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LOW-RANK COAL RESEARCH

Quarterly Technical Progress Report for the Period
April-June 1984

August 1984

Work Performed Under Contract No. FC21-83FE60181

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

By
University of North Dakota
Grand Forks, North Dakota

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Quarterly Technical Progress Report for the
Period April-June 1984

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August 1984

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Prepared For

United States Department of Energy
Morgantown Energy Technology Center
Morgantown, West Virginia

Under Cooperative Agreement No. DE-FC21-83FE60181

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1. HIGHLIGHTS

COAL CONVERSION RESEARCH

Gasification Wastewater Treatment and Reuse

- Following activated sludge (AS) treatment of stripped gas liquor, carbon adsorption was used to remove refractory organics, mainly hydantoin, in preparing makeup for the second cooling tower test. Optimum operating conditions for the granular activated carbon (GAC) columns were determined to be: hydraulic loading, 0.6316 l/sec/m^2 ; mass transfer zone (MTZ), 0.76 m; contact time, 75 minutes; carbon dosage, 9.0 kg/m^3 liquid; and service time, 15.19 hours/MTZ. Removal efficiencies for individual parameters were: TOC, 90%; COD, 90%; phenol, 100%; hydantoin, 95-98%; iron, 66%; copper, 84%; and manganese, 63%. Isotherms and breakthrough curves were determined for the organic species.
- Results from the Phase II cooling tower test showed that aqueous gasifier effluent treated by solvent extraction, steam stripping, AS processing, GAC adsorption, and multimedia filtration was not suitable as feed to a cooling tower operated at 10 cycles of concentration. This water was highly corrosive to carbon steel, caused severe fouling of carbon steel, resulting in large pressure drop increases and decreases in heat transfer coefficients for carbon steel heat exchange tubes. These results indicate that for this water to be used successfully as makeup to a cooling tower, the addition of chemicals for the control of corrosion and the associated fouling will be necessary, or substitution of stainless steel or some other corrosion resistant material for all carbon steel will be required.

Hydrogen Production from Low-Rank Coals

- An equilibrium thermodynamic model has been developed for the purpose of providing guidance in establishing the optimum conditions and system parameters for producing hydrogen from steam gasification of carbon. Efforts were directed to provide the capability to establish carbon conversions as well as the influence of excess steam on the shift reaction. The modifications made now give the model the capability to predict equilibrium gas compositions exiting each of two stages in steam gasification of coal. The gaseous species considered in the model are H_2 , H_2O , CO , CO_2 , and CH_4 .
- The 1-lb thermo reactor is operational and providing data necessary to assess the inherent reactivity of chars produced in-situ by steam gasification as a function of the feed coal. The initial tests were made with Indian Head lignite, reduced to a char under an inert atmosphere during heating from ambient temperature to a reaction temperature of 700°C . Upon reaching 700°C , steam gasification commenced and the gas composition and rate were measured until carbon depletion. Gas composition averaged about 61% H_2 , 37% CO_2 , <2% CO , and <1% CH_4 with excess steam.

Coal-Water Slurry Preparation

- Hot-water drying of Indian Head lignite at 330°C and pressure above the saturated steam pressure yielded a product with a low equilibrium moisture content (11.2%) which did not reabsorb moisture even when stored under water for 90 days. The hot-water-dried product could be concentrated in a pourable slurry at a bone-dry solids loading more than 40% higher than that possible with the raw lignite.
- Construction progress on the hot-water drying process development unit was highlighted by: completion of insulation of process heating units; completion of the product and makeup water storage areas, including tankage; pressure testing of process steam lines; and electrical wiring of the instrument control loops. An overall estimate is that the construction/installation is over 90% complete and shakedown testing is anticipated in September.

Low-Rank Coal Liquefaction

- An analysis using a deuterium-labeled chemical ionization reagent has been developed to aid in the identification of substituted benzenes. Using CH_3OD provides the basis for a method to determine the number of substituted positions on the aromatic ring. Under appropriate Chemical Ionization (CI) conditions the hydrogens attached to the aromatic ring of a substituted benzene undergo exchange with deuterium in the reagent gas. The number of exchanges that occur corresponds to the number of unsubstituted positions in the ring. Thus, in addition to the molecular ion + 2 ($M + 2$) peak which is the ionized species (resulting from the addition of D^+ , not exchange) the number of additional peaks to $M + 2$ is the number of exchangeable protons on the aromatic ring.
- Comparison of product slurry viscosity data obtained from the previously reported long bottoms recycle tests, two with Indian Head (Zap) lignite and one with Wyodak subbituminous coal, illustrated process specific as well as more subtle coal specific effects. Process specificity was demonstrated by the strong beneficial effect of periodic reactor blowdown on product slurry viscosity. In the first run with Indian Head which included reactor blowdown as a last resort to save the test, viscosities (measured at 70°C) as high as 3500 cp were seen. In the second test with Indian Head, with scheduled blowdown after every twelve cycles, the viscosity never surpassed 350 cp. Coal specificity was evident in the third test using Wyodak and scheduled blowdown, in which the viscosity never exceeded 210 cp and averaged around 150 cp.

