-DONOR

		<u>L004/L003</u>
Aromatic and Phenolic	^1H	1.10
	^2H	1.16
Alpha and Beta	^1H	0.98
	^2H	1.25
Other	^1H	0.92
	^2H	0.61

5.2.5.2.2 Processing with Labelled Gases, $^2\text{H}_2/\text{CO}$

Autoclave tests L004 and L005 were used to compare reactions with labelled and unlabelled syngas. Both tests contained the same small amount of added H-donor, tetrahydrophenanthrene; run conditions are shown in Table 5-13. The reaction using $^2\text{H}_2/\text{CO}$ (99 + atom % $^2\text{H}_2$) gave products that contained about 250-270 times the natural abundance of ^2H . The natural abundance ^2H NMR spectrum for Run L004 and the enriched ^2H NMR spectrum of Run L005 are compared in Figure 5-3 and Table 5-14. The ^1H NMR spectral distributions are also reported in Table 5-14. Again the ^1H spectra are much alike with test ratios of approximately 1. But the ^2H NMR distribution has changed for Run L005 as it did for L004, and the $\alpha + \beta$ regions are the most active. Based on the observations that the run with hydrogen shows no increase in the ^1H NMR $\alpha + \beta$ region ($\text{L005/L004} = 1.09$) while the ^2H NMR region shows an increase ($\text{L005/L004} = 1.21$), it is the effect of the gas entering the product that causes the observed differences. There is no competitive isotope effect of H_2 gas since nearly pure $^2\text{H}_2$ gas was used.

The most active area in H-transfer or exchange, as seen when comparing Runs L004 and L003, is also the site of largest hydrogenation (deuteration) seen when comparing Runs L005 and L004. The combined result is apparent in the increase of the $\alpha + \beta$ ^2H ratio ($\text{L005/L003} = 1.51$) and the corresponding decrease in ^2H other ($\text{L005/L003} = 0.42$).

To further compare the increase in ^2H distribution in the $\alpha + \beta$ ^2H NMR region and the corresponding decrease in the H_0 region, several separations were performed on the Run L005 ASTM D-1160 distillate using silica gel column chromatography. The results of the separation are shown in Table 5-15. The ^2H NMR distributions for the different fractions are shown in Table 5-16 and Figure 5-4. The aromatic fraction showed a large ^2H isotope enrichment at the $\alpha + \beta$ positions (51.1 pct), and the ratio for L005/L004 was 1.31; surprisingly, $^2\text{H}_0$ was also enriched ($\text{L005/L004} = 1.19$). The distribution in the polar fraction showed that the ^2H entering the product also is exchanging

TABLE 5-13

COMPARISON OF PROCESSING WITH LABELLED AND UNLABELLED
SYNGAS (CO/²H₂ AND CO/H₂)

Autoclave Run No.	<u>L004</u>	<u>L005</u>
<u>Additive, TH Phen:</u>		
Wt %, maf Coal	0.50	0.52
Wt % of Solvent	0.27	0.28
Processing Gas	CO/H ₂	CO/ ² H ₂
² H Enrichment	None	274 X Nat. Abund.

TABLE 5-14

COMPARISON OF RESULTS WITH LABELLED AND UNLABELLED
SYNGAS (CO/²H₂), (CO/H₂)

Area, % ASTM D-1160 Distillates	<u>L004</u> (unlabelled)	<u>L005</u> (labelled)	<u>L004/L003</u>	<u>L005/L004</u>	<u>L005/L003</u>
¹ H _{ar}	37.7	35.0	1.10	0.93	1.02
¹ H _{α+β}	31.4	34.3	0.98	1.09	1.07
¹ H _o	30.9	29.9	0.92	0.97	0.89
² H _{ar}	45.9	43.7	1.16	0.95	1.10
² H _{α+β}	35.7	43.1	1.25	1.21	1.51
² H _o	19.4	13.2	0.61	0.68	0.42

FIGURE 5-3. 30.7 MHz ^2H NMR of L004 and L005 product ASTM D-1160 distillates in CD_2Cl_2 .

TABLE 5-15
SEPARATIONS OF L004 AND L005 PRODUCT
ASTM D-1160 DISTILLATE

Silica Gel Column Chromatography

Solvent Schedule

	Wt % of Dist.	
	L004	L005
Pentane-----Alkanes	9.64	9.16, 10.4
CH_2Cl_2 -----Aromatics	51.0	51.9, 51.1
MeOH-----Polars	34.6	30.1, 27.8
Unrecovered	7.76	8.84, 10.7

TABLE 5-16
AREA PERCENTAGES OF SEPARATED FRACTIONS
OF L004 AND L005 PRODUCT ASTM D-1160 DISTILLATES

Integrated Area %, Column Fractions, ASTM Distillates		L004	L005	L005/L004
Alkanes	$^2\text{H}_o$	100.0	100.0	NA
Aromatics	$^2\text{H}_{ar}$	50.0	35.8	0.72
	$^2\text{H}_{\alpha+\beta}$	39.3	51.1	1.31
	$^2\text{H}_o$	10.7	13.1	1.19
Polars	$^2\text{H}_{ar}$	33.8	43.2	1.28
	$^2\text{H}_{\alpha+\beta}$	50.2	42.9	0.85
	$^2\text{H}_o$	16.0	13.9	0.87

FIGURE 5-4. 30.7 MHz ^2H NMR of silica gel fractions of L005 product.

extensively with that portion of the product containing polar aromatic compounds which are known to undergo exchange easily. The polar fraction is greater than 90 pct phenol plus the three cresols. The aromatic protons activated by the phenolic OH undergo exchange and this exchange is reflected in the comparative ^2H distributions for L005/L004 polars where aromatic $^2\text{H} = 1.28$. Undoubtedly there are other sites of exchange throughout the product since all regions are enriched.

Depletion of ^2H in the alkane fractions and H_2O alkyl regions relative to the rest of the products may be the result of less active hydrogen exchange and lower reactivity.

Another investigation carried out on all of the L005 products and fractions involved determining the ^2H incorporation into each fraction using ^2H NMR. The organic products were analyzed by a standard addition technique (Figure 5-5) and the D_2O incorporation into the H_2O by a direct comparison with standards (Figure 5-6). The standard lines are shown in Table 5-17 and the ^1H and ^2H NMR spectra are shown in Figures 5-7 and 5-8 respectively. The results show exchange or reaction to incorporate approximately 38 pct of the ^2H added in the labelled syngas into the reaction products.

5.2.5.2.3 Processing with Labelled Gases, $\text{H}_2/^{13}\text{CO}$ (99⁺ pct)

Autoclave tests L003 and L008 were performed to determine if any reaction gas (^{13}CO) was incorporated in the liquefaction products. Analyses of the gases are incomplete; however, analyses of the other products show no ^{13}C incorporation into the distillable products. Analysis of the vacuum bottoms is underway.

5.2.5.3 Conclusions

1. Differences in natural abundance ^2H NMR distributions result from differences in processing history of the sample.
2. The addition of small amounts of H-donor to a liquefaction reaction changes the natural abundance ^2H NMR distribution with respect to an identical run without added donor. The ^1H distribution and ^{13}C distribution are unchanged. Changes are probably the result of increased hydrogen transfer activity and the cumulative deuterium isotope effects. Most active are $\alpha + \beta$ regions.
3. Tests made using $^2\text{H}_2/\text{CO}$ show product incorporation of ^2H to >270 times the natural abundance as determined by standard addition ^2H NMR. The ^2H distribution is not the same as in the unlabelled test.
4. ^2H entered all fractions of the product including light oils, ASTM distillate alkanes, phenols and polars, H_2O and soluble vacuum bottoms. Polars and H_2O were the most enriched fractions, probably due to easy H-exchange.
5. When processed with $^2\text{H}_2/\text{CO}$ α and β ^2H NMR regions were sites of major ^2H enrichment. The control run processed with H_2/CO showed no increase in the ^1H α and β NMR regions.

FIGURE 5-5. Standard addition line for the determination of wt % ^2H in L005 product distillate.

FIGURE 5-6. Standard line for the determination of $^2\text{H}_2\text{O}$ in D_2O by 30.7 MHZ ^2H NMR.

TABLE 5-17

WT % ^2H , PRODUCTS FROM AUTOCLAVE TEST, L005

Product	Wt % ^2H	Wt % H in Sample	Enrichment Factor
Water	2.62	11.11	757
LLO	0.353		
ASTM D-1160 Dist.	0.606	7.17	274
ASTM D-1160 bottoms, CHCl_3 solubles	0.605		

Accounted for 38% of the ^2H addedWt % ^2H , L005 ASTM D-1160
Distillate Column FractionsWt % ^2H in Fraction

Alkanes

Aromatics

Polars

0.542

0.967

FIGURE 5-7. 200 MHz ^1H NMR and 30.7 MHz ^2H NMR of L005 product aromatic fraction.

FIGURE 5-8. 200 MHz ^1H NMR and 30.7 MHz ^2H NMR of L005 product polar fraction.

6. Addition of H-donor and labelled gas ($^2\text{H}_2/\text{CO}$ experiments show two separate ^2H distribution changes affecting mainly the most active α and β sites in the product.
7. ^2H NMR observations of ^2H enrichment and observation of deuterium isotope effects on ^2H distributions are useful tools for the investigation of liquefaction reactions, especially when comparisons are made with control reactions by natural abundance ^2H NMR.
8. In the test with labeled ^{13}CO syngas no ^{13}C incorporation into the product was observed, indicating interactions of ^{13}CO are either transitory or that labile addition products such as ketones, aldehydes or alcohols are formed and subsequently destroyed by the severe processing conditions.
9. The test with labeled ^{13}CO syngas ruled out a Fischer-Tropsch-type process for the formation of alkanes during liquefaction since no ^{13}C incorporation into products was seen.

5.2.6 Solvent Effects

Two "long" runs on the CPU were completed using two distinctly different startup solvents. The objective is to determine the effect, if any,

startup solvent has on product yields and to characterize the lined-out product. The startup solvents chosen were AO4 (7), a typical commercial anthracene oil and PDU Recycle solvent, a lignite derived solvent obtained by processing the same lignite in the Project Lignite PDU at UND (8). These solvents were selected as good startup solvents with sufficiently different composition to address the objectives. The analysis of these solvents are given in Table 5-18. The different solvents were used in Runs 101, 102, and 103. Runs 102 and 103 were at the same conditions with the startup solvent; a plug in the feed line caused premature termination in Run 102. A quick turn around allowed another startup, and the run number was changed to Run 103 to avoid sample-numbering problems.

Nominal run conditions for all the runs were: Zap lignite (from the Indian Head mine); 440°C reactor temperature; 4000 psig reactor pressure; H₂S addition at the rate of 5 lb/hr; coal feed rate of 5 lb/hr; 30 wt pct coal (as-received) in recycle feed; and about 5 mole pct CO in the feed gas with the remainder being hydrogen.

Run 101 lasted through 43 passes, each nominally four hours long, before a plug in a feed line forced an unscheduled shutdown. Viscosity of the recycle bottoms at various run periods is shown in Figure 5-9. The gradual, then rapidly increasing viscosity with run period is characteristic of what has occurred over the past many scheduled "long" runs. The bottoms eventually becomes so high that the unit can no longer be operated. The pass at which inoperability occurred depended on the operating conditions, the presence of H₂S, and on the coal feed. The rapid drop in viscosity seen after pass 25 was caused by blowing down the reactor contents, and then resuming the run. The smaller "oscillations" in viscosity are unexplained, but it is clear that the trend in viscosity is gradually, then precipitously, upward. Though termination of the run was because of a product line plug, it is clear that high viscosity would soon have prevented mixing the feed slurry.

Run 102 was begun using the recycle solvent from the Project Lignite Process Development Unit. It was decided that to help insure long-term operation, the reactor would be blown down when the bottoms product got too viscous. The reactor was blown down at pass 20, but before the effects were apparent a plug in the feed line caused shutdown. Turn around of the unit in preparation for the next run was very rapid; so Run 103 was begun using fresh PDU recycle solvent.

Operating procedures were modified for Run 103 so that the reactor was to be blown down every twelfth pass. The CPU operated very well through pass 43; 45 passes were scheduled. During pass 44, a feed line plugged, forcing a somewhat premature shutdown. If scheduled termination had not been imminent, the problem would have been relatively minor and the run could have continued.

5.2.6.1 Analyses of Products

Pass-to-pass analyses were carried out on the distillates of the product slurries. A schematic of the analytical characterization planned for CPU

TABLE 5-18

COMPARISON OF STARTUP SOLVENTS FOR 2 WEEK RECYCLE CPU RUNS WITH
INDIAN HEAD LIGNITE, H₂S, AND 95% H₂, 5% CO.

PDU Recycle Solvent (PDU) and Anthracene Oil (AO4)

Components Determined by 200 NMZ ¹H-NMR and Capillary
GC Analysis of Silica Gel Fractions

<u>Compound</u>	<u>% Whole Oil</u>	
	<u>PDU</u>	<u>AO4</u>
n-alkanes		
C-14	0.05	--
C-15	0.12	0.01
C-16	1.11	0.05
C-17	0.96	0.11
C-18	0.75	0.14
C-19	0.76	0.14
C-20	0.79	0.07
C-21	0.72	0.04
C-22	0.53	0.02
C-23	0.53	0.02
C-24	0.32	0.01
C-25	0.15	0.008
C-26	0.03	0.005
C-27	0.0001	--
C-28	0.0003	--
C-29	0.0003	--
C-30	0.0002	--
C-31	0.0002	--
Pristane	0.23	0.09
Phytane	0.03	0.11
Naphtahlene	--	0.75
2-methylnaphthalene	0.14	1.44
1-methylnaphthalene	0.03	0.86
2-ethylnaphthalene	0.04	0.32
1,3-dimethylnaphthalene	0.44	0.37
6-methylchrysene	0.03	--
benzo(e)pyrene	0.03	--
perylene	0.02	--
2a,3,4,5-tetrahydroacenaphthene	0.006	--
2,3-dimethylnaphthalene	--	0.16
1,6-dimethylnaphthalene	0.62	--
1,4-dimethylnaphthalene (1,5-,2,3-)	0.36	--
Acenaphthene	0.08	9.54

TABLE 5-18 (Continued)

COMPARISON OF STARTUP SOLVENTS FOR 2 WEEK RECYCLE CPU RUNS WITH
INDIAN HEAD LIGNITE, H₂S, AND 95% H₂, 5% CO.

PDU Recycle Solvent (PDU) and Anthracene Oil (AO4)

Components Determined by 200 NMZ ¹H-NMR and Capillary
GC Analysis of Silica Gel Fractions

<u>Compound</u>	<u>% Whole Oil</u>	
	<u>PDU</u>	<u>AO4</u>
(2,7-2,6-)dimethylnaphthalene	1.02	0.37
Dibenzothiophene	1.46	
Phenanthrene	6.99	16.59
9,10-Dihydrophenanthrene	0.23	
Octahydrophenanthrene	0.02	
Dibenzofuran	0.16	4.95
Fluorene	0.39	6.67
Anthracene	--	2.02
3-methylphenanthrene	3.06	0.66
2-methylphenanthrene	2.55	0.84
4,5-methylenephenanthrene	--	1.60
1-methylphenanthrene	0.82	0.52
Fluoranthene	0.46	6.87
Pyrene	0.50	2.69
Biphenyl	--	0.81
3,6-dimethylphenanthrene (?)	0.44	--
2-methylfluorene	0.55	--
1-methylfluorene (?)	0.80	0.45
4-methylfluorene	0.33	--
2-methylpyrene	0.29	--
4-methylpyrene	0.21	--
1-methylpyrene	0.24	--
1,2-Benzofluorene	0.26	0.48
2,3-Benzofluorene	0.13	0.48
Benz(a)anthracene	0.06	0.26
Chrysene	0.16	0.27
1,2,3,4-tetrahydrophenanthrene	0.18	--
C ₁ -dibenzothiophene (a) ⁺⁺	1.15	--
C ₁ -dibenzothiophene (b)	1.09	--
4-methylphenanthrene	0.72	--
4,5-dihdropyrene (?)	0.44	--
Unknown sulfur compounds (RT, min) ⁺		
28.42	0.18	--
28.79	0.26	--
28.92	0.48	--

TABLE 5-18 (Continued)

COMPARISON OF STARTUP SOLVENTS FOR 2 WEEK RECYCLE CPU RUNS WITH
INDIAN HEAD LIGNITE, H₂S, AND 95% H₂, 5% CO.

PDU Recycle Solvent (PDU) and Anthracene Oil (AO4)

Components Determined by 200 NMZ ¹H-NMR and Capillary
GC Analysis of Silica Gel Fractions

<u>Compound</u>	<u>% Whole Oil</u>	
	<u>PDU</u>	<u>AO4</u>
29.25	0.15	--
29.38	0.15	--
1,2,3,4-tetrahydrofluoranthrene	0.06	0.01
3-ethylphenanthrene	0.19	--
2-ethylphenanthrene	0.27	--
2,7-dimethylphenanthrene	0.47	--
Benzo(c)anthracene	0.03	--
Benzo(a)pyrene	0.02	--
Polars (phenols, bases, and polar aromatics)	21.4	18.3 (No phenols)

⁺ HD methylsilicone 50 in fused silica capillary, 40/min 100°-280°C.

⁺⁺ Designates isomer with shortest retention time, RT.

FIGURE 5-9. Run 101 recycle bottoms viscosity at 70°C.

Runs 101 and 103 is shown in Figure 5-10. All of the analyses listed in Figure 5-10 are completed for selected passes of Run 101 except the analyses of specific hydrocarbons by GC. Results are summarized in Table 5-19 through 5-23.

The increasing concentrations with pass number of coal-derived materials that are not present in the solvent (such as phenols and alkanes) are shown in Figures 5-11 and 5-12; it appears that lineout occurs much later (30-40 passes) than calculated from a theoretical dilution stand point. Figures 5-13 and 5-14 show that compounds in the start-up solvent (such as phenanthrene and acenaphthene) are being diluted in the product slurry. Figures 5-11 through 5-14 also show data from previous "long" runs carried out on the CPU; conditions for all of the runs are summarized in Table 5-20. Note that three start-up solvents are represented in these runs: SSOL, which contains about 12 pct phenols; A04, an anthracene oil; and HA061, hydrogenated A04 which contains no phenols.

FIGURE 5-10. Analytical characterization of slurry ASTM D-1160 distillates of CPU Run 101 and 103.

TABLE 5-19
SILICA GEL COLUMN DISTRIBUTION FOR RUN 101
(Wt % of Slurry Distillates)

Col Fn. No.	CPU Pass No.									
	1	3	5	7	9	13	17	21	30	38
2		1.9		2.8		2.4	3.7	3.9	9.7	6.6
3		0.8		2.8		1.4	1.6	0.8	2.6	2.1
4		10.8		12.4		11.4	10.6	7.2	8.1	10.1
5		12.8		11.5		10.0	7.6	8.2	6.8	5.9
6		14.6		12.5		12.0	9.7	9.5	6.0	4.3
7		11.7		9.4		9.9	7.5	8.0	4.3	4.1
8		11.5		8.9		7.8	7.8	7.1	5.5	5.2
9		5.7		5.0		4.6	4.8	4.1	3.9	4.1
10		3.4		2.9		3.4	3.0	2.7	2.2	3.7
11		1.1		1.0		1.9	1.0	1.2	0.4	1.6
12		26.7		29.0		38.0	40.6	--	44.9	50.9
% Recovery		101.0		98.2		102.8	97.9	--	94.2	98.5

TABLE 5-20
RUN CONDITIONS FOR CPU BOTTOMS RECYCLE RUNS

Run No.	<u>64</u>	<u>65</u>	<u>66</u>	<u>85</u>	<u>101</u>
Coal	BB1	B3	BB1	BB2	ZAP2
Processing gas	H ₂	H ₂	H ₂ /CO 50/50	H ₂ /CO 50/50	H ₂ /CO 95/5
Temp., °C	460	460	460	440	440
Pressure, psig	2600	2600	2600	280	4000
Startup solvent	*SSOL	SSOL	SSOL	HA04	AO4
Number of passes	13	14	13	13	43
Additive	-	-	-	-	H ₂ S

* 60% A04, 40% SRC MD

TABLE 5-21
COMPOUND CLASSES FOR CPU RUN 101 SLURRY DISTILATES

CPU Pass No.	Wt % of Distillate			% Recovery
	<u>Phenols</u>	<u>Hydrocarbons</u>	<u>Bases</u>	
1	10.1	83.4	5.66	99.1
3	9.57	77.6	5.54	92.8
5	12.8	78.6	4.58	95.9
7	16.7	77.4	5.03	99.1
9	16.3	75.2	4.10	95.6
13	21.5	76.6	5.86	103.9
17	21.9	69.4	4.54	95.8
21	27.6	67.7	4.86	100.2
24	29.3	72.3*	6.82*	108.4
27	26.4	85.2*	8.52*	120.2
30	27.2	60.6	--	--
38	31.3	61.4	--	--
40	32.4	60.6	--	--

* NMR shows solvent present.

TABLE 5-22

EXTRACTED PHENOLS FROM PRODUCT SLURRY DISTILLATE - RUN 101

Pass Number	101 PB1	101 PB3	101 PB5	101 PB7	101 PB9	101 PB13	101 PB17	101 PB21	101 PB24	101 PB27	101 PB30	101 PB38	101 PB40
Phenol	0.404	0.524	0.923	1.097	1.270	1.466	1.405	1.476	1.474	1.135	2.175	2.612	2.736
o-cresol	.209	.238	.338	.413	.470	.582	.563	.669	.784	.707	.999	1.097	1.102
m-cresol	.296	.391	.543	.648	.677	.831	.810	.961	.974	.982	1.369	1.426	1.479
p-cresol	.440	.485	.671	.759	.834	1.408	1.215	1.123	1.166	1.772	2.069	2.214	2.012
Phenols													
2-Et-	.098	.096	.139	.171	.178	.218	.214	.254	.265	.257	.329	.358	.384
2,4-DiMe	.145	.154	.226	.269	.286	.379	.370	.470	.524	.563	.722	.788	.798
2,5-DiMe	.090	.086	.127	.154	.163	.214	.214	.269	.297	.335	.401	.430	.426
4-Et-	.149	.229	.317	.381	.406	.500	.502	.566	.566	.606	.763	.923	1.010
3-Et-	.140	.161	.214	.250	.272	.338	.345	.377	.375	.516	.454	.457	.438
3,5-DiMe	.048	.053	.074	.092	.099	.122	.121	.150	.172	.175	.953	.983	.899
3,4-DiMe	.066	.081	.105	.123	.127	.163	.162	.195	.197	.244	.300	.332	.349
2-i-Pr-	--	--	.010	.012	.014	.018	.018	.021	.017	.020	--	.018	--
2-n-Pr-	.019	.035	.051	.067	.072	.097	.097	.109	.104	.112	.117	.129	.081
4-i-Pr-	.045	.076	.104	.128	.140	.172	.172	.199	.205	.223	.192	.232	.252
4-n-Pr-	.085	.131	.172	.219	.241	.294	.316	.346	.355	.378	.404	.520	.553
3-Et,5-Me-	.220	.251	.327	.389	.431	.544	.566	.619	.614	.868	1.379	1.579	1.557
4-t-Bu-	.011	.015	.019	.024	.024	.031	.031	.038	.041	--	.018	.011	--
4-indanol	.104	.128	.171	.207	.230	.293	.299	.327	.308	.384	.458	.473	.516
5-indanol	.169	.257	.346	.421	.462	.561	.582	.611	.555	.632	.888	.958	.974
2-phenyl-													
phenol	.069	.071	.090	.102	.108	.119	.116	.115	.084	.090	.102	.103	.103
α-naphthol	.113	.049	.041	.037	.032	.035	.036	.034	.034	.101	.027	.020	.016

TABLE 5-23

WT % SOLVENT-RELATED EXTRACTED HYDROCARBONS AND DIBENZOFURAN
IN RUN 101 SLURRY ASTM D-1160 DISTILLATES BY QUANTITATIVE 50 MHz ^{13}C NMR
WITH AN INTERNAL STANDARD AND 3 CONCENTRATION CALIBRATION CURVES

CPU Pass No.	Naphthalene	Phenanthrene	Fluorene	2-Methyl- naphthalene	Dihydro- phenanthrene	Dibenzofuran	n-alkanes as C-20	Acenaphthene
1	2.8	12.0	4.0	2.9	0.94	3.4	<1.0	3.7
3	3.2	10.2	3.9	3.3	1.5	3.5	1.2	2.9
5	2.6	8.1	3.4	3.5	2.1	3.3	1.5	2.1
7	3.1	9.4	3.4	3.5	2.0	3.1	1.5	2.4
9	3.0	7.9	3.0	3.0	1.9	2.9	1.5	2.1
13	3.5	8.3	3.0	4.0	2.0	2.9	2.3	2.3
17	3.7	6.8	2.3	3.5	1.8	2.0	2.2	1.8
21	3.0	6.3	1.8	3.0	1.2	1.3	2.3	1.2
24	2.9	5.5	1.7	3.7	0.98	1.4	2.5	0.96
27	2.5	3.2	1.2	3.0	1.7	0.57	3.1	0.79
30	2.7	4.0	1.4	2.1	1.8	0.59	3.4	0.70
38	2.8	3.0	1.1	2.0	1.7	0.33	3.6	0.62
40	2.7	3.2	1.2	2.1	1.7	0.42	3.8	0.76

S-33

FIGURE 5-11. Phenols in ASTM distillate versus number of reactor passes.

FIGURE 5-12. Weight percent n-alkanes in ASTM distillate versus number of reactor passes.

FIGURE 5-13. Weight percent phenanthrene in ASTM distillate versus number of reactor passes.

FIGURE 5-14. Weight percent acenaphthene in ASTM distillate versus number of reactor passes.

5.3 REFERENCES

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6. - COMBINED FLUE GAS CLEANUP/SIMULTANEOUS SO_x-NO_x CONTROL

Project No: 7202

B&R No.: AA0505000

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6.1 GOALS AND OBJECTIVES

The overall project objective is to develop an economical process for simultaneous control of SO_x/NO_x emissions derived from combustion of low-rank coals. The key to accomplishing this goal is the development of a dry process readily adaptable to retrofit situations and useful in areas of the West where water supplies are scarce. A promising process involves the direct injection of a calcium based sorbent material with subsequent collection of flue gas particulate (including the calcium based sorbent material) in a high temperature baghouse (1000°F). Use of a catalytic or noncatalytic NO_x reduction step in conjunction with the high temperature baghouse provides^x for simultaneous control of SO_x/NO_x emissions.

The specific goals of the project during the first year of the Cooperative Agreement are:

1. Identify and evaluate materials which have the potential for use as throwaway NO_x reduction agents.
2. Identify and evaluate additives or dopants for calcium-based compounds to enhance SO_x capture and sorbent utilization.
3. Investigate the use of a pressure hydrator as a means of combining additives and dopants with calcium-based compounds and increasing sorbent utilization.
4. Evaluate NO_x emissions control using an ammonia injection catalytic system incorporated into the 130 scfm propane-fired combustor/high temperature baghouse system.
5. Investigate simultaneous SO₂/NO_x emissions control by direct calcium injection for SO₂ control, and ammonia SCR and/or ammonia throw-away reagents for NO_x control, using the 130 scfm propane-fired combustor/high temperature baghouse system.

6. Investigate simultaneous particulate/SO_x/NO_x control using a high temperature baghouse and ammonia-SCR or ammonia throw-away system coupled with the pulverized coal-fired particulate test combustor.
7. Conduct an engineering/economic evaluation and begin work in preparation for a field test of simultaneous particulate/SO_x/NO_x control, to be cost-shared with a utility company in 1985.

The planned activities in the second quarter of FY 1983 and the first quarter of the Cooperative Agreement included the following:

1. Conduct literature surveys to identify throw-away reagents for NO_x control and additives enhancing calcium compound utilization for direct injection SO₂ control.
2. Collect throw-away NO_x reduction agents identified in the literature survey and evaluate them using a bench-scale packed-bed reactor system.
3. Investigate NO_x reduction capabilities of promising throw-away materials (as identified from bench scale packed-bed testing) on the 130-scfm propane-fired combustor/high temperature baghouse PDU.
4. Establish design criteria and construct a pressure hydrator to be used in the preparation of enhanced calcium-based dry sorbent materials.
5. Install a Selective Catalytic Reduction (SCR) NO_x control system for evaluation in the 130-scfm propane-fired combustor/high temperature baghouse PDU.
6. Perform preliminary testing of the 130-scfm SCR-baghouse system evaluating operability and NO_x emissions reduction with respect to vendor specifications.

6.2 ACCOMPLISHMENTS

6.2.1 Literature Search

A computer literature search was conducted to identify throwaway reagents for NO_x control and additives to enhance the utilization of calcium based sorbent materials for direct injection SO₂ control. As a result of the search several compounds were identified as potential throwaway reagents for control of NO_x emissions. The list of compounds include the following:

1. Magnetite (Fe₃O₄)
2. Iron Filings (Fe₂O₃, FeO)
3. Flue Dust (Fe₂O₃, FeO)
4. Nahcolite
5. Zeolite 900H (Synthetic Mordenite)

Additives which were identified as having the potential to enhance utilization of calcium based sorbent materials for SO₂ control include the following:

1. Sodium Hydroxide
2. Iron Oxide
3. Sodium Carbonate
4. Sodium Bicarbonate
5. Copper Oxide
6. Manganese Oxide

Although the literature search has essentially been completed, routine literature review may identify other potential throw-away NO_x control agents and additives to enhance utilization of calcium based sorbent materials.

6.2.2 Packed Bed Reactor Evaluation of Throw-away NO_x Reduction Agents

All of the throwaway NO_x reduction agents identified in the previous section were collected, and the bench-scale packed-bed reactor system was assembled and tested. Actual testing of throwaway reagents was begun in the first quarter of the Cooperative Agreement.

The bench-scale packed-bed reactor was constructed to evaluate the effect of various throw-away materials on the ammonia injection catalytic reduction of NO_x in a simulated flue gas stream. Table 6-1 provides data on inlet gas composition.

TABLE 6-1
PACKED-BED REACTOR INLET GAS COMPOSITION

<u>Constituent</u>	<u>Concentration (Vol. %)</u>
Nitrogen	78.3
Carbon Dioxide	16.0
Oxygen	5.7
Oxides of Nitrogen	1000 ppm
Anhydrous Ammonia	1500 ppm

Figure 6-1 illustrates the reactor configuration. The component gases are introduced at the top of the preheater, traversing downward through a 2-inch I.D. tube, heated by a Sybron/Thermolyne Model F21125 Tube Furnace. Hot gases then pass through the reactor, which consists of a 2-inch I.D. stainless steel tube externally heated by heat tape, a removable holder to contain bed material, and two type-K thermocouples. The holder is fitted with a wire mesh screen and porous Kaowool pads to prevent entrainment of bed material. Static pressure drop across the bed is measured by a manometer.

After passing through the reactor, the gas stream is cooled to 25°C and then flows through a gas metering device. Subsequently, the gas stream

FIGURE 6-1. Bench-scale packed-bed reactor.

enters a sample conditioner, from which slip streams are removed for analysis. NO_x concentrations are recorded by a Thermo Electron Model 10 Chemiluminescent Analyser, O_2 concentrations by a Beckman Model 755 Analyzer, and CO_2 concentrations by Beckman Model 865 Infrared Analyzer.

To conduct a test, about 50 g of minus 40 mesh material are placed in the bed; the weight of reducing agent used varies with its bulk density, since a fixed bed volume is desired. During heat-up, N_2 is purged through the system, and when the selected temperature is achieved, the sample gases are introduced into the preheater. The gas flow rate is kept at about 30 scfh, with the bed temperature operated from 400° to 750°F. Experimental conditions monitored throughout a run include bed and reactor wall temperatures, inlet and outlet gas flow rate and composition, and pressure drop across the bed. Space velocities are about 15,000 hr^{-1} .

Figures 6-2 and 6-3 illustrate the results of experiments conducted with a lignite fly ash and with iron filings. It is apparent that the iron filings activate at a lower temperature, but the slope of the curve decreases with increasing temperature. The reverse is true of the lignite fly ash: this material has virtually no catalytic activity at 400°F, but the activity increases markedly with increasing temperature.

Packed-bed reactor evaluation of the remaining identified throwaway NO_x reduction agents will be complete during the next quarter.

FIGURE 6-2. Activity of lignite fly ash versus temperature.

6.2.3 Evaluation of Throwaway NO_x Reduction Reagents in the 130-scfm PDU

Four runs (38 tests) were performed on the 130 scfm propane-fired combustor/high temperature baghouse PDU to evaluate throwaway NO_x reduction compounds during the two quarters being reported. The materials evaluated were a lignite fly ash, a subbituminous fly ash, and magnetite (Fe_3O_4). Injection was accomplished prior to the baghouse at temperatures ranging from 1000° to 1650°F.

A schematic of the 130-scfm combustor-baghouse is presented in Figure 6-4. The combustor burns propane gas to generate a flue gas containing approximately 11 pct moisture. Anhydrous ammonia (to produce NO) and SO_2 can be added to the flame at any desired rate. Sorbent or NO_x reduction materials may be injected through any sample injection port. The baghouse can be operated over a temperature range extending from the flue gas dew-

FIGURE 6-3. Activity of iron filings versus temperature from bench-scale packed-bed reactor.

point up to about 1000°F. Ceramic filters are used at flue gas temperatures ranging from 500°-1000°F.

A review of the literature indicated that iron compounds are effective catalysts for reducing NO_x emissions when combined with ammonia injection. The effective temperature range is reported to be 550° to 900°F, with maximum NO_x reduction occurring at 750° to 800°F.

The iron oxide content of lignite and subbituminous fly ash can vary from 2 pct up to 35 pct, with typical values for most ashes around 10 pct. Therefore, NO_x reduction may be possible by collecting the low-rank coal derived fly ash on ceramic filters in a flue gas temperature range of 550° to 900°F.

Experiments were conducted on the 130-scfm high temperature baghouse PDU to characterize NO_x reduction by iron oxide compounds collected on ceramic filters in the high-temperature baghouse. The results of the NO_x reduction experiments, with and without ammonia injection, are presented in Table 6-2.

Although overall NO_x reduction values reported in Table 6-2 are relatively insignificant the following conclusions can be drawn:

FIGURE 6-4. Dry sorbent unit, facility configuration.

TABLE 6-2

NO_x REDUCTION BY IRON OXIDE COMPOUNDS
IN A HIGH-TEMPERATURE BAGHOUSE

Test No.	Fly Ash ^a	Injection Temp., °F	Baghouse Temp., °F	Anhydrous ^d Ammonia, scfh	Reduction Total, %	A/C ft ³ /ft ²	Baghouse ΔP inch-WC
0183.1a	Lignite	1630	748	8.0	8	5.6	2.0-6.8
0183.2a	Lignite	1230	754	7.8	8	5.5	4.6-7.8
0183.3a	Lignite (pulv.)	1585	745	8.0	14	5.6	5.2-8.3
0183.4a	Lignite (pulv.)	1200	735	7.7	15	5.4	5.6-8.5
0183.1b	Subbit.	1585	745	7.8	6	5.5	5.0-8.6
0183.3b	Subbit. (pulv.)	1585	747	7.8	12	5.5	7.5-9.4
0183.2c	Subbit.	1210	739	7.8	16	5.5	7.9-10.5
0183.4c	Subbit. (pulv.)	1215	747	7.8	21	5.5	7.3-10.9
0283.1	Lignite (pulv.)	1630	611	5.3	0	4.9	2.1-5.0
0283.2	Lignite (pulv.)	1630	684	5.4	8	5.4	4.5-7.1
0283.3	Lignite (pulv.)	1630	749	5.4	14	5.7	6.6-9.6
0283.4	Lignite (pulv.)	1630	817	5.2	29	5.8	7.1-11.4
0283.6b	--	1080	761	5.3	21	5.7	8.2
0283.6c	--	1585	755	5.2	18	5.5	8.0
0383.1	--	1630	746	7.7	11	5.4	1.7
0383.2	Lignite (pulv.)	1630	746	7.8	2	5.5	1.7-4.7
0383.3	Lignite (pulv.)	1630	753	--	3	5.5	3.9-5.6
0383.4a	Lignite (pulv.) ^b	1630	749	--	3	5.5	4.5-6.4
0383.4b	Lignite (pulv.) ^b	1630	756	--	--	5.5	5.1-9.0
0383.5a	Lignite (pulv.) ^b	1630	755	7.7	13	5.5	4.7-7.4
0383.5c	Lignite (pulv.) ^b	1630	748	7.9	4	5.6	7.5-8.3
0383.5d	Lignite (pulv.) ^b	1630	750	7.7	7	5.5	5.4-8.6
0383.6	Lignite (pulv.) ^b	1630	745	15.5	2	5.5	5.1-8.1
0383.8	Lignite (pulv.) ^b	1550	875	7.6	12	6.0	5.7-9.4

TABLE 6-2 (Continued)

NO_x REDUCTION BY IRON OXIDE COMPOUNDS
IN A HIGH-TEMPERATURE BAGHOUSE

Test No.	Fly Ash ^a	Injection Temp., °F	Baghouse Temp., °F	Anhydrous ^d Ammonia, scfh	Reduction Total, %	A/C ft ³ /ft ²	Baghouse ΔP inch-WC
0483.1	--	1630	758	7.8	0	5.6	2.6
0483.2	Lignite (pulv.)	1630	751	7.8	2	5.5	3.4-4.7
0483.3	Lignite (pulv.) ^b	1630	745	--	0	5.6	3.7-5.1
0483.4	Lignite (pulv.) ^b	1630	753	--	0	5.6	4.2-6.0
0483.5	Lignite (pulv.) ^b	1630	750	7.9	8	5.6	4.8-6.7
0483.6	Lignite (pulv.) ^b	1630	753	15.8	12	5.6	5.0-6.9
0483.7	Lignite (pulv.) ^b	1600	815	7.8	5	5.8	4.9-7.9
0483.8	Lignite (pulv.) ^b	1550	865	10.5	15	6.1	4.8-8.6
0483.9	Lignite (pulv.) ^b	1600	829	7.9	11	6.0	4.6-7.9

^aParticulate concentration from fly ash injection was about 3.0 gr/scf.

^bMagnetite was injected in addition to fly ash. Total flue gas particulate concentration was about 6.0 gr/scf.

^cFlue gas NO concentrations maintained at about 1000 ppm with the exception of tests 0283.1 through 0283.6 for which NO concentration were maintained at about 700 ppm.

^dAll anhydrous ammonia was injected immediately upstream of the baghouse.

^eFe₂O₃ in lignite ash, 9.6 pct.

^fFe₂O₃ in subbituminous ash, 10.7 pct.

1. Maximum NO_x reduction was 29 pct using the pulverized lignite fly ash. Injection temperature, baghouse temperature, air-to-cloth ratio, and anhydrous ammonia injection rate were 1630°F, 815°F, 5.8 acfm/ft², and 5.2 scfh, respectively.
2. Reduction of NO_x emissions increased from 0 to 29 pct as baghouse temperature increased from 610° to 815°F for the pulverized lignite fly ash.
3. The flue gas temperature regime into which the lignite fly ash was injected did not affect the resulting NO_x reduction when injection temperatures were in the range of 1000° to 1800°F.
4. Fly ash materials injected into the 130 scfm PDU fouled flue gas piping when injected into temperature regimes in excess of 1800°F.
5. The subbituminous fly ash tested was more reactive when injected at 1200°F than at 1600°F.
6. Injection of pulverized fly ash increased the NO_x reduction values as compared to untreated fly ash.
7. The addition of magnetite to the flue gas stream with subsequent collection in the baghouse had no effect on NO_x reduction results.
8. Reduction of NO_x emissions by the fly ash iron oxide materials tested was essentially zero without anhydrous ammonia injection.

Additional testing will be performed with the subbituminous fly ash to complete the data set. Minimal testing will also be performed with the lignite fly ash to substantiate present data and clear up some inconsistencies. Additional testing of magnetite is not planned at this time. Future testing will also include some of the other additives identified in Section 6.2.2. An investigation will also be conducted into magnetic separation and recovery of iron oxide compounds from bulk baghouse ash if one of the iron oxide compounds tested proves successful.

6.2.4 Development of Continuous Bench-Scale Pressure Hydrator

Work conducted in SO_2 control during the past 6 months has centered around the development of a continuous bench-scale pressure hydrator. The apparent advantages of a SO_2 control scheme using a pressure hydrator for direct injection of calcium-based compounds include the following:

1. Very small particles (0.4-micron) are generated in the pressure hydrator, which are further reduced in size by dehydration reactions after injection into a flue gas stream. Small particle size provides large surface area for reaction.
2. Additives can be readily incorporated in the hydration process to increase overall sorbent utilization to meet changing coal sulfur levels.

From previous results calcium hydroxide has proved to be the most reactive calcium-based material for direct injection into high temperature flue gas. If the reactivity of the hydrated product can be increased by addition of other compounds during the hydration process overall sorbent utilization may be significantly increased from the 40 pct value previously observed. Sodium is one of the additives proposed for testing, and will be added by hydrating quicklime with a solution of sodium hydroxide. Other additives being considered include iron oxide, sodium carbonate, sodium bicarbonate, copper oxide, and manganese oxide.

Three system configurations have been tested in an attempt to develop a bench-scale pressure hydrator capable of producing about 5 lbs/hr of hydrated product having an average particle size of 0.4 microns. The basic reactor configuration has consisted of a continuously stirred cylindrical reactor. The reactor has an interior diameter of approximately 6 inches and an overall length of 12 inches. Operating conditions for the reactor are nominally 150 psig and 360°F.

The first configuration tested used the reactor described above and separate water and quicklime (CaO) feed locations. Quicklime was to be fed from a pressurized hopper through a rotating ball valve into the reactor. Water for the hydration reaction was to be injected into the reactor by a positive displacement piston pump. The reason for separating the quicklime and water feed streams was to eliminate the necessity for pumping a slurry and to prevent the hydration reaction from beginning outside the reactor. This configuration was found to be unworkable due to severe plugging in the rotating ball valve.

Separation of the quicklime and water feed locations was also attempted in the second configuration. The basic reactor configuration and water injection method remained the same. The quicklime feed system was changed from the pressurized hopper and rotating ball valve to a screw feeder. Again plugging problems made the screw feeder unworkable.

After failing twice to develop a working pressure hydrator system with separate quicklime and water feed locations, a decision was made to use the conventional method of premixing the water and quicklime and pumping the slurry into the reactor. The key to successfully operating a pressure hydrator in this manner is to thoroughly mix the slurry and pump the slurry into the reactor in a relatively short time (1-2 seconds). The rate of the hydration reaction can be controlled somewhat by adding carbon dioxide to the system. Testing of the new configuration will begin in early July. Upon successful operation of the pressure hydration system, hydration product evaluation will begin with X-ray Diffraction analysis and TGA techniques.

6.2.5 Acquisition and Installation of Selective Catalytic Reduction (SCR) System

After completion and review of the preliminary design for the SCR system to be incorporated into the 130-scfm high temperature baghouse PDU, discussions were held with two NO_x-catalyst vendors--Engelhard, Inc. and Midland-Ross, Inc.--regarding the purchase of catalyst material. As a result of those discussions, a decision was made to use a honeycomb array catalyst support configuration. The primary reason for adopting the honeycomb array

configuration was the pressure drop limitations of the 130-scfm high temperature baghouse PDU. Engelhard, Inc. was chosen to supply the base metal catalyst/honeycomb support/reactor system.

Modifications to the 130-scfm high temperature baghouse PDU necessary for installation of the SCR reactor began in late April and were completed in early May as scheduled. All work was performed by UNDERC's instrument and machine shops, and the combustion pilot plant operations personnel. Modifications made to the 130-scfm high temperature baghouse PDU included:

1. Separation of the baghouse bypass and outlet flue gas streams.
2. Installation of two water-cooled annular heat exchangers. Heat exchanger No. 6 is used to control the temperature of flue gas entering the SCR reactor. Heat exchanger No. 7 reduces the temperature of flue gas bypassing the baghouse prior to entering the ID fan.
3. An additional expansion joint was added to compensate for differential thermal expansion of the baghouse bypass and outlet piping.
4. Additional instrumentation was added to monitor flue gas temperature in the baghouse bypass, the SCR reactor inlet and the ID fan inlet flue gas streams. Pressure taps were added to the SCR reactor to monitor differential pressure.
5. A spool piece was constructed to replace the SCR reactor in the flue gas piping system when the use of the reactor is not desirable.

Figures 6-5 and 6-6 illustrate the inlet and outlet baghouse piping configurations before and after the installation of the SCR reactor, respectively.

6.2.6 Evaluation of Operability and NO_x Reduction Capabilities of SCR System

Three runs, each containing a series of tests, have been performed evaluating system operability and NO_x reduction capabilities of the SCR/high temperature baghouse system.

Run DS-SSD-0583 was performed specifically to evaluate operability of the 130 scfm propane-fired combustor/SCR/high temperature baghouse system following installation of the SCR reactor. No operability problems were identified during the run. System flow rates and pressure drops were acceptable. The new heat exchangers provided sufficient cooling to operate the SCR reactor in the desired temperature range (550°-750°F) and reduced flue gas temperatures sufficiently to increase the efficiency of the induced draft fan. Manufacturers specifications, as presented in Table 6-3, indicate that the SCR reactor will provide 80 pct NO_x reduction for reactor temperatures ranging from 550°-750°F.

FIGURE 6-5. Baghouse inlet and outlet flue gas piping prior to installation of SCR reactor.

FIGURE 6-6. Baghouse inlet and outlet flue gas piping after installation of SCR reactor.

TABLE 6-3
MANUFACTURERS SPECIFICATIONS FOR
SCR REACTOR

NO _x reduction:	80%
Flue gas flow rate:	130 scfm
O ₂ in flue gas:	Greater than 4%
Reactor temperature	550°-750°F
Ammonia injection rate:	1:1 (NH ₃ /NO in flue gas)
Pressure drop:	4 inches H ₂ O
Catalyst life:	2 to 3 years

Runs DS-SCR-0683 and DS-SCR-0783 were performed to evaluate the NO_x reduction capabilities of the SCR reactor with respect to reactor temperature, stoichiometric ratio (NH₃/NO) and location of ammonia (NH₃) injection. The data in Table 6-4 identify reactor temperature as the parameter having the greatest effect on overall NO_x reduction. Experimental data presented in Figure 6-7 show that 80 pct NO_x reduction was achieved at reactor temperatures exceeding 700°F. At reactor temperatures of 575°F, NO_x reduction

FIGURE 6-7. NO_x reduction versus reactor temperature.

TABLE 6-4

NO_x REDUCTION IN THE SCR REACTOR

Test No.	Date	Reactor Temp. °F	Reactor ΔP "WC	Stioc Ratio (NH ₃ /NO)	NH ₃ Inject Location ^a	NO _x Reduction %
0683.1	6/14	575	--	1.0	SP-11	63
0683.2	6/14	640	2.8	0.8	SP-11	68
0683.3	6/14	727	3.2	1.0	SP-11	86
0683.4	6/14	729	3.2	1.0	SP-7	86
0683.5	6/14	730	3.2	0.5	SP-11	73
0683.6 ^b	6/15	720	3.4	0.5	SP-11	73
0683.7 ^b	6/15	726	3.5	1.0	SP-11	80
0683.8 ^{b,c}	6/15	713	3.5	1.0	SP-11	84
0683.9 ^b	6/15	723	3.7	1.5	SP-11	86
0783.1	6/21	570	2.7	1.0	SP-11	59
0783.2	6/21	565	2.7	1.0	SP-7	59
0783.3	6/22	635	3.1	1.0	SP-7	68
0783.4	6/22	640	3.1	1.0	SP-11	68
0783.5	6/22	724	3.6	1.0	SP-11	86
0783.6	6/22	727	3.6	1.0	SP-7	82
0783.7	6/22	722	3.5	1.0	SP-10	79
0783.8 ^b	6/23	720	3.6	1.0	SP-11	77
0783.9 ^{b,d}	6/23	625	2.7	1.0	SP-11	72
0783.10 ^{b,c}	6/23	712	3.8	1.0	SP-11	84
0783.11 ^e	6/23	733	4.7	1.0	SP-11	81
0783.12 ^e	6/24	722	5.2	1.0	SP-11	81
0783.13	6/22	729	3.6	1.0	SP-17	84

^a Injection ports SP-7, SP-10, SP-11, and SP-17 correspond to locations in the flue gas system having temperatures of 1700°, 1200°, 1100°, and 775°F, respectively.

^b Flue gas contains a fly ash particulate loading of about 3 gr/scf.

^c Flue gas contains about 100 ppm SO₂.

^d Flue gas flow rate was only 129 scfm compared to 152 scfm to 165 scfm for all other tests.

^e Flue gas contains about 650 ppm SO₂ with hydrated lime injection.

values were as low as 59 pct. Although the reactor was operated at slightly higher flue gas flow rates than those specified by the manufacturer, 160 scfm compared to 130 scfm, a single test conducted at a flue gas flow rate of 129 scfm and reactor temperature of 625°F resulted in only 72 pct NO_x reduction. Several tests were also conducted with less than 4 pct O_2 in the flue gas, but even at 3.6 pct O_2 in the flue gas 84 pct NO_x reduction was achieved at a reactor temperature of 729°F.

Tests conducted with stoichiometric ratios (NH_3/NO) ranging from 0.5 to 1.5 resulted in relatively small changes in NO_x reduction as shown in Figure 6-8. At a reactor temperature of 725°F, stoichiometric ratios of 0.5, 1.0, and 1.5 resulted in NO_x reduction values of 73 pct, 80 pct, and 86 pct, respectively. These values are reasonable with the exception of 73 pct NO_x reduction at a stoichiometric ammonia injection rate of 0.5. Theoretically only 50 pct NO_x reduction should have occurred. Additional testing will be performed to substantiate or disprove these data.

FIGURE 6-8. NO_x reduction versus stoichiometric ratio (NH_3/NO).

Data presented in Table 6-4 indicate that the location at which the anhydrous ammonia was injected did not affect the overall NO_x reduction. Several tests were performed in which the reactor temperature, flue gas flow rate and stoichiometric ratio (NH_3/NO) were nominally constant. Four injection ports, located in temperature regimes ranging from 775° to 1700°F, were used. The results of the tests showed that for injection ports SP-7 (1700°F), SP-10 (1200°F), SP-11 (1100°F) and SP-17 (775°F) NO_x reduction

values were 82 pct, 79 pct, 86 pct, and 84 pct respectively. This information indicates that the location or temperature regime at which the anhydrous ammonia (NH_3) is injected is not critical as long as the NH_3 is thoroughly mixed with the flue gas prior to entering the SCR reactor. The limitation would be injecting NH_3 into a temperature regime in excess of 1700°F where oxidation of NH_3 to NO might begin to occur.

Future testing of the SCR system will be minimal until simultaneous SO_x/NO_x work begins in September or October 1983.

7. - PARTICULATE CONTROL AND HYDROCARBONS AND TRACE ELEMENT EMISSIONS FROM LOW-RANK COALS

Project No.: 7203

B&R No.: AA0505000

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7.1 GOALS AND OBJECTIVES

The purpose of the particulate characterization project is to measure and characterize particulate and trace element emissions to the atmosphere and relate these emissions to the fuel, ash, and particulate collector parameters, and to operation of upstream FGD, NO_x-reduction, or simultaneous SO_x/NO_x reduction devices. The long range goal of this work is to develop a detailed understanding of coal- and collector-specific emissions, in order to reduce these emissions by improved collector and station design, coal preparation, or other strategies, based upon reliable predictive models. Another goal is to assist DOE in preparing for new regulatory thrusts, primarily at the Federal level, which may relate to respirability, ultrafine particle emissions, or metal content.

The specific objectives for the first year of the UNDERC Cooperative Agreement are:

1. Characterization of combustion emissions with respect to composition, morphology, and particle size distribution, and relationships to upstream parameters such as fuel and control equipment. Characterization will include:
 - (i) Morphology (SEM)
 - (ii) Particle size distribution (SEM and multicyclone)
 - (iii) Bulk composition (XRF)
 - (iv) Composition as a function of size (SEM/microprobe)

With the procurement of a laser optical device (11/83), quasi real-time measurement of particle size distribution will also be included as part of the characterization effort. Although particle size distribution plays a role in affecting baghouse collection efficiency, other properties appear to have overriding effects. Morphology and particle cohesion need to be investigated. There are hints in existing data that sodium concentration may affect cake development and maintenance, and therefore emission levels.

One approach which will require a significant effort is to perform correlation studies (regression analyses) of a variety of inlet ash parameters and fabric characteristics in relation to outlet emission levels. Data already published, in press, or otherwise in hand include particulate size and composition distributions for a number of coals and fabrics, largely for shaker cleaned bags. This data set will be utilized first.

2. Spiking and dopant studies in the Particulate Test Combustor to determine origin of ash "minerals", and to determine fabric clearance rates. This task is also important to the Waste Characterization project, in which a goal is to understand the phase behavior transformations, and elemental associations, in order to devise strategies for immobilizing deleterious elements in fly ash. The testing of fabric clearance rates relates to: a) validation of sequential short term filtration tests, and b) understanding penetration rates of filter cake components through intact fabric.
3. Characterization of emissions from the high temperature ceramic baghouse on the dry sorbent unit. This task is to be performed in cooperation with the SO_x/NO_x control project. Filtration characteristics and emissions of high temperature ceramic filters in fossil applications have not been studied extensively, and require investigation in support of the SO_x/NO_x control goals.

7.2 ACCOMPLISHMENTS

7.2.1 Characterization of Beulah, ND Lignite

7.2.1.1 Background

Fort Union lignites represent one of the three major groups of low-rank western coals. The others are the Gulf Province lignites, mainly in Texas, extending into Alabama, and the diverse subbituminous coals, found on both sides of the Rocky Mountains from New Mexico to Montana and the southern provinces of Canada.

Previous reports in this series (1, 2, 3, 4) have presented detailed studies of three coals: Arapahoe subbituminous, an exceptionally high-grade western coal on the borderline between subbituminous A and high-volatile C bituminous (10,700 Btu/lb); San Miguel, Texas lignite, a high-ash, high-sulfur Gulf Province lignite of variable composition and low-heating value (4000-7000 Btu/lb); and Ledbetter, Texas, lignite, also a Jackson group lignite of moderately high ash (21 pct) and low Btu (6578 Btu/lb), having unusually high silica in the ash (58.7 pct).

Arapahoe and San Miguel are fuels used at full-size utility steam electric boilers at which this project has sponsored field tests by Southern Research Institute (5,6). By contrast, Ledbetter is a Texas Lignite for which no station and no mine exist. A plant is now in design stage. Our tests were performed on core drillings.

Beulah, North Dakota, lignite, was used in the combustion tests of interest to this report. This lignite is extraordinarily variable in its inorganic constituents. For example, the sodium content can have a tenfold variation within a few hundred meters in a single seam (7). The specific Beulah lignite used was selected for its high sodium content.

A subsequent report in this series will describe work in which this lignite was studied after removal of a portion of its sodium by ion exchange with H_2SO_4 .

7.2.1.2 The Particulate Test Combustor (PTC), Combustion Conditions, and Ash Sampling

Fly ash is generated at UNDERC using the Particulate Test Combustor, a pulverized coal-fired furnace having a nominal coal consumption of 75 lbs/hr. This device was illustrated and described in previous reports (3). The fuel combusted in the test burn reported here, PTC Run No. BA-220, was pulverized to 55.0 pct. "-220" mesh, 39.8 pct "-230" mesh. Combustor operating parameters, and flue gas and sampling conditions are summarized in Table 7-1.

7.2.1.3 Beulah Coal Analysis

Coal proximate and ultimate analyses and the coal ash analysis, appear in Tables 7-2 and 7-3.

The inorganics associated with the Beulah lignite consist of a complex mixture of cations bound to the humic acid groups, possible chelates or coordination complexes, minerals formed during coalification, and minerals accumulated during deposition. Several non-traditional methods were used to examine the coal characteristics.

One of the "non-traditional" methods used is low-temperature ashing in an oxygen plasma at $150^\circ C$, with x-ray diffraction analysis to determine the crystalline phases in the ash. The phases identified include SiO_2 (quartz), FeS_2 (pyrite), kaolinite, and $CaCO_3$ (calcite). The second method involves a chemical fractionation procedure which selectively removes inorganics (8). The ion-exchangeable cations and soluble salts are removed with 1M ammonium acetate. The coal is then extracted with 1M hydrochloric acid to remove chelated species, acid decomposable minerals such as carbonates, and oxides. The inorganics remaining in the coal can include FeS_2 , organically bound sulfur, quartz, and clay minerals. The elements found to be extracted with ammonium acetate are Na (100 pct of the total Na content), Mg (88 pct), Ca (41 pct), and K (57 pct). The elements removed by HCl are Mg (20 pct), Al (61 pct), Ca (50 pct) and Fe (30 pct). The elements which remain are Si (100 pct), Fe (70 pct), Al (40 pct), and S (100 pct). Table 7-4 summarizes data obtained on the inorganic constituents in Beulah lignite and its geologic formation.

TABLE 7-1
RUN AND SAMPLING CONDITIONS DURING
BEULAH TEST BURN PTC-BA-220

Coal Feed, lb/hr	74.0
Air Feed, scfm	117
Flue gas composition ^a :	
O ₂ , vol % dry basis	5.2 ($\sigma = 0.6$)
CO ₂ , vol % dry basis	13.8 ($\sigma = 0.7$)
N ₂ , vol % dry basis	81.0
CO, vol % dry basis	0 ($\sigma = 0$)
SO ₂ , ppmv dry basis	729 ($\sigma = 78$)
NO _x , ppmv dry basis	681 ($\sigma = 20$)
H ₂ , vol %	12.4
Inlet ^b dust loading	
gr/scf	2.81
Inlet ^b temperature, °F	355
% isokinetic	98.8

^aO₂ is measured with Beckman Model 741 electrochemical analyzer and Model 755 paramagnetic analyzer. NO_x by Thermo Electron Series 10 chemiluminescent instrument; SO₂ by DuPont Model 400 photometric analyzer; CO₂ by Beckman Model 864 and CO by Beckman Model 865 infrared analyzer. (Reference to specific brand names and models is done to facilitate understanding and neither constitutes nor implies endorsement by the Department of Energy).

^bAt ash sampling port, located on inlet side of baghouse. No statistically significant variation in any measured flue gas constituent occurred between combustor outlet, baghouse inlet, and outlet. Dust loading determined by total collection of Accurex SASS train at inlet ash port.

TABLE 7-2

PROXIMATE AND ULTIMATE ANALYSIS OF BEULAH, ND
LIGNITE COMPOSITE AS BURNED

C, %	46.29
H, %	5.29*
N, %	0.62
S, %	0.99
O, % (by difference)	45.99
Ash, %	8.2
H ₂ O, %	27.2
Volatile Matter, %	30.9
Heating Value (Btu/lb)	7512

*Includes H associated with H₂O

TABLE 7-3

COAL ASH ANALYSIS OF BEULAH, ND
LIGNITE COMPOSITE AS BURNED^a

SiO ₂ , %	26.4
Al ₂ O ₃ , %	12.4
Fe ₂ O ₃ , %	11.3
TiO ₂ , %	1.1
P ₂ O ₅ , %	0.4
CaO, %	18.2
MgO, %	4.5
Na ₂ O, %	13.0
K ₂ O, %	0.6
SO ₃ , %	12.2
	100.1

^aBy x-ray fluorescence analysis.

TABLE 7-4
INORGANIC CONSTITUENTS IN BEULAH
LIGNITE AND SENTINEL BUTTE FORMATION

	Beulah Lignite		Sentinel Butte Formation		
	Whole Coal	Sink Fraction	Overburden	Lignite	Underclay
Alkali feldspars	XXX		XX	X	X
Augite				X	
Barite	X			X	
Biotite	X		X		
Calcite/dolomite	X	XX	XX	X	
Chlorite			XX	X	X
Galena	X				
Gypsum		XX		XXX	
Hematite		X		XX	
Hornblende			X		
Illite	XXX		XX	X	X
Kaolinite	XXX	X	XX	XXX	XXX
Magnetite	X				
Montmorillonite			XXX	X	XXX
Muscovite	X				
Plagioclase		X	XXX	X	X
Pyrite	XXX	XXX		XX	
Quartz	XXX	XXX	XXX	XXX	XXX
Rutile	X				
Volcanic glass			X		

XXX Abundant
XX Common
X Minor

7.2.1.4 Beulah Fly Ash Sampling

Fly ash is sampled isokinetically in three ways in the PTC: 1) using a modified U.S. EPA "method 5" dust loading filters (9); 2) by collection in a Southern Research Institute 5-stage multicyclone which simultaneously samples isokinetically and size fractionates the ash (10, 11); 3) by collection in a three-stage cyclone module of an Acurex Source Assessment sampling system or "SASS-Train" (11, 12). Actual size ranges for the multicyclone and SASS-train appear in Table 7-5. They are expressed as aerodynamic diameters in μm and correspond to actual flow rates employed. The figures represent the mass median diameters (D_{50}) or "cut points", of the size distribution entering or leaving the stage.

7.2.1.5 Particle Size Distribution

University of Washington Mark III cascade impactors were used to more precisely determine particle size distribution (13). The cumulative particle

TABLE 7-5

ACTUAL SAMPLING FLOW RATES AND RESULTING AERODYNAMIC SIZE
RANGES OF AEROSOL SAMPLING/FRACTIONATING EQUIPMENT,
RUN PTC-BA-220

<u>Instrument</u>	<u>Southern Research Institute Multicyclone</u>					<u>Acurex/Aerotherm SASS Train</u>		
Flow rate employed STD 1/min	9.36					113.2		
Stage No.	1	2	3	4	5	1	2	3
Nominal size range (upper and lower D_{50}), μm	>10.3	10.3- 5.6	5.6- 4.15	4.15- 1.9	1.9- 1.55	>10	10-3	3-1

size distribution, expressed in aerodynamic diameters, appears in Figure 7-1. These data are used only for comparison. The bulk of the characterization work was done on the multi-cyclone and SASS Train samples because the masses of particles collected by the impactor are very small and inadequate for analysis.

FIGURE 7-1. Baghouse inlet particle size distribution determined with University of Washington Mark III Cascade Impactor.

However, both the SASS Train and the SoRI multicyclone can be used to determine particle size distributions. In order to display the relationship between the Beulah ash particle size distributions and that of other coals, several size distributions are displayed in Figure 7-2, as determined with the SASS Train.

FIGURE 7-2. Inlet particle size distributions determined with the Acurex/Aerotherm SASS train 3-stage cyclone system. Sarpy Creek is a Montana subbituminous coal, Arapahoe a Colorado subbituminous, and Big Brown, a Texas lignite.

7.2.1.6 Bulk Ash Analyses and Analyses of Fractionated Ash

Macroscopic ash samples are analyzed by x-ray fluorescence (XRF). Elemental trends determined by XRF analysis show increasing concentration of Na_2O and SO_3 and decreasing SiO_2 , CaO , Fe_2O_3 , and MgO with decreasing particle size. Very little change was noted for Al_2O_3 or the minor elements (TiO_2 , K_2O , and P_2O_5). These relationships are illustrated in Figure 7-3. X-ray diffraction was used to identify the crystalline species in each size fraction. The trends show the following relationships:

1. Na_2SO_4 and $\text{Na}_2\text{Ca}(\text{SO}_4)_2$ are present in the smaller size fractions.
2. SiO_2 and CaO are noted in larger size fractions and not in smaller fractions.

FIGURE 7-3. X-ray fluorescence analysis of bulk ash from each stage of the SASS Train Sampler.

3. Fe_3O_4 - MgFe_2O_4 - MgO phases decrease from larger to smaller size fractions.
4. Possible Al_2SiO_5 and K_2SO_4 phases are noted in smallest size fractions.

The most interesting trend is the increasing amount of Na_2O and SO_3 with decreasing particle sizes. Because of the importance of Na and SO_3 in moderating ash resistivity, this is a fortunate trend in the case of any coal whose fly ash is collected by electrostatic precipitation (ESPs). Fine particles are the most difficult to remove by ESPs and it is desirable to reduce resistivity of the difficult-to-control ash fractions to the maximum extent possible. On the other hand, the importance of these major elemental concentrations to fabric filtration remains unclear.

7.2.1.7 Scanning Electron Microscopy (SEM)

The SEM has been the major ash microcharacterization tool employed to date in this project, and it has assumed an importance equal to the SoRI multicyclone and the cascade impactor. Our methods have been described in detail previously (1, 2, 3, 4).

Briefly, the scanning electron microscope (SEM) equipped with an energy dispersive x-ray analyzer was used to image and analyze particles down to $\sim 1\mu\text{m}$ in size. The particles were selected at random for analysis by using a grid overlay of points generated by random numbers on the SEM photomicro-

graph. One hundred particles for each stage were analyzed, determining 10 elements per particle, and sized. All data were entered into a computing system for correlation analysis. Each particle is individually serial numbered, permitting various multivariate analyses to be performed.

Particle sizes measured by SEM are actual, rather than aerodynamic. The relationship between these descriptors is:

$$d_{\text{aero}} = d_{\text{actual}} \cdot \rho^{\frac{1}{2}}$$

where ρ , the particle density, is generally unknown. Mean particle densities can be measured by helium pycnometry; however, our observation of wide particle-to-particle variations in composition suggest that this mean density is not useful in understanding the aerodynamic properties of lignite fly ash.

The average particle size determined from the SEM photomicrographs for each SoRI multicyclone stage is listed in Table 7-6. Table 7-6 also lists the Na_2O and SO_3 concentration averages for all five stages along with the ratio of Na_2O to SO_3 . The concentrations of Na_2O and SO_3 increase as particle size decreases and the ratio of Na_2O to SO_3 is very close to that of pure Na_2SO_4 for stages 1, 3, and 4. The particles collected in stage 5 are not consistent with other stages in particle size or in the ratio of Na_2O to SO_3 . X-ray diffraction analyses revealed $\text{Na}_2\text{Ca}(\text{SO}_4)_2$ in the third stage of the SASS system.

TABLE 7-6
SIZE, SODIUM, AND SULFUR RELATIONSHIPS
FOR EACH STAGE OF THE SoRI MULTICYCLONE

Stage	Particle Size, μm	Na_2O , %	SO_3 , %	$\text{Na}_2\text{O}/\text{SO}_3$
1	5.48	8.60	10.98	0.79
2	1.99	10.78	12.53	0.86
3	1.29	13.20	17.02	0.78
4	1.20	13.98	19.43	0.72
5	1.38	14.99	23.05	0.65

$\text{Na}_2\text{O}/\text{SO}_3$ in pure $\text{Na}_2\text{SO}_4 = 0.78$

The first panel of Figure 7-4 displays the population distribution of actual particle sizes obtained by SEM. These results (and all of the histograms in Figures 7-4, 7-5, 7-6) are developed in the following way. The computational manipulation of SEM size or composition data for each multicyclone stage permits a population distribution histogram to be prepared for that stage. The data from all five stages are then combined by weighting data from each stage by the percent of total mass collected in that stage. This weighting is extremely important because unweighted combined stage data will be distorted to the extent that there are differences between stages.

FIGURE 7-4. Population distributions of particle diameter (expressed in micrometers) and alkaline earth concentrations (expressed as pct calcium and magnesium oxides and elemental barium).

FIGURE 7-5. Population distribution of several elemental concentrations, expressed as pct oxide.

FIGURE 7-6. Population distributions of several elemental concentrations, expressed as pct oxide.

Clearly this argument is especially cogent in the case of size data, since the multicyclone is by design a size fractionating instrument.

Although not shown here, another parameter measured by SEM is size factor (aspect ratio), which is the ratio of maximum to minimum diameter of a particle. For most pc-fired Western ashes that we have studied, a significant fraction of the ash particles are not spherical. For Beulah, the mean size factor of 494 particles was 1.003 ($\sigma = 0.016$). Microphotographs confirm the preponderance of spherical particles.

In each histogram of Figures 7-4, 7-5, and 7-6, the mean value of the parameter and its standard deviations are displayed.

Another way of displaying composition data is in correlation data maps, as in Figures 7-7, 7-8, and 7-9, in which composition vs. size for several elements (Figures 7-7, 7-8) and interelement composition for selected elements (Figure 7-9) are shown. The reader must be careful in interpreting these maps, in order not to confuse abundance of data at low particle size with a functional dependence of concentration upon size. Statistical analysis of the sodium and SO_3 data does confirm their increasing concentration in the fine particle range, consistent with the data in Figure 7-3 and Table 7-6.

For the ten major and minor elements, 45 element pairs could have been displayed. We have selected four whose interest derives from their functional form and the implied mineralogy (Figure 7-9). For example, the plot of Al_2O_3 versus SiO_2 reveals a cluster of points around a slope of approximately 0.8. Minerals have been identified in Beulah (8) including biotite, kaolinite, muscovite, and illite, where the Al/Si ratio is in the range of 0.67-1.0. From this it can be suggested that the aluminosilicate framework remains intact after combustion. The common clay minerals have a range in composition of 25-45% Al_2O_3 and 35-50% SiO_2 . Since most of the particles in Figure 7-9 contain less than these percentages, either the aluminosilicates combined with additional elements or became coated. Dehydrated illites, formed by decomposition of kaolinite (14) fall outside the bulk of the Al_2O_3 - SiO_2 data, near muscovite. This is in contrast to the observations in the case of Arapahoe ash (1). Etching and microscopic investigation of Eastern bituminous ashes (15) has demonstrated the presence of mullite, $3\text{Al}_2\text{O}_3$, 2SiO_2 . This would fall near 72% Al_2O_3 , 28% SiO_2 , far outside the range of Beulah data, as well as all other Western coal ashes we have studied in detail.

The plot of Na_2O versus CaO in Figure 7-9 shows an inverse relationship which is supported by the XRF data in Figure 7-3. This observation is consistent with the suggestion that sodium and calcium compete for anions in chemical processes.

In the plot of SiO_2 versus SO_3 , and Al_2O_3 and SO_3 , there is a negative correlation between SiO_2 or Al_2O_3 and SO_3 . Many of the points lie in the region along lines connecting clay minerals, at 0% SO_3 , with Na_2SO_4 or glauberite at 0% SiO_2 . This is consistent with clay-like particles becoming coated with Na_2SO_4 .

7-15

FIGURE 7-7. Correlation data maps of concentration (in pct) versus particle size (in μm) for three elements which moderate resistivity (Na, Fe, S) and for barium, a RCRA element.

FIGURE 7-8. Correlation data maps of concentration (in pct) versus particle size (in μm) for several elements. Ca and Mg normally cause increases in ash resistivity; Al and Si appear together in clay-derived species.

FIGURE 7-9. Interelement correlation data maps for four element pairs. Stoichiometric locations of several coal and ash minerals, identified by XRD, are indicated.

7.2.1.8 Auger-ESCA Observations

Surface analysis of the particles was performed utilizing ESCA. The ESCA analysis technique analyzes to a depth of 20 to 30Å. The major constituents found on the surface of SoRI multicyclone stage 5 particles included Ba, O, Ca, Na, C, S, and Si. The published binding energies (16) of the elements detected by the detailed ESCA scans show that Na, Ca, and Ba are present as sulfates. The Al and Si may be tied up as silicates, but detailed binding energies for such compounds are unavailable in the literature.

The surfaces of the particles were characterized by a sputter-etching technique used to remove surface layers followed by subsequent ESCA analysis. It was found that carbon and sulfur were concentrated on the surface of all five stages of the multicyclone samples. The presence of sodium was noted on the surface of the larger particles but in the smaller size fractions (<1.5 µm) the sodium concentration was more uniform throughout the depth analyzed by sputtering. Campbell and others (17) also showed that Na, S, and C were found on the surface of ash particles. In all cases, except for Stage 5, Ca, Al, and Si were found to increase after sputtering.

7.2.1.9 Conclusions

The most significant trend noted by all techniques was the increase of sodium and sulfur with decreasing particle size. The relatively more volatile sodium salts may sublime to form very small particles of pure salt or they may condense on the surfaces of other particles such as aluminosilicates originating from clay minerals of the coal. These results support the validity of a vaporization-condensation mechanism of particulate formation.

7.2.2 Publications and Presentations

During this reporting period, two manuscripts were prepared. One on Beulah ash, from which significant portions have been extracted for this report, was:

MICROANALYTICAL CHARACTERIZATION OF NORTH DAKOTA FLY ASH
by S. A. Benson, D. K. Rindt, G. G. Montgomery, and D. R. Sears
(DOE/FE/60181-13).

This was presented by S. A. Benson to the March 1983 meeting of the American Chemical Society in Seattle. Upon invitation of the editor, it has been submitted to Industrial and Engineering Chemistry - Product Research and Development.

A second unrelated paper deals with Beulah ash generated during atmospheric fluidized bed combustion, entitled:

MUTAGENICITY IN SALMONELLA OF NITRO-ORGANIC COMPOUNDS IN EXTRACTS OF FLY ASH FROM A LIGNITE-FIRED ATMOSPHERIC FLUIDIZED-BED COMBUSTOR, Joyce F. Remsen, Wesley R. Harris, and D. Richard Sears. Remsen and Harris are at the DOE Laboratory for Energy-Related Health Research-University of California, Davis. The paper is being submitted to Environmental Mutagenesis.

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8. WASTE CHARACTERIZATION

Project No.: 7204

B&R No.: AA0515000

Submitted by: M.L. Jones, Manager, Coal Utilization Research Division

Prepared by: D.R. Sears, Research Supervisor, Particulates and Waste Characterization

Assigned UNDERC Personnel: H.M. Ness (through 4/8/83)
G.M. Schelkoph
D.R. Sears

8.1 GOALS AND OBJECTIVES

The goals of the Waste Characterization project are to characterize and develop suitable techniques for environmentally satisfactory disposal of waste materials derived from burning low-rank western coals. Specific project objectives during the first six months of 1983 were to: 1) complete reports on previous laboratory studies on the chemical and physical characteristics of fly ash and fly ash alkali FGD sludge materials; and 2) establish a laboratory effort to characterize distribution and form of deleterious major and trace elements through chemical etching and selective leaching experiments, leading to possible future tests of coal additives in a pilot-scale combustor to immobilize deleterious elements in the ash.

8.2 ACCOMPLISHMENTS

8.2.1 Reports on Previous Investigations of FGD Wastes

During this reporting period, the major effort was the collation, interpretation, and reporting of previously completed laboratory and field studies. This effort has resulted in the preparation of three draft manuscripts, from which the data and the bulk of the text appearing here have been extracted:

1. "Characterization of a Fly Ash Alkali FGD Sludge" by Harvey M. Ness, Gwen M. Schelkoph, Allen F. Volesky, and Sherold Y. Johnson."
2. "Physical Characterization of FGD Wastes From a Parametric Study of Scrubber Operating Conditions" by Harvey M. Ness and Gwen M. Schelkoph.
3. "Chemical and Physical Characteristics of Raw and Stabilized FGD Sludge Materials" by Harvey M. Ness and Gwen M. Schelkoph.

The first two of these papers report the results of studies of sludges obtained from a 5000-acfm (saturated) pilot plant wet scrubber located at the

Minnkota Power Cooperative Milton R. Young Generating Station at Center, North Dakota. The pilot plant was designed and constructed by Combustion Equipment Associates and Arthur D. Little Co. Cooperating organizations included CEA-ADL, Square Butte Electric Cooperative (SBEC), Minnkota Power Cooperative (MPC), Minnesota Power and Light Company (MP&L), and Grand Forks Energy Technology Center (GFETC).

In the parametric study, sulfur dioxide removal efficiency was investigated as a function of liquid-to-gas (L/G) ratio, inlet sulfur dioxide concentration, calcium oxide-to-sulfur dioxide stoichiometric ratio, and recirculated suspended solids. Ten representative sludges were selected for the program.

In the fly ash alkali FGD sludge study, the waste materials selected for chemical and physical characterization were collected from the vacuum filter waste dewatering apparatus. Solid waste from this system was produced by the demister loop varifier underflow, and by the wash tray loop thickness underflow.

The fly ash utilized in the ash alkali wet scrubbing process was recovered from the cyclone-fired furnace which burned lignite from the Baukol-Noonan mine at Center, ND. Large within-seam variations are common in North Dakota lignites. A typical analysis of the fly ash employed during the pilot plant tests is given in Table 8-1.

TABLE 8-1

TYPICAL ANALYSIS OF FLY ASH PRODUCED BY THE
CYCLONE-FIRED BOILER ON CENTER UNIT #1

	Percent of Ash As Received		Percent of Ash As Received
Silica, SiO ₂	29.8	Aluminum Oxide, Al ₂ O ₃	12.7
Ferric Oxide, Fe ₂ O ₃	10.6	Titanium Oxide, TiO ₂	0.5
Phosphorus Pentoxide, P ₂ O ₅	0.3	Calcium Oxide, CaO	25.7
Magnesium Oxide, MgO	4.5	Sodium Oxide, Na ₂ O	2.2
Potassium Oxide, K ₂ O	2.0	Sulfur Trioxide, SO ₃	6.4

8.2.1.1 Description of Pilot-Scale Wet Scrubber

The 5000-acfm (saturated) pilot plant wet scrubber (equivalent to about 1.4-MW) was operated on a slipstream of flue gas collected downstream of the electrostatic precipitator (ESP) on Center unit #1, a 238-MW cyclone-fired boiler. It consisted essentially of two liquor loops: the primary sulfur dioxide loop, and the wash tray-mist eliminator loop. The fly ash alkali (FAA) sludge used as the absorbent in the scrubbing of the sulfur dioxide gas from the flue gas came from the power plant ESP. In addition, a fly ash-limestone (FAA-LS) and limestone (LS) sludge were studied. The sludge materials produced by the fly ash alkali FGD process has some unique properties when compared to lime or limestone wastes.

In the 5000 acfm pilot plant, the wash tray-mist eliminator loop was designed to operate on a clear liquor at approximately pH 3 and consists of a wash tray above the absorber tower, a tray recycle tank, clarifier and clarifier overflow tanks, and a demister. The wash tray, constructed of 316L stainless steel, was designed to remove entrained droplets of scrubbing liquor which could otherwise foul the demister. Liquid from the wash tray drained to a flakeglass-lined recycle tank and was then pumped back to the wash tray or to a flakeglass-lined clarifier. Overflow from the clarifier was used to wash the bottom of the wash tray. Liquid from the clarifier not used for washing was drained by gravity to a flakeglass-lined overflow tank. Makeup water from nearby Lake Nelson was added to the pilot scrubber at the clarifier overflow tank at an average rate of 1.3 gpm (about 1.5 acre-ft/MW/yr) and the combined liquid used to wash the polypropylene demister. Makeup water was added to this loop to lower calcium sulfate supersaturation and suspended solids. Underflow from the clarifier was pumped to a drum-type vacuum filter.

The scrubber loop was operated on a slurry of alkali ash in recycled liquor at a characteristic pH of from 2 to 7. It consisted of an absorber tower which contained banks of stainless steel nozzles spraying scrubber liquid countercurrent to the gas flow. The scrubber liquid drained from the absorber tower to a retention tank equipped with stainless steel agitator. Retention tank liquid was pumped back to the spray nozzles and also to a thickener used to control the level of suspended solids. Reducing the liquid flow from the retention tank to the thickener increased the level of suspended solids; increasing the flow rate lowered the level of suspended solids. Overflow from the thickener drained by gravity to an overflow tank. Thickener underflow was pumped to the vacuum filter. The vacuum filter was operated only when the concentration of suspended solids in the thickener underflow exceeded 55 pct; filtration was stopped when the solids were reduced to about 20 pct. Liquid from the thickener overflow tank was pumped to the retention tank. Fly ash was stored in a hopper and fed to the preparation tank using a screw feeder; retention tank liquor was primarily used to slurry the fly ash, since scale formation in the preparation tank, slurry pump, and feed lines was a problem when thickener overflow liquor was used. Hydrated lime was fed directly into the retention tank. The total amount of liquid in the entire pilot plant scrubber was about 12,000 gallons.

8.2.1.2 Experimental Methods

Many different techniques were utilized to characterize the sludges obtained from operation of the pilot-scale wet scrubber. Both physical and chemical properties were measured. A short description of the parameters examined follows. Physical properties of sludges measured during this study included:

- bulk density,
- dry density,
- moisture content,
- specific surface area,
- permeability,
- porosity/void ratio,
- unconfined compressive strength, and
- particle size distribution.

Chemical characterization of the waste materials included major, minor, and trace element analyses. Analytical methods included x-ray fluorescence (XRF) and diffraction (XRD), inductively coupled argon plasma spectroscopy (ICAP), atomic absorption spectroscopy (AA), pH measurements, and column leaching.

The column leaching tests were designed to simulate the release of chemical pollutants from waste material in a disposal site. All equipment was inert with respect to the waste material and leaching solution. The apparatus consisted of a plexiglass column, approximately 61 cm high with an inside diameter of 3.0 cm, containing two plates, one a porous sample support, and the other supporting a Teflon stopcock. An inert, porous plastic pad was placed on the support plate to retard the movement of solid particles from the column, thus simulating the conditions at an actual disposal site, which would provide similar filtration conditions. The column was charged by adding known quantities of waste material to deionized water, and pouring the slurry into the column. After allowing the material to settle, deionized water was passed through the waste sample at a rate controlled by the natural permeability of the waste sample. For this study approximately 25 cm of distilled deionized water was maintained above the waste bed. Chemical background concentrations were determined by running distilled water through a column without sample at a similar rate. Samples were split into aliquots and preserved depending on the analyses to be performed on the aliquot. The metals (cations) were preserved in Ultrex nitric acid, while the anions were either analyzed immediately after collection or required no preservation. All samples were stored at 4°C until the analyses were performed. All leaching experiments were performed under aerobic conditions.

8.2.1.3 Results

The very voluminous results will be described briefly here; the three manuscripts referred to earlier contain complete details of sampling conditions, results of chemical and physical characterization and leaching experiments, as well as interpretive discussions.

Table 8-2 summarizes the composition of typical sludges used in the parametric study. Table 8-3 presents the actual analyses of individual sludges. Table 8-4 summarizes the physical properties.

Examination of the bulk density of the sample as received from the rotary vacuum filter indicates values ranging from 1.55 to 1.76 g/cm³. The average value was 1.68 ± 0.07 g/cm³ which is also the average value for the sludges taken during a material balance test using normal scrubber operating conditions. The dry density ranged from 2.45 to 2.59 g/cm³. The average value was 2.54 ± 0.04 g/cm³. The value for sludge dry density under normal operating conditions was 2.51 g/cm³. These results indicate that there is essentially little variation in density values with differences in scrubber operating conditions since the values fall within the range for an average type of sludge.

TABLE 8-2

TYPICAL ANALYSIS OF A SLUDGE WITH COMPARATIVE RANGES FOR THE
SLUDGES FROM THE PARAMETRIC STUDY

	Percent of Ash, As Received	
	<u>Typical Sludge</u>	<u>Parametric Study Ranges</u>
SiO ₂	29.0	14.9 - 29.5
Al ₂ O ₃	12.4	6.5 - 14.1
Fe ₂ O ₃	7.6	3.8 - 10.2
TiO ₂	0.5	0.3 - 0.5
P ₂ O ₅	0.4	0.3 - 0.6
CaO	18.4	13.5 - 28.4
MgO	3.3	2.4 - 5.4
Na ₂ O	2.8	0.6 - 4.8
K ₂ O	1.3	0.7 - 13.7
SO ₃	22.9	19.8 - 38.7

TABLE 8-3

ACTUAL X-RAY FLUORESCENCE VALUES FOR THE PARAMETRIC STUDY SLUDGES

Test*	Percent of Ash, As Received									
	<u>SiO₂</u>	<u>Al₂O₃</u>	<u>Fe₂O₃</u>	<u>TiO₂</u>	<u>P₂O₅</u>	<u>CaO</u>	<u>MgO</u>	<u>Na₂O</u>	<u>K₂O</u>	<u>SO₃</u>
1-3	29.4	13.2	7.8	0.5	0.3	21.4	4.4	0.9	1.4	20.5
3-1	29.1	12.1	8.3	0.5	0.3	20.8	3.6	0.8	1.6	22.9
3A-2 (1000 ppm SO ₂)	29.5	13.1	8.2	0.5	0.3	22.3	4.2	0.6	1.5	19.8
3A-3 (lime added)	21.2	9.7	6.1	0.4	0.5	22.0	2.8	2.4	4.8	29.7
3A-4 (1800 ppm SO ₂)	26.3	13.5	5.0	0.4	0.4	13.5	2.7	2.2	13.7	21.3
3A-7 (lime added, 1800 ppm SO ₂)	14.9	6.5	3.8	0.3	0.6	28.4	3.0	2.4	0.7	38.7
5-4 (High Sodium)	22.4	12.2	7.9	0.4	0.4	17.4	3.1	4.8	1.1	30.2
5-14 (High Magnesium)	26.9	14.1	10.2	0.5	0.4	15.1	5.4	3.1	1.3	22.9
6-4 (Low pH)	24.0	8.2	8.0	0.4	0.3	24.1	2.4	1.8	1.5	29.1
6-5 (Low pH)	26.7	8.2	10.1	0.5	0.3	20.9	2.5	1.7	1.9	27.1

*Inlet value of SO₂ is 1000 ppm unless otherwise noted.

TABLE 8-4

PHYSICAL CHARACTERISTICS OF THE PARAMETRIC STUDY SLUDGES

Test*	Bulk Density (g/cm ³)	Dry Density (g/cm ³)	Surface Area (m ² /g)	Permeability (cm/sec)	Pore Volume (ml)	Porosity (%)	Void Ratio	Moisture %
1-3	1.65	2.59	26.89	3.47×10^{-5}	13.28	61.1	1.57	37.7
3-1	1.76	2.45	25.31	1.43×10^{-5}	33.31	53.2	1.14	31.7
3A-2	1.75	2.57	26.92	1.24×10^{-5}	28.02	54.6	1.20	31.9
3A-3 (lime used)	1.74	2.53	26.88	1.69×10^{-5}	33.90	57.3	1.34	34.7
3A-4 (1800 ppm SO ₂ , lime used)	1.65	2.49	20.12	1.58×10^{-6}	34.09	61.6	1.60	39.2
3A-7 (1800 ppm SO ₂ , lime used)	1.69	2.55	14.67	1.86×10^{-5}	26.41	59.1	1.45	36.2
5-4 (high sodium test)	1.55	2.57	25.31	3.48×10^{-6}	29.98	63.9	1.77	40.7
5-14 (high magnesium test)	1.69	2.55	14.72	5.23×10^{-6}	24.51	55.7	1.26	33.0
6-4 (low pH test)	1.67	2.54	17.08	5.19×10^{-6}	18.14	56.9	1.32	34.2
6-5 (low pH test)	1.60	2.50	23.01	8.2×10^{-7}	25.29	63.0	1.70	40.5

*Inlet value of SO₂ is 1000 ppm unless otherwise noted.

The test results for surface area indicated significant variability with scrubber operating conditions. The surface area was usually around 27.0 m²/g. However, lower values are seen for low pH tests, the high magnesium test, and in tests where the inlet SO₂ level was 1800 ppm. Differences in surface area are related to particle size distribution.

The only differences in permeability from that of usual operating conditions occurred in the high sodium and magnesium tests and in the low pH tests, for which the permeability values were considerably lower. The sludge permeability may also be related to differences in particle size distribution. Freshly placed mixtures have permeabilities on the order of 10⁻⁶ cm/sec. As the material cures, permeability is further reduced.

Values for the pore volume, porosity, and the void ratio showed no major differences for the sludges obtained from tests with different operating conditions.

For the parametric study sludges, the unconfined compressive strengths ranged from 1.56 ksf to 3.25 ksf. The unconfined compressive strength of a sludge is affected by two independent parameters, namely strain rate and degree of saturation. The unconfined compression test results for the parametric study sludges are given in Table 8-5.

TABLE 8-5

UNCONFINED COMPRESSIVE STRENGTH VALUES

<u>Test*</u>	<u>Test Conditions</u>	<u>qu (ksf)</u>	<u>Strain unit*</u>
1-3	1000 ppm SO ₂	2.78	0.020
3-1	1000 ppm SO ₂	2.54	0.019
3A-2	1000 ppm SO ₂	2.62	0.010
3A-4	1800 ppm SO ₂	3.20	0.021
3A-7	1800 ppm SO ₂ , lime added	3.25	0.017
3A-3	1000 ppm SO ₂ , lime added	1.56	0.028
5-4	High sodium	2.23	0.025
5-14	High magnesium	2.34	0.026
6-4 and 6-5	Low pH	2.74	0.015

*Inlet value of SO₂ is 1000 ppm unless otherwise noted.

From the study, the following conclusions can be drawn: a) addition of lime causes variations in sludge strength, b) higher levels of SO_2 will cause a significant increase in strength, c) high sodium and magnesium levels cause decreased strength, d) low pH has no effect on strength, and e) drier samples have decreased strength. High SO_2 level and the low pH conditions of the test are definite favorable factors for increasing the unconfined compressive strength of the sludge.

In the investigation of raw and fixed sludges, a salient observation is that the property most significantly affecting the release of chemical pollutants was sludge moisture content. When a leach solution is passed through the sludge, the occluded moisture would be flushed; therefore, the initial fixed and raw leachate would be expected to contain higher concentrations of chemical pollutants. After flushing occluded moisture, the level of chemical pollutants would be governed by the solubilization or diffusion kinetics. Generally, the cumulative leach profile demonstrates a stable or decreasing leach rate. The latter indicates decreasing availability of pollutant. For most chemical species in the raw FGD sludge tested in this investigation, the leach mechanism appears to be solubilization kinetics controlled. The data imply pH changes play a dominant role in fixation and solubilization. This should be related to the observed pollutant mobility, particularly for the metals which are less mobile at a high pH due to formation of insoluble hydroxides. The effect of fixation upon leachates is more complex than is stated above, but the pH effect is one which can be documented by observed data.

8.2.2 Laboratory Studies on Deleterious Elements in Waste Materials

During the reporting period, the planning of this activity was accomplished, a laboratory was established, and a laboratory chemist was selected to join the UNDERC staff upon the completion of his MS thesis in geology in July.

9. - COMBUSTION RESEARCH AND ASH FOULING

Project No.: 7205

B&R No.: AA1505000

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9.1 GOALS AND OBJECTIVES

The Combustion Research and Ash Fouling project has two primary goals. The first is the development of fundamental data and correlations on the combustion reactions of low-rank coals. Special attention will be given to effects related to the unique properties of low-rank coals such as high moisture content, lower heating value, highly variable and alkaline ash, and high porosity.

The second objective of the project is to maintain and expand the technical data base at UNDERC on ash fouling and slagging behavior in pulverized fuel and cyclone-fired furnaces burning low-rank coals.

The specific objectives of the project in the current budget year are:

1. Completion of the construction and checkout of the bench-scale combustor and its diagnostic and sampling systems.
2. Initial testing and calibration of the bench-scale combustor with model compounds, and with low-rank coal particles.
3. Pilot-scale testing to evaluate the effects of ultra-fine coal grinding on ash fouling.
4. Evaluation of systems for in situ examination of deposits.
5. Completion of the ash fouling topical report.
6. Examination of alkali species in combustion systems, focusing on analysis of gas and solid phases to be sampled and collected by Midwest Research Institute.
7. Testing of selected low-rank coals to expand the existing data base on fouling and slagging maintained at UNDERC.

The planned activities for the current quarter included the following:

1. Complete construction of bench-scale combustor.
2. Continue work on the topical report on ash fouling in low-rank coal combustion.
3. Examination of alkali species in low-rank coal combustion systems.
4. Combustion testing of selected low-rank coals.

9.2 ACCOMPLISHMENTS

9.2.1 Construction of Bench-Scale Combustor

To obtain information on single low-rank coal particles as they experience devolatilization, ignition, and char burn out, a bench-scale combustor has been constructed at the UNDERC. The combustor is designed to provide non-obtrusive probing of an entrained flow of coal particles in a simulated combustion gas using photography and three-color optical pyrometry. The combustion environment experienced by the coal particles can be controlled with respect to both gas temperatures and gas composition.

Construction on the combustor has proceeded to the point where only the coal feed system remains to be added. This should be completed early in the fourth quarter of FY 1983, thus allowing initial testing to proceed during this fiscal year. The following is a description of the systems which have been completed at UNDERC.

An overview of the conceptual design of the bench-scale combustor is shown in Figure 9-1. A gas mixing system blends N_2 , O_2 , CO_2 , and SO_2 to simulate a combustion environment. The gas mixture is heated to the desired temperature in two preheaters and a resistance-heated furnace. Water is metered into the gas stream after the first preheater where it flashes to steam. The hot gas stream exits the furnace through a ceramic distribution plate into a vertical quartz observation chimney. Uniformly-sized coal particles are entrained at a constant rate in a small fluidized bed and injected into the hot gas stream through a water-cooled tube terminating at the top of the distribution plate. The square quartz chimney allows photography and optical pyrometry along the other axis, along the axes perpendicular to the particle's trajectory. Data from the pyrometer, thermocouples and other instruments are acquired, stored, and manipulated using an IBM 5150 micro-computer.

The following sections provide a description of the components of the bench-scale combustor and performance data.

9.2.2 Gas Mixing System

The composition of the gases entering the heating zone is regulated by a Brooks Associates custom-built mixing system. The system employs thermal mass flow detectors to control metering solenoids. Concentration ranges for the four gases used are 5 to 25 pct for O_2 , 1 to 5 pct for CO_2 , 0 to 0.5 pct

FIGURE 9-1. Schematic of bench scale combustion system.

for SO_2 with the balance N_2 . Metering accuracy is 1 pct of the maximum range for each gas. The feedback signals from the metering solenoids (0-50 V DC) are used by the IBM microcomputers to monitor the flow rates for each gas.

The mixing system was constructed with dual O_2 and CO_2 inlets to allow cylinder changes without interrupting gas flow. N_2 is obtained from the house supply. The system can also be switched from the gas mixture to house compressed air, which is used during furnace heatup and cooldown. Water is metered with a peristaltic pump (0-7 cc/min with the present unit) and injected into the gas stream after the first preheater.

9.2.3 Gas Heating System

A specialized gas heating system was constructed to achieve the goal of heating various gas mixtures with a flow rate of 140 slm (5 scfm) to a maximum temperature of 1650°C (3000°F). A schematic of the system is shown in Figure 9-2.

The gas mixture is preheated in two conventional Thermolyne tube furnaces. The gas passes through 5 cm (2 inch) diameter pipes (304 ss) filled with 0.95 cm (3/8 inch) diameter tubing bundles to increase the effective heat transfer surface before entering the specially-designed high-temperature furnace. A cross-sectional view of the furnace is shown in Figure 9-3.

FIGURE 9-2. Gas heating system.

FIGURE 9-3. Cross-sectional view of high temperature.

The high-temperature furnace consists of four sections of heating elements with twelve elements per section. The inner heating chamber is formed from a high temperature alumina insulating board (Zircar SALI) capable of withstanding temperatures up to 1700°C (3100°F). A secondary layer of insulation (Fiberfrax Hot-board) maintains the stainless steel outer furnace wall at ~100°C (212°F). The resistance heating elements are made of molybdenum disilicide (Zircar Super Kanthol 33) with excellent chemical resistance and with the ability to withstand a maximum temperature of 1800°C (3273°F). Vertical mounting is necessary, as these heaters soften and lose structural strength at operating temperature.

The heating elements are connected in a series-parallel arrangement. Power is supplied by two DC supplies with an output of 9.6 KW each. Temperatures are monitored by thermocouples located at the exits of the second and final furnace sections and at the base of the ceramic distributor plate. Thermocouples located throughout the system, as well as the output voltage and amperage of the power supplies, are monitored by the IBM microcomputer.

Difficulties were encountered during assembly of the furnace primarily due to the extreme fragility of the Kanthol heating elements; approximately 30 pct of which were broken in the process of installation. The wiring configurations were modified slightly to allow operation with the surviving elements.

The furnace and associated elements are being currently operated in a series of shakedown runs, gradually working up to the 1650°C design limit, to test the equipment and determine operating parameters. Table 9-1 gives operating parameters and temperatures reached in these tests.

TABLE 9-1

Test No.	1	2	3	4
Gas (scfh)	300 air	200 air	200 air	200 air
Water (ml/min)	None	7	5	5
<u>Preheater,</u> <u>Temp. °C</u>				
No. 1	--	300	300	300
No. 2	--	400	400	400
Furnace elements	12	30	30	30
<u>Maximum:</u>				
Volts				
Amps				
Temp., °C	760	1200	600 (Instrument tests)	1100 (Coal feeder failure)

9.2.4 Coal Feed System

A small fluidized-bed coal feeding system (Figure 9-4) has been designed to achieve a uniform coal feed at a nominal rate of 10 g/hour. A portion ($\sim 0.1\%$) of the gas exiting the gas mixing system is diverted to fluidize and transport the coal. The coal is transported through a 1 mm diameter water-cooled feed tube and isokinetically injected into the hot gas stream at the top center of the distributor plate. To monitor coal feed rate, the fluidized bed is mounted on an electronic balance; connections being made using flexible plastic tubing.

9.2.5 Reaction Chamber

The combustion chamber itself (Figure 9-5) consists of a square chimney constructed of $30.5 \times 8.9 \times 0.3$ cm quartz plates supported at the edges with a stainless steel framework and resting on the distribution plate. The ceramic distribution plate is a 2 cm thick honeycomb with ~ 1 mm² square holes designed to produce a laminar flow in the chimney with the coal particles moving vertically upward along the centerline.

The optical instruments are mounted on optical benches around the combustion chamber. The instruments are capable of 7.6 cm of vertical translation to observe particles at different stages of combustion. To avoid disturbing the instrument alignments, larger translations necessary to observe the upper part of the chimney will be achieved by vertical movement of the table on which the furnace assembly is mounted.

9.2.6 Photographic System

Images of individual coal particles will be obtained using a high-speed flash and a long-range microscope fitted with a camera. The flash (Arenberg-Sage Model 550) is capable of generating up to four Joules of light energy in 75 μ s pulses. The Questar M1 microscope employs Maksutov-Cassegrain optics with an 89 mm clear aperture. It has excellent depth of field and a magnification of 65X at a minimum focal distance of 56 cm. A set of eyepieces allows a range of magnifications.

Due to the difficulty of observing coal particles by reflected light, the photographs will be shadowgraphs of the particles silhouetted against the light source. Even in a flame, the only useable light at high magnification is the short strobe pulse. Although no particles have yet been photographed in the combustor, good photographs of a variety of stationary and moving targets have been obtained. No blurring of the image occurred in the photographs of test objects moving at ~ 1 m/sec.

The flash and microscope will provide a photographic record of physical changes and devolatilization behavior during the combustion of individual coal particles. Other researchers have observed soot-like material forming jets and clouds around burning bituminous coal particles as well as changes in this behavior with particle size. Changes in the physical behavior of coal particles have also been observed with different coal rank (1, 2).

FIGURE 9-4. Fluidized bed coal feeder.

FIGURE 9-5. View of reaction chamber and arrangement of optical equipment.

9.2.7 Optical Pyrometer

Three color optical pyrometry will be used to determine surface temperatures of individual coal particles. This technique uses the spectral radiance emitted to determine the average surface temperature of the objects being observed.

The pyrometry system used with the bench scale combustor is shown in Figure 9-6. The optical head focuses on a $\sim 1\text{mm}^2$ path through the vertical centerline of the quartz chimney. Adjustment of the head to various heights above the distributor plate allows a time history of the particles to be obtained. Particles traveling at $\sim 1\text{ m/sec}$ traverse the viewing area of the optical head in $\sim 1\text{ msec}$. A transient pulse of light is observed and delivered to three pyrometer channels via a trifurcated fiber optics cable. Such a fiber optics cable eliminates much of the critical alignment necessary with beamsplitter arrangements as well as transmitting more light from the region of interest.

FIGURE 9-6. Optical pyrometer and photographic system used in conjunction with bench-scale combustion devices.

Wavelengths of 700 nm, 800 nm, and 850 nm are observed by the 3 channels of the pyrometry system using filter monochrometers with 10 nm bandpasses. The light pulses are detected and converted to a 0-2V DC signal by photomultiplier tubes, with high sensitivity and good response in the 700 nm to 900 nm region. Amplifiers are an integral part of the photomultiplier socket assembly.

The amplifier outputs are captured by a Data 6000 universal waveform analyzer. The Data 6000 digitally records signals on one to four input channels at a 100 KHz A/D conversion rate. A pretrigger recording capacity allows capture of the baseline and the portion of the transient signal occurring before the trigger threshold is reached. The Data 6000 is equipped with disk drives for storage of the raw signals. The unit also contains powerful processing features to smooth and reduce the acquired data.

9.2.8 Computer System

Data acquisition is controlled by an IBM 5150 microcomputer. The 5150 has a 16-bit CPU and a 5 MHz clock. Additionally, it has been upgraded with an extra 256 KB of memory (yielding a total of 320 KB), 2 RS-232 asynchronous communication ports, a parallel printer port, and a real-time clock. Other features include dual 320 KB floppy disk drives and a matrix printer with graphic capabilities. A schematic of the system is shown in Figure 9-7.

FIGURE 9-7. Computer system for combustion apparatus.

One of the RS-232 ports is used to communicate via modem with an IBM-370 computer network. This allows for transfer and storage of generated data to tapes or hard disk, as well as access to statistical languages such as the Statistical Analysis System (SAS).

Data acquisition from the pyrometer is handled through the Data 6000 signal analyzer. Data from other sensors are scanned at regular intervals by

a Tecmar Lab Master board. The Lab Master allows for up to 16 12-bit A/D inputs. A multiplexer expansion board attached to the Lab Master provides an additional 48 input ports. Input ranges and gains need not be the same for all ports, as both are software programmable. Data from the Lab Master will be stored by the 5150's disk drives as it is received. Other features of the Lab Master available but not now in use include 2 12-bit D/A converters, 5 independently programmable timer/counters, and 24 digital I/O channels.

Basic programs have been written to control the Data 6000 and to acquire data from the Labmaster board. The use of the IBM microcomputer with the A/D converter boards for data collection provides a system which is far more versatile and flexible than conventional data loggers.

Currently twenty input signals from thermocouples, voltmeters, ammeters, and gas flow controllers are connected to the A/D board. To minimize signal noise, the A/D board is configured in a differential mode, each signal occupying two input channels. The inputs are scanned at 1 minute intervals, with each input value taken as the average of 100 readings of that channel. After appropriate scaling, the data are displayed on the CRT monitor along with warnings if preset values are exceeded. The data are also logged to a disc at 2 minute intervals, and to the printer at 5 minute intervals. A copy of the monitor display may also be printed at any time. An example of the information displayed on the monitor is shown in Figure 9-8.

During a given run, data from the pyrometer will be collected by the Data 6000 and stored by its own dual 1.5 megabyte floppy disk drives. Upon completion of the experiment, some preliminary data manipulation will be performed on the Data 6000. The pyrometry data and the data received from the Lab Master system will then be transferred via the 5150 to the larger IBM 370 computing facility, where existing statistical and graphics capabilities can be utilized.

9.2.9 Future Plans

The combustion system and experimental plan just described are an attempt to begin obtaining data which will provide a more detailed understanding of the combustion of low-rank coals. Initial work will involve examination of physical changes to the coal particles, surface temperatures of individual particles, and with the addition of a particulate probe, chemical changes to the coal particle. The chemical changes noted will involve both the organic and inorganic portion of the coal matrix.

The variables to be considered in monitoring the coal particles will involve a combination of fuel-related and system-related parameters. In examining the physical changes it is expected the particle size, gas temperature, composition of the gas environment and moisture content will be critical parameters. Surface temperatures, as an indicator of reaction rates, are expected to respond to those same variables, and in addition, ash composition may play a prominent role.

Materials to be examined will include a wide variety of lignite and sub-bituminous coals. These coals will be chosen to represent the wide variety of fuels classified as low-rank coals. In addition, material subjected to different beneficiation processes will be examined. The effects which hot-water drying or ion exchange have on reactivity of the coal particles will be studied.

LAB MASTER READINGS AS OF 00:01:01

07-14-1983

1	GMIX	25.50007	DEG C	18	Furnace 1	158.5938	DEG C
2	GCYL	25.27648	DEG C	19	Furnace 2	141.5527	DEG C
3	Hood	28.95319	DEG C	20	Amp 1	26.95093	Amps
4	6000	24.77963	DEG C	21	Amp 2	41.0625	Amps
5	Chimy	127.5081	DEG C	22	Volt 1	4.417969	Volts
6	Furex	115.3794	DEG C	23	Volt 2	5.711426	Volts
7	Probe	2466.822	DEG C	32	N ₂	.29702	Slpm
16	Pre 1	340.4199	DEG C	33	CO ₂	-.02114	Slpm
17	Pre 2	214.1602	DEG C	34	O ₂	.14	Slpm
				35	SO ₂	.017	Slpm

Warning: Channel Number 7 has a value of 2466.822.

FIGURE 9-8. Sample of information logged during operation of bench-scale combustor.

This information will be incorporated into both physical and mathematical models of the combustion process. Knowledge of the behavior of low-rank coals in combustion environments will lead to cleaner and more efficient means of making use of the resources available.

9.2.10 Topical Report on Ash Fouling in Low-Rank Coal Combustion

Compilation of data generated by the pilot-scale test facility at UNDERC has been completed by Northwest Research, Inc. Correlation of these results with observations during field testing is well under way. Additional data describing analytical studies performed at the Energy Center are being compiled. It is anticipated that the report will be completed by the end of this calendar year.

9.2.11 Examination of Alkali Species in Low-Rank Coal Combustion Systems

Work is under way to examine the fate of the alkali metals in low-rank coal combustion systems. This project is a joint effort with Midwest Research Institute operating a laminar flame on low-rank coals and obtaining gas phase samples of the alkali in this flame. In addition, particulate samples are obtained using free-jet sampling within the flame. These samples are being analyzed by the UNDERC using ESCA.

At this time only preliminary measurements showing relative concentrations of the alkali species in the solid phase are available. Examinations of particulates using ESCA indicate phases present at different levels above the burner as indicated in Table 9-2.

As can be seen in the table, both calcium and sodium sulfates are noted. At this time relative concentrations, as a function of height above the burner, have not been determined.

It is expected that future data on the alkali species present in coal flames will include data on vapor species. This information should help in defining the role of alkali metals in ash fouling in low-rank coal fired systems.

9.2.12 Combustion Testing of Selected Low-Rank Coals

Maintenance and expansion of the UNDERC data base of fouling and slagging behavior of low-rank coals is one of the stated goals of the research program at the Energy Center. This is being accomplished in two ways: first, by testing of selected low-rank coals and potential fouling remedies at government expense and second, by allowing the test facility located in Grand Forks to be available to industry on a fee basis. Both methods have been used during the second and third quarters of FY 1983.

A test burn was completed on a sample of lignite from Pike County, Alabama. This coal had an ash value of ~12 pct with sodium in ash <0.5 pct. Very little ash (~24 g) was collected on the probes during the test run. Due to the small deposit strength, tests could not be completed for this coal. This coal would be classified as a very low fouling coal.

TABLE 9-2

PHASES IDENTIFIED ON PARTICULATES COLLECTED DURING
COMBUSTION OF 10-20 μ M DECKER COAL

<u>Distance Above Burner (mm)</u>	<u>Phases Identified</u>
3	Na_2SO_4
6	Na_2SO_4 , CaSO_4 , Fe_2O_3 , $\text{Fe}_2(\text{SO}_4)_3$
9	$\text{Na}??$, Na_2SO_4 , CaSO_4 , Fe_2O_3
16	$\text{Na}??$, Na_2SO_4 , $\text{Fe}_2(\text{SO}_4)_3$, CaSO_4
25	Na_2SO_4 , Silicates, $(\text{NaPO}_3)_3$, CaSO_4 , Fe_2O_3
38	$\text{Na}??$, NaPO_3 , $\text{Fe}_2(\text{SO}_4)_3$, CaSO_4
63.5	$\text{Na}??$, NaPO_3 , Na_2SO_4 , FeSO_4 , $\text{Fe}_2(\text{SO}_4)_3$, CaSO_4 , $(\text{NaPO}_3)_3$
101	$\text{Na}??$, NaPO_3 , $\text{Fe}(\text{SO}_4)_3$, CaSO_4

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10. - FLUIDIZED-BED COMBUSTION OF LOW-RANK COALS

Project No.: 7206

B&R No.: AA3505450
AA3510100

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10.1 GOALS AND OBJECTIVES

The Fluidized-Bed Combustion (FBC) project at the University of North Dakota Energy Research Center (UNDERC) has two major goal: first, to resolve identified problems such as bed agglomeration, low turndown ratio, and utilization of SO_x sorbents; and second, to continue the development of a data base on the FBC process and systems utilizing low-rank coals.

Other specific objectives of the Fluidized-Bed project for the first year of the Cooperative Agreement which contribute to these major goals are:

1. The preparation of a comprehensive topical report on the performance of low-rank coal in Atmospheric Fluidized-Bed Combustion.
2. The development of a data base on the formation of bed material agglomeration, including pilot plant testing with various levels of ion exchanged lignite, effects of operation under reducing conditions, design and construction of a gas and particulate sampling probe for insertion into the 2.25 sq ft combustor bed, and analytical studies to formulate a mechanism and define the role of sodium in the formation of agglomerates.
3. An engineering evaluation of alternative coal feeding systems, and possible testing of an alternative system for effects on agglomeration.
4. The examination of advanced FBC concepts being developed under METC contracts for applicability to low-rank coals.
5. Evaluation of heat transfer coefficients in AFBC of low-rank coals.

10.2 ACCOMPLISHMENTS

During the second quarter of FY 1983 and the first quarter of the Cooperative Agreement, work was completed in the following areas:

10.2.1 Pilot-Scale Testing to Examine Bed Agglomeration

A scheduled 480-hour run was successfully completed with high-sodium Beulah, North Dakota lignite and a gabbro (plagioclase feldspar) bed. This test concludes the series of two tests for comparing the effects of alternate bed materials (to silica sand) on agglomeration. Dolomite was added at a rate of approximately 0.04 lb/lb coal. A 315-hour period of steady state operation with dolomite injection was observed. Two additional short periods of steady state operation without sorbent addition--one before dolomite injection and one after the prepared dolomite was exhausted--were also identified. Ash reinjection was scheduled for the run, but not accomplished because of problems encountered with the gravity-fed ash reinjection system.

A second 480-hour run was successfully completed with ion exchanged high-sodium Beulah, North Dakota lignite (~10 pct of original sodium removed) and a silica sand bed. This is the second in a series of three tests to determine what effect different amounts of sodium present in the coal have on agglomeration. A total of 303 hours of steady state operation, 16 hours without ash reinjection and 287 hours with ash reinjection, were observed. The pneumatic ash reinjection system was used for the first time during this run. Data from both Runs BU3-0183 and B15-0283 are presented in Table 10-1.

The coal used for Run BU3-0183 was high-sodium Beulah, North Dakota lignite containing approximately 7.5 pct sodium in the ash. The same high-sodium Beulah, North Dakota lignite was ion exchanged to remove approximately 10 pct of the sodium before combustion in Run B15-0283. The coal was prepared with the pilot scale ion exchange unit using a sulfuric acid solution as the exchange medium. The sodium was reduced from approximately 7.4 to 6.4 pct Na_2O in the ash and the coal was dried to 15.4 pct moisture after the ion exchange process. The coal and ash analyses for the lignites used in the two runs are shown in Table 10-2.

Bed agglomeration did not shorten either of the two tests, BU3-0183 or B15-0283. Both tests ran 400 hours as scheduled. No bed material agglomeration was observed during the runs or on post-run inspection of the gabbro bed material run; however, growth of bed particles was noted throughout the run. There were some deposits on the combustor walls, heat exchanger tubes, and thermocouples. These deposits appeared to be composed primarily of ash material and little or no parent bed material. Some bed material agglomeration was noted during post-run inspection of the bed after the ion exchange run (B15-0283). The agglomeration was localized and was apparently caused by a leak in one of the bed cooling coils. The remaining areas of the bed showed no signs of bed agglomeration.

Bed composition is plotted as a function of run time in Figure 10-1 (BU3-0183) and Figure 10-2 (B15-0283). One significant point is noted. The end-of-run sodium concentration in the bed for the ion exchange run (B15-0283), 9.4 pct Na_2O , was well above levels where bed agglomeration would normally occur with a silica sand bed when burning untreated Beulah lignite. This suggests that the ion exchange process has altered the distribution of inorganics in the coal rather than just reducing the sodium content, and that the form of the sodium in the coal structure might have a more

TABLE 10-1
RUN CONDITIONS AND RESULTS FROM
BU3-0183 AND B15-0283 AFBC RUNS

Run Number	BU3-0183		B15-0283	
Purpose of Test	Agglomeration with high-sodium Beulah lignite and gabbro bed with dolomite addition		Agglomeration with ion-exchanged Beulah lignite and silica sand bed	
Bed Material	Gabbro		Silica sand	
Description	Dolomite addition	No sorbent addition	No ash reinjection	Ash reinjection
Average Bed Temp., °F	1644	1649	1643	1636
Velocity ft/sec	6.1	6.1	6.1	6.2
Excess Air %	20.1	20.8	20.0	20.3
Sulfur Retention %	59.8	43.4	51.9	49.5
Heat Transfer Coefficient Btu/hr ft ² °F	50.2	48.9	51.4	47.7
NO _x Emissions lb/MM Btu	0.43	0.50	0.40	0.39
Additive type and lb/hr	Dolomite 5.9	N/A	N/A	N/A
Alkali/Sulfur Ratio	1.3	0.9	1.0	
Recycle Rate lb/hr	N/A	N/A	N/A	43.3

FIGURE 10-1. Change in bed composition with time (FB2-BU3-0183).

FIGURE 10-2. Change in bed composition with time (FB2-B15-0283).

TABLE 10-2
COAL AND COAL ASH PROPERTIES
BEULAH HIGH-SODIUM AND ION-EXCHANGED BEULAH SAMPLES

<u>Coal Type:</u>	<u>Beulah High-Sodium</u>		<u>Ion-Exchanged Beulah</u>	
	<u>Dry Basis</u>	<u>As Burned</u>	<u>Dry Basis</u>	<u>As Burned</u>
<u>Proximate Analysis:</u>				
Moisture	N/A	18.0	N/A	15.4
Ash	12.8	10.5	12.6	10.5
Volatile Matter	40.6	33.3	42.8	36.2
Fixed Carbon	46.6	38.2	44.6	37.7
Heating Value Btu/lb	10,246	8,402	10,134	8,573
<u>Ultimate Analyses:</u>				
Carbon	61.8	50.7	58.3	49.3
Hydrogen	3.5	4.9	4.1	5.2
Nitrogen	0.9	0.7	0.8	0.7
Sulfur	1.8	1.4	1.7	1.4
Ash	12.8	10.5	12.6	10.7
Oxygen (diff.)	19.2	31.8	22.5	32.7
<u>Elemental Ash Analyses:</u>				
SiO ₂	20.0		21.9	
Al ₂ O ₃	14.5		15.2	
Fe ₂ O ₃	8.0		9.7	
TiO ₂	0.8		0.8	
P ₂ O ₅	1.0		0.8	
CaO	16.1		17.8	
MgO	6.1		5.3	
Na ₂ O	7.5		6.4	
K ₂ O	0.2		0.1	
SO ₃	26.0		22.0	

significant effect on agglomeration than the total quantity of sodium in the coal or in the bed.

10.2.2 Lignite Symposium Paper

A paper entitled "AFBC Bed Performance with Low-Rank Coals" was presented at the twelfth Biennial Lignite Symposium at Grand Forks, North Dakota. The authors were G.M. Goblirsch, S.A. Benson, F.R. Karner, D.K. Rindt, and D.R. Hajicek. The major emphasis of this paper was on results from pilot plant testing and the associated analytical studies on the agglom-

eration of bed materials that occurs with the use of high-sodium coals in an atmospheric fluidized bed combustor. A summary of approaches that, based upon results obtained in the agglomeration test program, can be used to reduce or eliminate agglomeration tendencies is as follows:

1. With regard to bed material selection, quartz or silica materials should be avoided. Gabbro with limestone or dolomite addition is a good combination for extended run time. It is possible that a gabbro bed can provide successful long-term operation with a high-sodium fuel if process upsets can be avoided.
2. The reduction and possible modification of the sodium in the coal by ion exchange has been demonstrated to be highly successful for the control of agglomeration even with a troublesome bed material such as silica sand. Modification of the way sodium is bound in the coal matrix is suspected because extended runs can be performed at higher-total sodium levels with the ion-exchanged coal than could normally be used without causing severe agglomeration.
3. The natural size fractionation of the fluidized bed process will tend to concentrate any agglomerates at or near the distributor plate. If the formation of agglomerates is slow enough to provide for the selective removal of large particles by draining material from the distributor plate level, the agglomeration process may be controlled. When the drained bed material is replaced with fresh material significant changes in bulk composition will result. For some bed materials, this may be of value because it reduces the probability that ash-coated particles will come together.

The following research and testing were also recommended in the symposium paper:

1. Further detailed microanalytical study of specimens of bed material and agglomerates to evaluate the role of melting versus solid state recrystallization in their formation.
2. Laboratory bench-scale experimentation with bed material and coal ash constituents under reducing or oxidizing conditions to determine more precisely the phase relationships that lead to agglomeration.
3. Further identification of sodium species involved in the agglomeration process.
4. Material balances on the alkali species to determine the extent of the reactions of these species with bed materials.
5. Evaluation of additional alternate bed materials that are low in available silica.
6. Evaluation of a system for withdrawal of large bed particles (initial stages of agglomeration) from the distribution plate level of the combustor.

10.2.3 Heat Transfer

Bed material size and overall heat transfer coefficient are plotted as a function of run time in Figure 10-3 for Run BU3-0183, in which high-sodium Beulah lignite was burned with a gabbro bed and dolomite addition. A significant increase in bed material size was noted throughout the entire run. The overall heat transfer coefficient increased earlier in the run but decreased very gradually in the later stages. The gradual decrease was probably caused by the increase in bed particle size. No explanation is available for the early increase in overall heat transfer coefficient.

The bed material size and overall heat transfer coefficient are plotted versus run hour in Figure 10-4 for the ion exchange run, B15-0283. A significant drop in the overall heat transfer coefficient was observed in the early stages of the run. This drop in overall heat transfer coefficient closely parallels an initial increase in bed particle size. Beyond this initial period, the bed material size did not increase significantly and the overall heat transfer coefficient remained stable.

10.2.4 2.25-Ft² AFBC Modifications

Previously, the AFBC baghouse had been modified to separate the discharge plenum into two gas streams so that tests on two different bag materials could be carried out at the same time with identical inputs. The tests were successfully completed and the baghouse was restored to its original configuration. At this time 18 new cages and felted fiberglass bags were installed in the baghouse.

A new pneumatic ash feed system was constructed and installed. The system uses the same educator design used for coal feed and was installed to alleviate feeding problems that were encountered with the gravity feed system. During installation of the pneumatic feed system, a constriction was discovered in the piping used for the gravity feed. This was possibly the source of the feeding problems with the gravity system. At this time it is planned to remain with the pneumatic feed system, based upon its highly satisfactory performance in the last run.

10.2.5 Topical Report

At the time of the transfer of the Center to the University of North Dakota, several of the personnel that had been assigned responsibility for completion of various sections of the topical report were assigned new positions with added responsibilities and in different areas, resulting in their being unavailable to work on the topical report. Several actions were taken to correct this problem.

A modification to the CPC contract makes CPC responsible for completion of the sections dealing with the pilot-scale test facility that had previously been drafted by EG&G. In exchange for performing this task, the editing function was dropped from the CPC contract. Either UNDERC personnel will perform the editing function or it will be let out as a separate contract. A decision on this point will be made early in the next quarter. Another contract through the Federal Project Office will make a contract group responsible for completion of the Solid Waste Characterization section. With additional

FIGURE 10-3. Heat transfer coefficient versus run hour (FB2-BU3-0183).

FIGURE 10-4. Heat transfer coefficient and bed material size versus run hour (FB2-BI5-0283).

reassignments of UNDERC personnel it is expected that the topical report will be ready for publication by the end of December 1983.

11. - COAL/WATER SLURRY COMBUSTION

(New project; no work planned during this reporting period.)

12. - ASH AND SLAG CHARACTERIZATION

Project No.: 7302

B&R No.: AA1515050

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12.1 GOALS AND OBJECTIVES

The goal of the Ash and Slag Characterization project is to develop a fundamental understanding of the properties and behavior of the inorganic constituents of low-rank coals at high temperatures. The project is therefore directed at studying the chemical changes occurring when low-rank coals are ashed and at measuring thermophysical properties of the resulting ashes and slags, with observed chemical changes or measured data then correlated with the chemical and mineralogical composition of the inorganic species in the coals.

A second goal of the project is to investigate slag-refractory interactions in the UNDERC slagging fixed-bed gasifier. This aspect of the project seeks to take advantage of opportunities to study actual slags and refractories in an actual operating gasifier--as opposed to laboratory simulations--and hence to add to the coal conversion data base on slag and refractory behavior. The slag-refractory interaction study is "target of opportunity" research in that it is wholly dependent on the operating schedule of the gasifier and on interesting or unusual effects arising during the run.

The objectives of the Ash and Slag Characterization project during this reporting period were, first, to initiate work on ashing of low-rank coal samples under controlled laboratory conditions, with attendant chemical and mineralogical analysis of the ashes; and, second, to continue measurements of the viscosity-temperature relationships of low-rank coal ash slags, with collateral development of mathematical relationships of viscosity to composition.

12.2 ACCOMPLISHMENTS

12.2.1 Ashing of Low-Rank Coals

12.2.1.1 Background

Low-temperature ashing of coals was developed to separate mineral matter and organics in coal while retaining the original mineral character. The ashing procedure, as introduced by Gluskoter (1965), deals primarily with low-temperature ashing of bituminous coal. Subsequent studies by Frazer and Belcher (1973) and Miller and others (1979) also deal with ashing of bituminous coals. Miller and Given (1979) and Robert N. Miller (personal communication, June 1983) have addressed the specific problems of alteration of inorganic matter during low-temperature ashing of low-rank coals. New inorganic species, or artifacts, may form from the breakdown of organic-inorganic complexes and the recombination of combustibles with the ash. The resulting ash may contain unaltered minerals, minerals whose elemental composition is unchanged but has undergone a crystallographic change, newly formed crystalline phases from gas-solid decomposition and oxidation reactions, and unburned residual organic matter (Robert N. Miller, personal communication, June 1983). The degree to which mineral alteration occurs is greatly affected by ashing conditions and sample treatment.

Oxidation Effect--Species present in reduced states are unstable in an oxidizing atmosphere; therefore, any minerals containing elements in a reduced state may be altered, producing new mineral species. Pyrite oxidizing to hematite is one such problem transformation. Miller and others (1979) have found that pyrite oxidation is directly related to RF power, the original pyrite content of the coal, and ashing time. Reduced metallic cations in clay structures can also be oxidized, altering the original mineral state.

Fixation Reactions of Combusted Organic Matter With Reactive Minerals--Oxides of nitrogen, carbon, and sulfur are all products of organic combustion and can react with other minerals forming new inorganic species not present in the original coal sample. Of major concern in low-rank coal is the fixation of organic sulfur as sulfates. The extent to which SO_4 is fixed in the ash is believed to be inversely related to the RF power and directly related to the amount of original sulfur in the coal sample. In addition, alkali or alkali earth metals associated with carboxyl groups are abundant in lignites and tend to trap combustion gases forming carbonates, nitrates and sulfates (Miller and Given, 1979).

During combustion, ion-exchanged inorganic salt cations are released as basic oxides or hydroxides and have an affinity for generated SO_3 , NO_2 or CO_2 . As a result, new inorganic species are formed as artifacts of the ashing process. Fortunately the alteration of original inorganic species in low-temperature ashing of lignite can be controlled by regulating ashing conditions and pre-treatment of samples.

12.2.1.2 Operating Conditions

A standard low-temperature ashing technique was established based on published literature (Frazer and Belcher, 1973; Miller and others 1979) and trial runs with the low-temperature asher (LTA). Robert Miller of Air Prod-

ucts and Chemicals, Inc. was also consulted. To date no standard procedure for the LTA has been established in coal research due to the variation of equipment and coal types.

A LFE Corporation LTA-504 asher is being used for this study. The radio-frequency generator operates at 13.56 MHz and delivers an output level variable up to 500 watts. The LTA has 4 Pyrex chambers approximately 102 mm in diameter and 216 mm in length. Pyrex boats are used for combustion and have a surface area of 5100 mm². A 1.5 gram sample ground to 60 mesh is weighed into a combustion boat, giving a layer density of approximately 0.29 mg mm⁻². One sample is placed into each chamber which is then evacuated to 0.2 mm Hg. Oxygen is then introduced into each chamber at a total flow rate of 100 cm³ min⁻¹ at 2 psi. The chamber pressure will stabilize at 0.9 mm Hg. The total RF power is increased to 150 W (approximately 37.5 W per chamber), igniting the oxygen plasma. Temperature during ashing ranges from 100° to 150°C.

During the first eight hours of operation samples are stirred every two hours to expose unoxidized coal. During the remaining ashing time samples are stirred and weighed every 24 hours. Prior to weighing, samples are cooled to room temperature in a vacuum dessicator. Ashing is considered to be complete when two consecutive weights obtained after a two-hour ashing period differ by less than 2 mg.

12.2.1.3 Pre-treatment of Samples

Samples are treated prior to ashing with ammonium acetate to extract exchangeable alkali ions from the organic portion of the coal. Approximately 20 grams of 60 mesh coal is added to 75 ml of 1 N ammonium acetate and stirred for 24 hours at 70°C. This process decreases the total ashing time by removing those alkali ions which tend to deactivate the oxygen plasma. In addition, these same alkali ions, if present, tend to recombine with combustion gases forming new minerals.

12.2.1.4 Preliminary Results of Trial Ashing

The purpose of the trial test was to standardize ashing conditions, and to determine the effects of pretreating samples on ashing time and mineral analysis. Two coals were ashed under the previously described conditions: Absaloka subbituminous coal from Montana and Indian Head lignite from North Dakota. For each coal two samples were ashed. One sample was pretreated with ammonium acetate while the other sample was left untreated.

Results were as follows in regard to relative ashing times:

Coal Type	Ashing Time (Hrs.)
Absaloka (untreated)	92
Absaloka (ammonium acetate)	87
Indian Head (untreated)	420
Indian Head (ammonium acetate)	265

From these results, the benefit of pretreating samples as part of the standard ashing procedure is obvious in reducing the total ashing time due to the removal of exchangeable cations. The difference in ashing time between

the untreated Absaloka subbituminous and Indian Head lignite is due to the greater abundance of inorganics associated with functional groups in lignites versus subbituminous coals.

X-ray diffraction analysis of low-temperature ash is currently being conducted to determine if any differences in mineralogy exist between treated and untreated samples.

12.2.1.5 ASTM and High Temperature Ashing

Currently seven samples included in the project have been ashed under standard ASTM conditions and are being analyzed by x-ray diffraction:

Absaloka Subbituminous, Sarpy Creek, Montana
Indian Head Lignite, Zap, North Dakota
Beulah Lignite (High Sodium), North Dakota
Velva/Coteau Lignite, North Dakota
Choctaw Lignite, Alabama
Pike City Lignite, Alabama
Center-Hagel Lignite, North Dakota

High-temperature ashing of samples at 1000°C has not been completed due to equipment problems.

12.2.2 Slag Viscosity

12.2.2.1 Background

The slag viscosity work is a continuation of research previously funded directly through the slagging fixed-bed gasification project of the former Grand Forks Energy Technology Center (FY82 PTPA No. 624). The viscosity-temperature curves are measured under contract by Bituminous Coal Research, Inc., Monroeville, PA (DOE Contract No. DE-AC18-80FC10159); supplemental analytical data are obtained at Grand Forks. At the time of transfer of the Grand Forks Energy Technology Center to the University of North Dakota, the technical direction of the Bituminous Coal Research contract remained with the new Grand Forks Project Office. Nevertheless, the viscosity data are an integral part of the UNDERC Ash and Slag Characterization project and are therefore reported here. UNDERC continues to supply analysis of ash and slag samples, and to collaborate extensively on development of correlative equations.

12.2.2.2 Viscosity Measurements

Tests were run on Baukol-Noonan slag in an oxidizing atmosphere (air), neutral atmosphere (N_2), and reducing atmosphere ($20 H_2 : 80 N_2$). The cooling curves in the Newtonian region for the oxidizing and neutral atmospheres are virtually identical within experimental error, although the oxidizing atmosphere curve is consistently slightly higher (e.g. 165 versus 140 poises respectively at 2400°F). The oxidizing and neutral curves were significantly higher than the one for the reducing atmosphere (58 poises at 2400°F). The curves are shown in Figure 12-1.

FIGURE 12-1. Baukol-Noonan--Oxidizing, reducing, and inert atmosphere tests.

The difference between the reducing versus oxidizing or neutral atmosphere behavior has some interesting implications for slagging gasifier operation. As a rule-of-thumb, it has been assumed that a slag will give satisfactory tapping if the viscosity is no greater than 100 poises at 2400°F, based on measurement in a reducing atmosphere. (Although the tuyere blast itself is obviously strongly oxidizing, it is presumed that the oxygen is consumed almost instantaneously, so that the actual atmosphere in the gasifier hearth is overall reducing.) In a reducing atmosphere viscosity test, Baukol-Noonan slag meets the 100 poises/2400°F rule and would be predicted to tap easily; in fact many successful runs have been made with this coal. However, the viscosity at 2400°F is well above 100 poises in oxidizing or neutral atmosphere. Thus if a process upset occurs, such as fuel bed bridging, that would result in a large "cavern" from which the coal has been consumed and which hence now has an oxidizing atmosphere, the slag will be much more difficult (if not impossible) to tap and hence contribute to shut-down.

Another interesting comparison among the three atmospheres is the relative hysteresis between the cooling curve and the reheating curve. The reducing atmosphere test shows significant hysteresis, as is not uncommon with low-rank coal ash slags. Hysteresis is diminished in the inert atmosphere test, and virtually nonexistent in the oxidizing atmosphere test. Except for atmosphere, the three tests were run as nearly similarly as could practically be accomplished. It has been assumed that hysteresis was a result of slow dissolution of a second phase formed during the cooling cycle; these results, however, suggest that another factor might also be at work.

A similar set of three tests was run with Kemmerer slag (Figure 12-2). In this case, the curves for the three atmospheres were virtually coincident, although at lower temperatures the oxidizing atmosphere system had the highest viscosity and reducing, the lowest, as was seen with Baukol-Noonan. Kemmerer, however, showed hysteresis in all three atmospheres, with the extent of hysteresis roughly the same, each time.

FIGURE 12-2. Kemmerer--Oxidizing, reducing, and inert atmosphere slag viscosity tests.

Any concerns about the effects of atmosphere naturally focus on iron, since Fe_2O_3 and FeO should have significantly different effects on the liquid structure and hence viscosity. Although analytical data are not complete on the most recent tests, it is interesting that a previous sample of Kemmerer slag was found to contain only 0.9 pct " Fe_2O_3 " whereas Baukol-Noonan slag runs about 8-10 pct " Fe_2O_3 ".

A test was run on "low-sodium" Beulah lignite slag (Figure 12-3). Beulah lignite is particularly noteworthy for large variations of sodium content within the mine. Two samples have been tested in the viscosity program, being called for convenience "low-sodium" and "high-sodium" and having respectively 4.2 pct and 8.1 pct Na_2O in the slag. The viscosity of the low-sodium sample was significantly lower at a given temperature than that of the high-sodium sample, e.g., 19 vs. 280 poises respectively at 2400°F . This result was surprising, since Na_2O would be expected to be an oxide donor in the melt, thereby helping to cleave aluminosilicate polymers and reduce the viscosity.

Although the observed viscosity behavior of the two Beulah samples is the reverse of what would be predicted from polymer-maker/polymer-breaker theory, the results do corroborate some work reported previously by the National Bureau of Standards (5). The NBS work involved the addition of K_2O to synthetic slags. The viscosity at a given temperature actually went through a maximum as a function of amount of K_2O added, the maximum occurring around 15 to 20 wt pct K_2O , depending on original SiO_2 content. Substantial increases in viscosity were noted in the NBS work. For example, at $1400^\circ C$ going from 10 to 20 wt pct K_2O increased the viscosity from 2512 to 4786 poises. The differences between the two Beulah samples are within those attributable to an increase in Na_2O , assuming that Na_2O acts in the same way as K_2O and that the Beulah slag is on the increasing-viscosity side of the viscosity versus Na_2O concentration curve.

FIGURE 12-3. Beulah low-sodium.

The work with the two Beulah samples is also relevant to gasifier operation. The low-sodium Beulah produces a slag which easily satisfies the 100 poises/ $2400^\circ F$ criterion, and, on the basis solely of slag properties, low-sodium Beulah might be an attractive coal for gasification tests. However, process upsets or inhomogeneities in the feed coal that alter the slag composition to that something like the high-sodium slag could easily result in the slag becoming too viscous to tap.

A test was made with Indian Head slag actually produced in the gasifier. (All other tests in the program have used slag prepared by melting ash prepared from the coal at 1000-1100°C. This curve is given in Figure 12-4). As might be predicted from the many successful gasifier runs with Indian Head Lignite, the slag was quite fluid, having a viscosity of 100 poises at 2215°F and about 14 poises at 2400°F. It was noted by the contractor that "the molten slag was unusually fluid."

FIGURE 12-4. Indian Head slag.

12.2.2.3 Correlation with Composition

A considerable effort is devoted to testing published correlations of viscosity-temperature behavior with composition, and, where initial results seem promising, modifying published equations to improve their applicability to low-rank coal ash slags.

A review of 18 published correlation methods has been compiled as an UNDERC Internal Report. The methods which seemed particularly useful were those of Bills (6), Bottinga and Weill (7), and the dolomite ratio method (8). Each has some limitations; for example, the Bills method is restricted to slags where $\text{CaO} + \text{MgO} + \text{Al}_2\text{O}_3 + \text{SiO}_2 \geq 90$ pct, and the dolomite ratio method gives only the temperature at which the viscosity is 250 poises.

The most promising correlation method developed so far is a modification of a method published by Urbain (9) for metallurgical slags. Full details of the modification, and of the application of this method to low-rank coal ash slags will be found in a paper entitled "Measurement and Prediction of Low-Rank Coal Slag Viscosity" by R. C. Streeter, E. K. Diehl, and H. H. Schobert, scheduled for publication in the Preprints of the Division of Fuel Chemistry for the Washington, D.C. American Chemical Society Meeting, August 28-September 2, 1983. A brief synopsis is given below.

The Urbain equation has some theoretical (or at least aesthetic) advantages over more traditional approaches. It is based on the Frenkel viscosity relation,

$$\eta = AT \exp (B/T)$$

rather than the Arrhenius

$$\eta = A \exp (E/RT).$$

It includes all slag constituents, rather than just a few of the major elements. Slag constituents are expressed as mole fractions instead of weight percentages. Finally, the Urbain correlation is based on the $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CaO}$ ternary, three constituents which frequently predominate in low-rank coal ash slags.

The logarithmic form of the Urbain equation is

$$\ln \eta = \ln A + \ln T + 10^3 B/T$$

where T is in $^\circ\text{K}$, B is a parameter defined by composition, and A is a function of B . The modification was developed by first adding a term, Δ , to account for the difference between the actual viscosity and that computed by the logarithmic equation above. Thus, for a force fit,

$$\ln \eta = \ln A + \ln T + 10^3 B/T + \Delta.$$

Since $\ln \eta$ is a linear function of temperature, Δ must be also; that is,

$$\Delta = mT + b.$$

For each slag m and b can be derived from the experimental viscosity data in the linear or Newtonian range. Then m and b must be correlated with a slag property. b can be determined from m via a regression equation.

To find a suitable correlation of m , it was necessary to divide the slags into three classes based on silica content. As an example, the calculation is shown here for Burns and McDonnell slag, a "high silica" slag. The slag composition, in mole fraction, is

SiO_2	.579	CaO	.081
Al_2O_3	.172	MgO	.053
Fe_2O_3	.090	Na_2O	0
TiO_2	.008	K_2O	.016
P_2O_5	0	SO_3	.002

The Urbain equation is

$$\ln \eta = \ln A + \ln T + 10^3 B/T + \Delta$$

where

$$\ln A = -(0.2693B + 11.6725)$$

and

$$B = B_0 + B_1N + B_2N^2 + B_3N^3$$

where N is the mole fraction of SiO_2 . The B_i are given by

$$\begin{aligned} B_0 &= 13.8 + 39.9355\alpha - 44.049 \alpha^2 \\ B_1 &= 30.481 - 117.1505\alpha + 129.9978 \alpha^2 \\ B_2 &= -40.9429 + 234.0486 \alpha - 300.04 \alpha^2 \\ B_3 &= 60.7619 - 153.9276 \alpha + 211.1616 \alpha^2 \end{aligned}$$

where

$$\alpha = M/(M + \text{Al}_2\text{O}_3)$$

and

$$M = \text{CaO} + \text{MgO} + \text{Na}_2\text{O} + \text{K}_2\text{O} + \text{FeO} + 2\text{TiO}_2 + 3\text{SO}_3$$

with all components expressed as mole fractions.

Recall that

$$\Delta = mT + b$$

For this class of slag

$$b = -1.7137 \times 10^3 m + 0.0509$$

where

$$10^3 m = -1.7264F + 8.4404$$

and

$$F = \text{SiO}_2 / (\text{CaO} + \text{MgO} + \text{Na}_2\text{O} + \text{K}_2\text{O}).$$

Substituting and solving gives the following typical results, with absolute temperature reconverted to Fahrenheit:

<u>T, °F</u>	<u>η calc'd, poises</u>	<u>η obs'd., poises</u>
2535	304	272
2690	105	94

It is interesting to note that for these high silica slags the alkali and alkaline earth oxides show an inverse relationship to silica in the term F, which is consistent with the polymer-maker/polymer-breaker theory.

12.2.3 Slag-Refractory Interactions in Gasification

A series of slag and refractory samples have been collected after shut-down from several recent gasifier runs. These samples are being studied by a variety of techniques including x-ray fluorescence for bulk composition; x-ray diffraction and optical microscopy for phase identification; and electron microscopy/microprobe analysis for surface morphology, composition mapping, and micro-analysis. Data are being accumulated but so far have not been brought together in such a way as to provide working hypotheses to account for some of the observed effects.

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13. - ORGANIC STRUCTURE

Project No: 7303

B&R No.: AA1515100

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13.1 GOALS AND OBJECTIVES

Our approach to the study of the organic structure of coal has been to use a model based on substructures, the same as were present in the original wood (cellulose, hemicellulose, lignin) and those derived from these original substructures. We have concentrated on the original substructures in the first quarter, since these structures are well known. The extraction of these substructures from the coal required much investigation, since the methods applicable to wood did not necessarily work with coal. New methods incorporating gas chromatography were developed for the analysis of the components derived from depolymerization of the macromolecular substructures.

13.1.1 Cellulose

Cellulose has long been thought to be the most easily degraded component of wood (1). The theory that coal was formed by reactions of cellulose or glucose from the hydrolysis of cellulose was suggested long ago by Maillard and (2) and Bergius (3) who converted carbohydrates into materials resembling coal. A later theory advanced by Enders (4) considered humic acids to have formed from cellulose and lignin via conversion of carbohydrates to methylglyoxal which then further condensed with other decomposition products to give insoluble quinone-type polymers. How much of the humic acid or coal molecule is derived from cellulose is still an important question, however the intent of our initial studies was to determine how much cellulose remains in the coal. The significant quantities of acetone and other low molecular weight aliphatic ketones present in products resulting from gasification, liquefaction and steam-drying of North Dakota lignites may have resulted from heating of cellulose, lignin or possibly some other precursor, since pyrolysis of either cellulose or lignin gives ketones (5).

The cellulose contents of a number of European brown coals and Japanese lignites have been determined with values from 0.2 to 45 pct having been reported (6). The method used for isolation of the cellulose in most of these studies was extraction with sulfuric acid, such as in the Klason method (72 pct H_2SO_4). The cellulose was hydrolyzed with dilute sulfuric or other acid and the glucose and other monosaccharides were analyzed in various ways.

13.2 ACCOMPLISHMENTS

13.2.1 Cellulose Extraction And Analytical Methods

The Klason method using 72 pct sulfuric acid was investigated with a lignite sample. After stirring the concentrated acid slurry, it was diluted with water and refluxed. The filtered solution was neutralized with BaCO_3 , filtered to remove BaSO_4 and excess BaCO_3 , and evaporated. Reduction of any monosaccharides present to the alditols was carried out with NaBH_4 . The alditols were esterified with acetic anhydride. The resulting alditol ester mixture was analyzed by gas chromatography.

A method using a solution of cadmium oxide in ethylenediamine and water (cadoxen) (7) was effective in extracting cellulose from the coal. Coal was stirred with cadoxen at room temperature. The suspension was centrifuged and the supernatant cadoxen solution was diluted with methanol to give a precipitate of cellulose, hemicellulose and other "humic acid" material. This mixture was isolated by centrifugation and hydrolyzed by dilute sulfuric acid as in the method above. The alditol esters were prepared and analyzed by gas chromatography.

Hydrolysis was studied using cellulase enzymes, however there was a residue of cellulose in the enzyme preparation which made it useless for analytical determinations of cellulose.

An enzyme system was also investigated for the analysis of glucose resulting from the hydrolysis of cellulose. This system (Sigma Chemical Co.) was composed of hexokinase and glucose-6-phosphate dehydrogenase and produces NADPH which is determined at 340 nm. This worked with standard glucose solutions; however the amounts of glucose obtained from the coal samples were too low for this method.

13.2.2 Gas Chromatographic Methods For Carbohydrate Analysis

The two most popular derivatives for GC analysis of monosaccharides are trimethylsilyl (TMS) derivatives (8) and alditol acetates (9). A silylation reagent (hydroxy-Sil-AQ) was obtained from Regis which effected the conversion of damp saccharide syrups to the TMS derivatives. The TMS derivatives gave well-resolved peaks in chromatography on a DB1701 capillary column. The peak shapes were very sharp and symmetrical. The only problem with this method is that each monosaccharide gave 2 peaks, the α - and β -anomers, thus complicating the quantitation by an ISTD method (the TMS derivative of each pure anomer would have to be prepared).

The alditol acetates were chromatographed on a number of capillary columns with various oven temperature programs. The derivatives of the common five and six carbon sugars were resolved on a DB1701 column except for those of ribose and arabinose. Derivatives of glucose and galactose were not resolved on an OV351 column. A PCPS polar column gave broad peaks. Only with an SP2330 capillary column were all the peaks resolved. A calibration using inositol as the internal standard was performed with five different levels of concentration of ribose, arabinose, xylose, mannose, galactose, and glucose. Peak shapes were very good with this column and excellent results were obtained in a calibration test.

13.2.2.1 Results of Extraction and Analysis

1. A composite lignite sample from the Beulah 3 mine gave no detectable amount of glucose when treated with 72 pct H_2SO_4 and hydrolyzed.
2. An identical sample of lignite (Beulah 3) gave peaks corresponding to galactose, xylose, ribose and arabinose as well as glucose when treated with cadoxen, hydrolyzed, and converted to alditol acetates.
3. A second Beulah 3 sample gave 0.003% glucose (analyzed as the alditol acetate) on an as-received weight basis.
4. A Velva composite sample and a Velva vitreous lithotype gave no glucose.
5. The identities of the alditol acetate peaks from the Beulah 3 sample were confirmed as 5 and 6 carbon sugar derivatives by gcms.

13.2.2.2 Conclusions of Extraction and Analysis

1. The Klason method for extraction of cellulose was not effective for coals.
2. The cadoxen method was able to extract cellulose and hemi-cellulose which gave a mixture of sugars on hydrolysis.
3. The amounts of cellulose and hemi-cellulose extracted from ND lignite was extremely small (0.003% as received). We do not know yet if all the cellulose in the coal was extracted with cadoxen.
4. The amount of cellulose present appears to be too small for it to have been a precursor for the acetone found in coal conversion products.

13.2.2.3 Future Experiments with Carbohydrates

1. Determine the carbohydrate content of three Beulah lithotypes: vitreous, dull, and fragmentary.
2. Exhaustively extract a lignite sample with cadoxen and employ various alternatives such as sonication to see if higher yields of extractions of cellulose can be obtained.
3. Extract coal with KOH before the cadoxen to remove the hemicellulose fraction.

13.2.3 Lignin

The lignin theory of the origin of coal is also very old (10). Hatcher (11) has recently examined a series of humic substances with ^{13}C nuclear magnetic resonance, and has shown that plant lignin is first concentrated, then modified in the conversion to lignite. Since lignites yield appreciable quantities of methanol on pyrolysis, the presence of guaiacol units from lignin can be presumed. Examination of the phenolic products from gasification of

lignite showed that significant amounts of a very limited series of guaiacols were present (12). This series was composed of guaiacol, 4-methylguaiacol, 6-methylguaiacol, 4-ethylguaiacol, and 4-propylguaiacol. Some of the guaiacol units of the plant lignin have survived the lignin modification process and are present either as unaltered lignin substructures in the coal matrix or possibly as isolated guaiacols resulting from changes in the lignin structure which did not affect the methoxy group or the side chain carbons. Since thermal treatments of the lignin generally involve loss of methoxy groups and conversion of the side chains to ketones, carboxylic acids, etc., the hypothesis that unaltered lignin is present seems more likely.

13.2.4 Methoxy Determination

One approach to determining how much lignin remains in a sample is to measure the methoxy ether groups using a Zeisel method. Blom and coworkers showed that the methoxy content decreased from 1.1 to 0.2 pct in a series of coals of increasing carbon percentages (65, 72, 75, and 80) (13). In the method as modified by Vieböck and Schwappach (14), phenol is used as a solvent with the HI, and the liberated methyl iodide is determined by a complicated titration method.

We sought to simplify the Zeisel method by determining the methyl iodide by a calibrated GC method, since the determination by capillary gas chromatography would not permit interferences and is easier to carry out than the titration. 1,2-Dimethoxyethane was used as the internal standard and a multi-level calibration was performed with a DB1701 thick phase (1 μ) column. The method was tested with a wood sample. Since part of the coal did not dissolve in the phenol-HI mixture, a method was sought where the coal would become solubilized. A lignite sample was heated overnight with a mixture of phenol and p-toluenesulfonic acid, then HI was added and the methyl iodide determined. Unfortunately part of the coal still had not dissolved and the methoxy content came out even lower than when phenol alone was used as the solvent.

In order to effect dissolution of the coal so that all methoxy groups would be subjected to ether cleavage, the oxidation of lignite with CF₃CO₃H was carried out (15). This reagent converts methoxy groups to methyl trifluoroacetate. An attempt to determine this ester directly failed because of its high volatility. An attempted conversion of the ester to methyl iodide failed since the conversion was incomplete. Finally a simple hydrolytic method was used to convert the ester to methanol which was distilled and then determined on a DB1701 thick phase (1 μ) capillary column by a calibrated method using 1,2-dimethoxyethane as the internal standard.

13.2.4.1 Results of Methoxy Determinations

1. Modified Zeisel methoxy determinations of two Beulah 3 lignite samples gave 0.45 pct methoxy on an as-received weight basis. Some coal was undissolved.
2. Modified Zeisel determination after heating a Beulah 3 lignite sample in phenol plus p-toluenesulfonic acid gave 0.33 pct methoxy. Some coal was undissolved.

3. Trifluoroperacetic acid oxidation of a Beulah 3 lignite followed by hydrolysis gave 0.75 pct. methoxy on an as-received weight basis.

13.2.4.2 Conclusions of Methoxy Determinations

1. Hydrolytic methods for determination of methoxy ethers with HI give low values, presumably because of incomplete dissolution of the coal.
2. Attempted dissolution of the coal in a mixture of phenol and p-toluenesulfonic acid failed and gave an even lower value for methoxy, probably due to loss of methanol from oxidation or evaporation during the "dissolving" stage.
3. A value for methoxy of 0.75% (determined by oxidation with $\text{CF}_3\text{CO}_3\text{H}$) corresponds to the middle of the range of values published by Blom (13). If this methoxy content is assumed to come from the guaiacol units of a lignin composed of poly (coniferyl alcohol) it corresponds to 5% lignin in the coal.

13.2.4.3 Future Experiments of Methoxy Determination

1. Methoxy determinations on three lithotypes of Beulah 3 coal will be performed.
2. Various lignin extraction schemes will be attempted, using the methoxy determination and spectroscopic methods to analyze the products.

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14. - DISTRIBUTION OF INORGANICS

Project No: 7304

B&R No.: AA1520150

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14.1 GOALS AND OBJECTIVES

The goals of this work are to better understand the distribution of inorganics in low-rank coals and examine the geochemical factors which affect their distribution. Methods will be developed to selectively remove inorganics in ways dependent upon their association in the coal. Knowledge of how these inorganics are associated can be used to predict the fate or impact of the elements during utilization.

The objectives for this reporting period are:

1. Begin extending the chemical fractionation procedure used to selectively extract inorganics to include more steps which would possibly determine more inorganic associations.
2. Examine methods used to determine carboxylic acid groups in low-rank coals.
3. Begin examining the organic and inorganic recognizable features in coals by macroscopic and microscopic techniques. Coal minerals and lithotypes will be examined by a variety of analytical techniques.

14.2 ACCOMPLISHMENTS

14.2.1 Collection and Storage of Low-Rank Coals

Samples of low-rank coals have been carefully collected from freshly mined seams to minimize oxidation, loss of moisture, and contamination from overburden. The samples are crushed, split, and stored under argon atmosphere. These samples are then made available to all Coal Science projects at the Center. The samples collected from North Dakota mines include Indian Head, Center, Beulah high-Na, Beulah low-Na, Velva, Gascoyne, Glenharold, and Falkirk. Samples of two Montana subbituminous coals, Absaloka and Spring Creek, have also been added to the coal sample bank.

14.2.2 Chemical Fractionation

The chemical fractionation procedure (1) used at present involves the ion-exchange of the cations associated with organic acid groups (probably carboxylic acids) with 1M ammonium acetate. The same sample is subsequently extracted with 1M hydrochloric acid to remove coordinated inorganics and acid soluble carbonates and oxides. The inorganics that remain in the coal include quartz, clays, and pyrite.

Washed and unwashed samples of Choctaw lignite from Alabama were examined using this technique. The coals were analyzed by x-ray fluorescence (XRF) before and after each extraction. The accuracy of XRF is limited for low atomic numbered elements, such as Na. The results are summarized for Choctaw and washed Choctaw in Tables 14-1 and 14-2 respectively.

Present extraction techniques involve two extractions with 1N NH_4OAc at 70°C and two with 1N HCl. An initial extraction with H_2O prior to NH_4OAc is being tested to determine the level of cations present as H_2O soluble minerals or complexed with fulvic acids (a water soluble fraction of the humic material). Distinguishing between these is difficult because demineralization techniques would also dissolve some of the fulvic acids.

TABLE 14-1
CHEMICAL FRACTIONATION RESULTS
FOR CHOCTAW, ALABAMA LIGNITE

Element	Before Extraction, Wt % In Dry Coal	% Extracted by NH_4OAc	% Extracted by HCl	& Remaining in Coal
Na	1.287	14.9	--	--
Mg	3.2	27.8	0	72.2
Al	0.386	0	28	72
Si	1.22	0	0	100
S	2.6	32.2	0	67.8
K	.105	5	30	65
Ca	1.18	46.4	53.6	0
Ti	436*	0	28.0	72
Cr	--	--	96	4
Mn	82*	5	0	95
Fe	1.87	10.0	90	0
Ni	0	0	--	--
Cu	13*	--	26	74
Zn	--	--	--	--
Sr	46*	47.5	50	2.5
Zr	9*	--	50	50

*ppm

TABLE 14-2
CHEMICAL FRACTIONATION FOR WASHED
CHOCTAW, ALABAMA LIGNITE

Element	Before Extraction, Wt % in Dry Coal	% Extracted by NH_4OAc	% Extracted by HCl	% Remaining in Coal
Na	1.2	--	--	--
Mg	3.107	28.9	3	68.1
Al	0.5	9.7	0	90.3
Si	0.96	4.0	0	96
S	2.07	18.11	15	66.9
K	0.193	61.4	10.9	27.7
Ca	1.8	54.8	49	0
Ti	427*	10	5	85
Cr	--	--	--	--
Mn	51*	20	--	~(80)
Fe	0.96	8	75	17
Ni	--	--	--	--
Cu	13*	7.7	8.3	84
Zn	8*	--	25	~(75)
Sr	96*	60	30	10
Zr	6*	20	17	63

*ppm

Indian Head and Velva lignites were stirred for 24 hours in 70°C H_2O . Approximately 25 to 50 pct of the extractable Na and all of the extractable K was found in the filtrate whereas a very small fraction of the extractable Ca and Mg was found. These cations were probably dissolved rather than exchanged with H^+ ions, because the level of cations in the filtrate was much greater than the corresponding decrease in H^+ ions.

A major problem with a 70°C H_2O extraction is the subsequent flocculation of the more insoluble humic acid (HA) fraction. If the solution is filtered immediately upon cooling, some of the HA is flocculated to a very fine size, leading to filter clogging and ~2 hr filtration times. If filtered hot, filtration is completed within a few minutes with less subsequent flocculation, although this observation is based on only one sample. The pH of the hot-filtered filtrate (measured 3 weeks later) was the highest however, which may explain the low level of flocculation. In general, the pH of the H_2O extraction filtrates (measured 3 weeks after filtration) was approximately 2 pH units higher than the pH of the subsequent NH_4OAc filtrates. This may explain the lack of precipitation problems with NH_4OAc extractions. Lower initial pH of NH_4OAc extraction would lead to less HA dissolved, hence lower amounts of subsequent flocculation.

Recommendations for future extractions of the type performed on the Indian Head and Velva lignites include:

1. H₂O extractions should be performed at room temperature to decrease amounts of dissolved humic acids.
2. Additional NH₄OAc extractions be performed to determine the completeness of the divalent cation exchange, exchanging until the pH of the filtrate equals that of the initial NH₄OAc solution.

14.2.3 Carboxylic Acid Group Determination

Methods used to determine the carboxylic acid content in coals were examined. The following experiments have been attempted using between .3 and 1 gram of demineralized coal from Center Mine, ND:

1. Shaking with 10 ml 1N calcium acetate + 50 ml water
2. Shaking with 10 ml 1N barium acetate + 50 ml water
3. Shaking with 100 ml 1N calcium acetate
4. Shaking with 100 ml 1N barium acetate
5. Refluxing with 100 ml 1N barium acetate with argon purge

The basic principle used in these experiments was to exchange either Ca²⁺ or Ba²⁺ with H⁺, releasing acetic acid. The acid formed was determined by titrating with a dilute base. The results are reported as the number of milliequivalents per gram of demineralized coal.

In experiments 1 and 2 the samples were placed in a mechanical shaker for 24 hours, filtered and washed. The filtrate was then titrated with base to a pH of 8.25. The results obtained were significantly lower than those reported by Schafer (2) who has studied a North Dakota lignite. Shaking the sample with either acetate did not produce a constant pH of 8.25 even after 5 days. The problem is probably due to oxidation of the phenols in the presence of air and transition metals. To eliminate or reduce oxidation a reflux exchange using barium acetate in argon was carried out (experiment No. 5). The result obtained was a constant pH of 8.2 to 8.3 after 24 hours of refluxing. At this point air was introduced into the system; after refluxing for 4 days, more acid could be titrated. The results of these tests are summarized in Table 14-3.

14.2.4 Mineral Analysis by Scanning Electron Microscopy

Minerals have been analyzed and identified by use of a scanning electron microscope/microprobe (SEM) in coal samples mounted in epoxy blocks. The samples were collected from a vertical section in the Beulah mine, North Dakota. Size and compositional analysis are being performed on samples collected at various depths within the seam.

The minerals identified include pyrite and/or marcasite, aluminum silicates such as kaolinite or montmorillonite, quartz, gypsum, and hematite or goethite.

TABLE 14-3
CARBOXYLIC ACID DETERMINATIONS FOR
CENTER MINE, ND LIGNITE

<u>Method</u>	<u>-COOH, meq/gram</u>
Shake 24 hours w/10 ml 1N Ca(OAc) ₂ and 50 ml H ₂ O	1.45
Shake 24 hours w/10 ml 1N Ba(OAc) ₂ and 50 ml H ₂ O	1.37
Shake 8 days w/100 ml Ba(OAc) ₂	5.6
Reflux with Ba(OAc) ₂ under argon	3.58
Continued refluxing above sample in air	1.75

To a lesser degree the following minerals have been identified: barite, feldspars, calcite, ankerite, rutile, and zircon. The size of the mineral grains ranges from ~5 to 23 microns. The shape of the pyrite in the coal can suggest either a syngenetic or epigenetic origin. Spherical and framboidal shapes have been observed which suggest a syngenetic origin. On the other hand, banded and interstitial pyrite has been observed in the basal section of the seam which is possibly epigenetic in origin. Quartz is mainly angular in shape; however, some crystals were observed. The aluminum silicates appear as larger masses of small particles agglomerated together which appear very dull under the SEM.

14.2.5 Lithotypes

Lithotypes are macroscopically recognizable constituents of coals. The lithotypes which have been identified and separated in the coals at UNDERC include vitrain (vitreous), durain (dull), and fusain (fragmental). The average concentrations of these lithotypes in Beulah lignite, North Dakota, are ~5 pct fusain, 40 pct durain, and 45 pct vitrain. Samples of these lithotypes are being used by other Coal Science projects.

14.2.6 Pressure Differential Scanning Calorimetry (PDSC)

The PDSC work is used to examine the structural characteristics of coals and their lithotypes. The PDSC experiments involve heating a sample linearly from 150° to 600°C in 500 psl oxygen. A complete description of the tech-

niques and results obtained have been reported by Benson and Schobert (3). Aromaticity values can be calculated by use of the ratio of the high temperature peak to the sum of both peaks. Figure 14-1 represents thermograms of Beulah lignite and three lithotypes separated from the coal. The most aromatic lithotype is the Fusain ($fa=0.80$) which is a highly oxidized fraction of the coal. Vitrain is the least aromatic of the lithotypes. A paper was written for the 12th NATAS/38th Calorimetry Conference entitled "Pressure Differential Scanning Calorimetry of Coals, Organic Compounds, and Polymers," by Steven A. Benson, Kathleen S. Groon, and Harold H. Schobert, to be presented in September 1983. This paper discusses the PDSC work with lithotypes, polymers and organic compounds.

FIGURE 14-1. PDSC thermograms of Beulah lignite and three lithotypes.

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15. - PHYSICAL PROPERTIES AND MOISTURE

Project No.: 7305

B&R No.: AA1520150

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15.1 GOALS AND OBJECTIVES

There are three major goals of this project. The first is to develop methodologies and data on mechanical properties of crushed and finely-ground low-rank coals and their mineral residues, relevant to their behavior and handling problems. The second is to relate observed mechanical or physical properties to the three-dimensional structural arrangement of the coal macromolecules via the theories and models of polymer science. The third is to determine the distribution and modes of incorporation of water in low-rank coals, and to develop approaches for the measurement of "moisture" which can be interpreted in ways meaningful for low-rank coal utilization.

Major objectives for the current budget year are as follows:

1. Establish credible testing procedures to define the following properties of coals:
 - a. Free sliding, bulk shear strength, as a function of particle size;
 - b. Permeability to gas flow, as a function of particle size;
 - c. Mechanical friability as a function of dryness; and
 - d. Thermal friability.

These properties define the behavior of a coarsely-crushed coal in a fixed-bed gasifier. Tabulate these properties for selected lignites and subbituminous coals, to establish their relative suitability as gasifier feeds.

2. Determine the pore size distribution in coals by small angle x-ray scattering, and any change therein that results during heating, drying, and pyrolysis, which is relevant to the release and reabsorption of moisture during processing. (This study is being done under a subcontract with Dr. Harold Bale of the UND Physics Department.)

3. Establish a methodology and simple apparatus to measure the relative hardness of finely-ground solids, such as coal and its ash in slurry streams, and candidate materials of construction. The hardness will be expressed on Mohs scale, which has hitherto been applied only to large surfaces by means of a scratch test. Process and equipment materials will thus be characterized with respect to the rates of erosion to be expected in slurry handling systems.
4. Apply physical characterization methods of polymer science, such as measurements of internal friction, elasticity, or solvent swelling, to elucidation of three-dimensional structural order of low-rank coals.

The objectives for the current reporting period have focused on measurements of shear strength, permeability, mechanical and thermal friability, and pore size distribution.

15.2 ACCOMPLISHMENTS

15.2.1 Shear Strength

Tests have been completed to define the free-sliding shear strength of lignite, which is defined as the shear stress applied to a failure plane, which increases in some proportion to the normal or perpendicular compressive stress applied to the same plane. The experimental method was unique in that it used a direct shear test cell of 8.5-inch diameter, with particle sizes up to 0.75-inch. Established procedures for direct shear measurements use a test cell on the order of 2- to 3-inch diameter, for materials in particle size ranges seldom greater than 20 mesh (0.03 inch). Data showed that the shear strength of loosely compacted lignite decreases significantly with decreasing particle size, in the range of 0.75 inch to 12 mesh (0.065 inch), and that the shear strength of mixtures is dominated by their finer components. Observations of plastic deformation, both normal and perpendicular to the shear plane, were made for increasing loads leading to shear failure. The shear strength of a packed bed of coal is a rough indication of the weight that can be sustained by a bridge or dome in a gasifier fuel bed. While sensitive to particle size, it is not expected that this property will vary detectably with kinds of coal.

15.2.2 Permeability

Apparatus has been assembled and tested to measure the pressure drop associated with flows of air through a column of crushed coal, for a range of flow rates per cross section and of particle sizes extending well above and below those encountered in fixed-bed gasifier operation. By application of basic, hydraulic dimensional analysis, such data can be extrapolated to predict pressure drops for the higher pressures and temperatures of variable gas mixtures encountered in gasifier operation. The effective weight of a fuel bed is reduced by the upward pressure drop through it, thus reducing the minimum shear strength that the material must develop to result in impeded settling of the fuel bed as throughput capacity approaches its upper limit. Plans are being formulated for a more elaborate cold simulation, in which steady downward flow of solids can be maintained, to approximate more accurately the settling behavior of a real gasifier fuel bed.

15.2.3 Mechanical and Thermal Friability

As originally conceived, mechanical friability was defined as the fraction of a +0.5 to 0.75-inch sample of coal reduced to -0.5 inch after tumbling for 30 minutes. Similarly, thermal friability was defined as the fraction of an identical sample reduced to -0.5 inch after simply being heated to 1000°F. Combined friability is the fraction of the +0.5-inch material surviving the heating that is reduced to -0.5 inch by a subsequent 30 minutes of tumbling. Using these definitions, based on a single data point for each test, preliminary data showed a striking correlation with type of coal, suggesting a simple positive test for the relative tendency of coals to crumble and form excessive dust during gasification. More recent data indicate that the mechanical friability of lignite is strongly and repeatably dependent on the extent of pre-drying, as occurs even in fairly brief open storage, prior to tumbling. It also appears that the thermal fracture response of lignite is significantly different from that of higher-rank coals, as indicated by their particle size distribution following the tests defined above. It now appears that the arbitrary definitions above may not be adequate to characterize and compare coal friabilities.

15.2.4 Pore Size Distribution

A four-slit Beeman-type collimation system and a rotating iron or copper anode x-ray source were used to obtain experimental small angle x-ray scattering curves for Beulah lignite treated as explained in a following paragraph. With copper K_{α} radiation the angular range was greatly increased from $h_{\max} = 0.13$ to $h_{\max} = 0.4$. The scattering curves were actually composites of two experiments. The inner part of the scattering curve was obtained with narrow slits and the outer part was obtained with wide slits. All scattering curves were corrected for slit effects.

The scattering curves we have obtained from coal do not have the necessary characteristics to uniquely determine any parameters from the scattering curves. Consequently, we have followed the procedure adopted by Schmidt (ACS Symposium Series 169, 1981, 1-22) and have interpreted the scattering in terms of a pore model. The basic premise of the model is that the coals contain three distinct classes of pores; macropores, transition pores, and micropores. The theoretical scattering curve expected from this model is,

$$I(h) = I_0 \left(\frac{S_{ma}}{h^4} + \frac{S_{tr}}{(h^2 + a^2)^2} + \frac{S_{mi}}{(h^2 + b^2)^2} \right)$$

where $h = 2\pi \sin(\theta/2)/\lambda$ and I_0 is a calibration constant which must be evaluated for the apparatus used. S_{ma} , S_{tr} , and S_{mi} are respectively the specific surfaces for the macropores, transition pores, and the micropores. The reciprocal of the parameter a , L_{tr} , is a characteristic length for the transition pores. Likewise, the reciprocal of b , L_0 , characterizes the micropores. Initially, a five parameter least-square fit of the above equation to our experimental data was used. In more recent work a constant term has been added to account for the atomic scattering contribution, which becomes the dominant term at the larger angles ($h > 0.3$). Hence the data are now being analyzed in terms of a six parameter least-square fit of the model to the experimental scattering curve.

The current series of experiments was designed to study structural changes of the lignite that result from exposure to elevated temperature. Each sample was heated for 4 hours in an argon atmosphere and then sealed before exposure to air. Six samples were prepared, each having a different thermal exposure ranging up to 550°C. The lignite used for this study was a size fraction of Beulah lignite which had been ground sufficiently to pass through a 200-mesh screen. The portion of this material retained on a 325-mesh screen was the size fraction actually used for the study. Approximately 40 pct of the powder was retained on the 325-mesh screen. Finely-powdered coal may contain a significant number of very small particles in the size range below a micron. These small particles in turn could contribute to the observed small angle scattering. Since our present interest is concerned with the pore structure rather than particle size, we chose to study a size fraction with particles greater than 45 microns.

Changes in the micropore structure occur upon heating above 225°C. L_0 changes from 10 Å to about 2 Å and S_{mi} increases from about 1 m²/g to over 200 m²/g. The changes may be related to the escape of volatile matter, CO₂, as the temperature is raised. The new micropore structure formed by the heating process has an L_0 value of 2 Å. In terms of spherical pores, this value of L_0 corresponds to an average sphere diameter of about 8 Å. As the heating temperature is raised above 300°C, the surface area of the micropores continues to increase but the micropore size remains nearly constant. Freeze drying, on the other hand, has little effect on the micropore structure but may give rise to an increase in the surface area of the transition pores.

Although the method of data analysis we have used is probably as meaningful an interpretation as can be made at this time, it is apparent that the pore model used in the analysis does not agree exactly with the lignite scattering structure. Future work directed toward a pore size distribution should be very helpful in establishing the pore model that should be used.

16. - SUPERCRITICAL SOLVENT EXTRACTION

Project No.: 7306

B&R No.: AA2530100

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16.1 GOALS AND OBJECTIVES

The two main goals of the Supercritical Solvent Extraction (SCSE) project at the University of North Dakota Energy Research Center (UNDERC) are to:

1. Use SCSE as a means for determining the composition of various molecular fractions present in low-rank coals.
2. Evaluate the use of the SCSE process as a method of obtaining liquid fuels and chemical feedstocks from coal.

Within these two major areas of research, the project has the following objectives for the current budget year:

1. Determine the yields and compositions of products from the SCSE process applied to low-rank coals as functions of the solvent properties (i.e., T_c , P_c , ρ_c , and solubility parameters), operating conditions, solvent flowrate, and the residence time of the coal.
2. Characterize the extraction products by the following analytical methods: 1H NMR, IR and GC-MS on the extract, C/H ratio on the extract and residue, thermogravimetric analyses on the residue, and GC on the product gas.
3. Determine the effects of adding reducing gases to the supercritical solvent or using a solvent with H-donor capabilities.
4. Conduct basic studies on the thermodynamic properties and fluid behavior in the supercritical regime particularly with respect to selected solvent mixtures and recycled solvents.
5. Perform a limited number of autoclave or tubing bomb tests using the optimum extraction conditions and solvents determined previously.

Objectives for the current reporting period (January through June 1983) were as follows:

1. Construct an experimental apparatus and perform some initial experiments to determine the effects of different solvents and operating conditions on product yields and composition.
2. Characterize the SCSE products obtained from these tests using ^1H NMR, IR, GC-MS, and C/H ratios on the extract, C/H ratio and thermogravimetric analyses on the residue, and GC analyses on the product gas.

16.2 ACCOMPLISHMENTS

Construction of a semicontinuous Supercritical Solvent Extraction (SCSE) process was completed in late March. Figure 16-1 is a flowsheet of the process showing the major pieces of equipment and process piping. A Ruska positive displacement pump is used to displace the solvent from a one-liter accumulator through a Varian GC oven containing a preheating coil and an extraction vessel which consists of a piece of 9/16-inch O.D. tubing located between two fittings press fitted with 65 micron sintered metal discs. The extraction vessel is capable of holding approximately 10 gms of coal. The supercritical solvent and entrained extractate pass through the Grove Mity Mite back pressure regulator located in a second Varian GC oven where the pressure of the solvent is reduced to atmospheric pressure upon which the extract separates out of the solvent into the sample cylinder located in the second oven. The solvent, which is still in the vapor phase, is then collected in the cold traps while the product gas is collected in a sample cylinder located at the end of the process.

FIGURE 16-1. Flowsheet for supercritical solvent extraction process.

Four runs using toluene ($T_c = 319^\circ\text{C}$, $P_c = 596$ psia) as the supercritical solvent were performed at approximately 330°C and 700 psia. These runs were made to check out the operability of the SCSE process and to allow suitable product workup and analytical techniques of the extraction products to be developed. The amount of the Indian Head lignite extracted was between 8.1 and 16.5 wt pct. These results were found to be comparable to results obtained elsewhere (1). The use of toluene as a supercritical solvent was not pursued further because of toluene's tendency to react with phenols and itself to form both biphenyls and dibenzyl, respectively, and also because of the large amount of work done by the British National Coal Board using supercritical toluene to extract various coals.

Eight runs using benzene ($T_c = 289^\circ\text{C}$, $P_c = 710$ psia) were performed under various operating conditions. The run conditions, density of the solvent at operating conditions, and the coal conversions obtained are summarized in Table 16-1. The reduced temperatures ($T_R = T/T_c$) were approximately 1.02 to 1.10, and the reduced pressures ($P_R = P/P_c$) were 1.02, 1.50, and 3.00. Figure 16-2 is a plot of the percent conversion versus the reduced pressure at the two different reduced temperatures. Figure 16-3 is a plot of the reduced pressure versus the reduced density of benzene at various reduced temperature isotherms ranging from $T_R = 0.933$ (slightly subcritical) to $T_R = 1.10$ based on data from the literature (2). This figure shows how large increases in the solvent density can be achieved with small or moderate increases in the pressure when the solvent is in the near supercritical region. Because of these density effects, the conversion obtained for Run SCSE No. 9 is believed to be erroneous since the conversion should show an increase with an increase in pressure. The higher conversions at 350°C compared to those at 300°C are due primarily to the greater degree of thermal decomposition of lignite which occurs at higher temperatures.

Four runs have been made using water ($T_c = 374^\circ\text{C}$, $P_c = 3209$ psia) as the supercritical solvent. The operating conditions and the results of these runs are summarized in Table 16-2. The higher conversion for Run 13 is due to a longer residence time at operating temperature than in the other runs (7 hours versus 6 hours). Runs 14 through 16 indicate the reproducibility of the results obtained from the SCSE unit. Extracts were analyzed using 200 MHz ^1H NMR on the CDCl_3 soluble portion of the extent. These analyses showed a small amount (10 to 15 pct) of aromatic hydrogen and a large variety of types of aliphatic hydrogen.

TABLE 16-1
OPERATING CONDITIONS AND CONVERSIONS FOR
SCSE RUNS USING BENZENE
(TC = 289°C, Pc = 710 psia)

Run Number	5	6	7	8	9	10	11	12
Operating Temp., (°C)	296	300	300	300	350	350	300	350
Operating Press. (psia)	735	730	725	1065	725	1065	2130	2130
Solvent Flowrate (cc/hr @ R.T.)	480	120	160	200	200	200	200	200
Solvent Density @ Operating Conditions (g/ml)	.18	.16	.16	.47	.11	.20	.57	.48
% Conversion (maf basis)	3.8	--	3.7	6.7	20.7	13.9	7.0	18.0
% Closure	93.04	106.6	100.05	102.79	96.28	96.51	95.44	93.84

FIGURE 16-2. Plot of % conversion versus reduced pressure at reduced temperatures of 1.02 and 1.11 using benzene as the supercritical solvent.

FIGURE 16-3. Plot of reduced pressure versus reduced density of benzene at various reduced temperature isotherms.

TABLE 16-2

OPERATING CONDITIONS AND CONVERSIONS FOR SCSE RUNS USING WATER

($T_c = 374^\circ\text{C}$, $P_c = 3209$ psia)

Run Number	13	14	15	16
Operating Temp., ($^\circ\text{C}$)	377	377	378	379
Operating Press. (psia)	3225	3245	3225	3260
Solvent Flowrate (cc/hr)	120*	200	200	200
% Conversion (maf basis)	54.7	48.7	45.5	47.0
% Closure	93.56	78.0	88.8	95.5

*Increased residence time of the coal.

16.3 REFERENCES

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2. Vargaftik, N.B. Tables on the Thermophysical Properties of Liquids and Gases. John Wiley and Sons, Inc., New York, NY, 2nd Ed., 1975.

17. - PYROLYSIS AND DEVOLATILIZATION

Project No.: 7307

B&R No.: AA8545050

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17.1 GOALS AND OBJECTIVES

The primary goal of the Pyrolysis and Devolatilization project is to determine the product compositions, mechanisms, kinetics, and thermodynamics of the pyrolysis or devolatilization of low-rank coals under heating rates, particle sizes, and atmospheres typical of low-rank coal processing. The experimental conditions will be chosen to complement, rather than duplicate, existing work already reported in the literature.

A second goal of this project is to use the pyrolysis experiments to simulate effluent production from fixed-bed gasification, and thereby to examine the nature of products as a function of reaction conditions and of coal type. This would allow potential downstream effluent treatment requirements to be assessed without having to run full-scale gasification tests.

The objectives of the Pyrolysis and Devolatilization project during this reporting period were: 1) to review pyrolysis and devolatilization reactions in the UNDERC slagging fixed-bed gasifier, to compare observed product compositions with other types of processes; 2) to conduct preliminary experiments in thermal analysis equipment and small tube furnaces; and 3) to design, construct, and initiate installation of a large-scale thermogravimetric analyzer capable of operation on 1-lb samples to 1000°F and 1000 psi.

17.2 ACCOMPLISHMENTS

17.2.1 Review of Pyrolysis in Slagging Gasification

It has been suggested that coal pyrolysis results in formation of alkyl-benzenes, naphthalenes, and higher aromatics at 200°-370°C and phenols and naphthols above 370°C. (See, for example, H.C. Howard, "Pyrolytic Reactions of Coal" in H.H. Lowry, Chemistry of Coal Utilization, First Supplemental Volume, chapter 9, p. 355.) This suggestion raises the question of whether a higher coal throughput rate in the SFBG would result in less "cooking" at 200°-370°C and, hence, relatively greater phenols and naphthols in the tar. To address this question, the low-voltage mass spectrometric data for tars from nine gasifier runs were examined. The ratio of oxygenated compounds (mostly phenol, naphthol, and their alkylated derivatives) to hydrocarbons

(containing no heteroatoms) was correlated against the coal residence time. Deleting one set of data which seemed to be an outlier still gave a correlation coefficient of only 0.58 suggesting at best a very weak correlation. A refined calculation in which phenols and cresols in the wastewater were added to the oxygenated compounds in the tar, also showed no evident correlation.

Tar yields from lignite as a function of gasification pressure were compared with those of German brown coal. The German data (Lowry, 1st Suppl. Vol., p. 356) do not show the basis of the calculation (i.e., yield per what?); the SFBG data were calculated on tar produced per lb of fixed carbon in the feed. On that basis, the relationships are very similar, being described by an equation of the form $Y = a \exp(bP)$ where Y is the yield, P the pressure in atmospheres, a the intercept, and b the "slope". The two cases are shown below:

	<u>a</u>	<u>b</u>	<u>R²</u>
German brown coal	10.3	-0.018	0.820
Indian Head lignite	8.8	-0.014	0.885

The important point is the very similar "slope"; if the German data were calculated on a different basis, the intercept might change, but the shape of the curve should remain relatively unchanged.

One view of pyrolysis is that the initial thermal cracking reactions of the coal "structure" would produce hydroxylated and alkylated aromatics, which would undergo subsequent cracking to the parent unsubstituted structures. This view suggests that the shorter the residence time, the smaller should be the quantity of unalkylated aromatics. To test this view, low-voltage mass spectrometric analyses (LV-MS) of nine tars were correlated against coal residence time. There was no correlation of unalkylated aromatics or of (unalkylated + unhydroxylated) aromatics versus residence time for a linear least squares fit. Even when the correlation was restricted to one- or two-ring aromatics, which should be the type of ring structures present in the coal, the best R² value observed was 0.10.

There should be a direct correlation between volatile matter and pitch content of the tar. Since pitch content is measured by the Hempel distillation, which was abandoned here in 1977, data are pretty scarce. Nevertheless, for six runs (RA-21 and earlier) the linear correlation coefficient is 0.82 for as-received volatile matter versus pitch. Curiously, the correlation coefficient drops to 0.51 if maf volatile matter is used as the independent variable. Some other suggested tar composition correlations with coal volatile matter content are phenol content and naphthalene/anthracene ratio (both directly proportional) and toluene/phenol ratio (inversely proportional). No correlations were found for phenol or toluene/phenol ratio. The naphthalene/anthracene ratio appears to be inversely, rather than directly, proportional to volatile matter, since a least squares line has a negative slope (R² = 0.731).

For low-temperature tars, alkylated naphthalenes should be the most prevalent compound class. Based on available LV-MS data, this is indeed the case for most tar samples. For unsubstituted hydrocarbons, the order of concentrations is naphthalene > phenanthrene > fluoranthrene for eight of nine

cases checked; this ordering agrees with other types of coal tar. The relationship breaks down if one compares the sums of all naphthalenes (i.e., including alkylated derivatives), all phenanthrenes, and all fluoranthenes.

For runs made at 200 psi, the hydrogen content of the tar increases with increasing partial pressure of hydrogen. This relationship holds for both Indian Head and Baukol-Noonan lignites, although the data for the two lignites do not fall on the same line. At 400 psi the hydrogen content of the tar seems roughly constant versus hydrogen partial pressure. These comparisons are made on the basis of limited data, since the tar hydrogen analyses beginning in the mid-RA-30's and running at least through RA-66, are highly suspect.

Further correlations of experimental data from gasifier runs will be made in conjunction with preparation of a chapter on processes leading to organic emissions for the forthcoming gasification topical report.

17.2.2 Small Scale Pyrolysis Experiments

17.2.2.1 Thermogravimetric Analysis

Experimental work in lignite devolatilization in a standard laboratory thermogravimetric analyzer was started. Indian Head lignite is being used as the test coal. The first series of experiments used -28+40 mesh particles heated in argon. The initial results were difficult to interpret because of varying moisture levels in the coal. Two approaches to correcting this problem were tested; air drying the coal to approximately 9 pct moisture before starting an experiment; or drying the coal by slow heating to 250°C in Ar right in the TGA, followed by "rezeroing" the instrument and then running the devolatilization experiment. In both cases, it is now possible to get reproducible results. Remarkably, the devolatilization chemistry, as followed by the first derivative of the weight loss curve, is noticeably different between the two methods of drying. The coal dried at 250°C in the TGA shows a slow, steady weight loss with a smooth first derivative plot resembling a classic decay curve. Devolatilization of the air-dried coal gives an irregular weight loss versus temperature, suggesting a complex devolatilization chemistry. While the latter case is likely to be much more interesting chemically, it was felt that the former (i.e., in situ drying in the devolatilization apparatus) more closely simulates conditions in a fixed-bed gasifier and thus was the method adopted.

However, the work with the air-dried lignite showed some very interesting effects of sample aging. As observed by following the first derivative of the TGA curve, freshly air-dried lignite shows a rich variety of reactions, with major reactions occurring around 200°, 400°, 500°, and 750°C and some evidently small changes in the regions 600°-700° and 800°-1000°C. As the samples are allowed to stand in the laboratory, the behavior becomes much simpler. For example, after three to four days there are major reactions only around 200° and 450°C with small changes occurring at 550° and about 850°C. After two weeks, the only evident reactions occur at 200° and 450°C, and there are virtually no other indications of reactivity up to 1100°C. The reasons for this behavior are not yet understood. However, this work does suggest that there may be very fruitful applications of TGA in studying drying and aging phenomena.

Using the apparatus in its differential scanning calorimetry mode, the most interesting finding so far has been the observation of exothermic heats of carbonization around 500°C. This observation agrees with some work previously reported by P.L. Walker at Penn State (Fuel, 1976, 55, 63-69). It also corroborates similar results obtained here in the early 50's which were not published because the finding contradicted the prevailing conventional wisdom that pyrolysis processes have to be endothermic.

17.2.2.2 Tube Furnace Experiments

Other small scale pyrolysis experiments have been carried out using a standard laboratory tube furnace, with the sample heated in a vessel made of pipe or tubing and various traps attached to collect or scrub out the reaction products. For convenience this unit will be referred to as the small pyrolysis reactor (SPR).

The initial experiments in the SPR were made to check heat transfer calculations for the large-sample thermogravimetric unit discussed in the following section. However, the feed coal and resulting chars were collected for analysis. In the baseline experiment, the total weight loss from the sample agreed very well with the sum of moisture and volatile matter determined by proximate analysis of the feed coal--47.66 pct versus 47.30 pct respectively. It was found that the weight loss from the sample was virtually unaffected by heating rate (as determined by the setting of the furnace controller) but was inversely proportional to the flow rate of nitrogen purge gas, as shown in the table below:

<u>Experiment</u>	<u>Furnace Heater Setting</u>	<u>N₂ Flow ml/min</u>	<u>% Wt Loss of Sample</u>
1	3	60	47.66
2	3	120	46.73
3	3	220	46.48
4	6	60	47.59
5	6	220	45.88

It was also noted that the char, when re-analyzed by the ASTM proximate analysis, still had some residual "volatile matter," running from 6.4 to 9.6 pct.

Elemental composition data for the chars were used to prepare Figure 17-1, in which the percent of the original O, H, N, or S remaining in the char is plotted versus the final temperature. The lines in Figure 17-1 are "eyeball" fits of data summarized by Jack Howard (see Chapter 12, Chemistry of Coal Utilization, Second Supplementary Volume, P. 778) for hydrolysis and pyrolysis reactions at much higher heating rates. The solid squares are data from one experiment at a heating rate of 0.5°C/sec; the open diamonds are the "best" data (i.e., closest to Howard's trends) from the set of five experiments but not necessarily all from the same run. The points to be emphasized are: a) there is a reasonable fit in most cases, which indicates at least that the experiments in the SPR are not out of line with other work; and b) Howard's data points (not shown in the Figure) themselves show considerable scatter and represent heating rates higher by a factor of 2,000, which suggests that we could hardly hope to achieve any better fit.

FIGURE 17-1. Percent of original concentration remaining in char as a function of final pyrolysis temperature; SPR data compared with literature trends for pyrolysis and hydrolysis reactions.

A second series of experiments in the SPR has used Beulah, Indian Head, and Velva lignites, with particle size and moisture content (as-received or freeze-dried) as variables and heating rates held constant. At present not all of the supporting analytical work is complete, so conclusions based on this work are tentative. All of the chars produced contain some residual volatile matter, based on the ASTM proximate analysis, running about 4-8 pct on an maf basis. The differential scanning calorimetry thermograms show that the aliphatic peak, which is prominent in the parent coal, has essentially vanished from the chars. The only aliphatic character evident in the chars is a low-temperature tailing of the aromatic peak.

For the Beulah lignite, comparison of the pyrolysis of freeze-dried coal shows virtually no effect of particle size when -8 and -60 mesh samples are used, the chars having 7.0 and 6.7 pct maf volatile matter, respectively. However, if freeze-dried coal is compared with as-received coal, char from the latter contains more volatile matter, 7.0 versus 5.0 pct (maf).

Further conclusions from this series of experiments will be discussed in the next report, when the analytical data will be in hand.

17.2.3 Large Sample Thermogravimetric Unit

An apparatus has been designed to allow pyrolysis of samples of up to 1 lb of coal at temperatures to 1000°F and pressures to 1000 psi. It will be possible to run experiments over a matrix of variables including pressure, heating rate, particle size, final temperature, and atmosphere composition. The sample container will be suspended from a load cell to obtain weight loss data as a function of time (or temperature). The outlet of the main vessel will be able to accommodate a variety of condensers or traps to collect samples of tars, water, or oils. Provisions will also be available for on-line gas analysis. The internal features of the unit can be changed fairly easy, in order to accommodate sample containers or reaction chambers of various configurations. When complete, this apparatus will be a very versatile unit capable of obtaining thermogravimetric data over a range of sample weights and pressures not normally accessible in laboratory-scale equipment.

The main pressure vessel has been fabricated. Virtually all of the internal parts or accessories that are commercially available have been ordered and are being received. Some non-commercial items have been designed and await fabrication. As the backlog in the machine shop permits, the vessel will be tested for compliance with design specifications and final assembly and check-out will proceed.