COAL UTILIZATION RESEARCH

SO_x/NO_x Control

- Pilot scale testing of hydrated lime injection using a pc-fired combustor with a high-temperature baghouse for SO_x control resulted in 80% reduction of SO_x. A Ca/S ratio of 1.67 was used, indicating 48% Ca utilization. Use of an NH₃/SCR system resulted in 70% reduction of NO_x for reactor temperature, NO_x concentration, and NH₃/NO ratio of 735°F, 700 ppm, and 1.0, respectively.
- Testing of calcium-based sorbent injection using a pc-fired combustor indicated an optimum injection temperature of approximately 1900°F. Utilization values of up to 55% were noted at a Ca/S ratio of 1.

Particulate Characterization

- Clear differences in particle morphology were noted between high and low sodium ashes. First, for larger particles in the range of 2 to 20 μm there are surface deposits on the high Na fly ashes which are noticeably absent in low Na ash. Second, for particles in the size range of 0.3 to 1 μm, high-Na ashes consist largely of non-spherical and irregular shapes while the low-Na ashes are predominantly spherical particles. These morphological differences probably contribute to the collection efficiency differences noted between the high and low Na ashes.

Waste Characterization

- Of the 15 pulverized-coal fly ash leachates evaluated during the quarter, none exceeded the RCRA limits for the elements evaluated (As, Ba, Cd, Pb, Cr, and Ni).
- Evaluation of the use of lime to reduce concentrations of leached B (not regulated by RCRA but included in various irrigation water criteria) indicates that this technique will work only if Na and Al are present at adequate levels.
- Preliminary studies of surface area of pulverized coal, AFBC, and fixed-bed gasifier fly ashes indicates that the surface area per unit mass for AFBC and fixed-bed gasifier fly ashes are significantly greater (~8X) than for pc fly ash from the same coal.

Fine Coal Cleaning

- Four coals have been chosen for in-depth fine coal cleaning studies to determine the limits of physical cleaning on western coals. The coals chosen are: Martin Lake, Gulf Coast lignite; Beulah-Zap, North Dakota lignite; Navaho, San Juan Basin subbituminous; and Eagle Butte, Wyoming subbituminous.

Combustion Research and Ash Fouling

- A slagging probe for the UNDERC ash fouling furnace has been completed. The probe will be used to examine ash-metal substrate bonding in the radiant section of a furnace. The device allows for gas velocities in the range encountered in full-scale facilities.
- Surface temperature measurements for 75-106 μm petroleum coke particles have been determined in the bench-scale combustor. Measurements indicate diffusion controlled burning which is consistent with results found in the literature.

Fluidized Bed Combustion

- A sampling probe to remove bed material from the operating pilot scale AFBC at UNDERC has been used successfully. The probe uses nitrogen and water cooling for rapid quench of the samples removed from the system.
- High temperature dilatometry has been used to examine the ash particle-particle bonding properties of AFBC bed material as a function of Na_2O concentration. The temperature at which bonding is initiated has been observed to decrease with increasing Na_2O concentration in the bed.

Coal/Water Slurry Combustion

- Modifications to the ash fouling furnace have been completed to allow combustion of coal/water slurries. A successful combustion test was completed using a commercial coal/water slurry. Future work will focus on combustion of hot-water-dried, low-rank coal/water slurries.

COAL SCIENCE

Ash and Slag Characterization

- The mineralogical composition of several low-rank coal ash slags was studied by scanning electron microscopy/microprobe analysis and by x-ray diffraction. The microprobe is particularly helpful in identifying minerals which are present below the detection limits of x-ray diffraction and in identifying the phases present in solid solution series. The results obtained confirm that the principal role of alkali and alkaline earth cations is to participate in the formation of relatively low-melting complex aluminosilicates, such as melilites. These results help provide a basis, in terms of chemical and mineralogical structures, for empirical observations that ashes with high alkali or alkaline earth content generally produce low-melting, low-viscosity slags and significant slag or ash deposits.

Organic Structure

- A low-angle laser light scattering photometer was procured and installed. The purpose of this instrument is to determine the average molecular weight of coal-derived macromolecules such as humic acids. Polystyrene standards were run to confirm that the instrument was working properly. In the first application of the instrument a humic acid fraction was extracted from Beulah (ND) lignite, methylated and then reduced under mild conditions. This material had an average molecular weight of 14,700. This value is in the range of molecular weights reported in the literature for soil humic acids.

Distribution of Inorganics

- Studies have begun to extend the chemical fractionation technique to separated lithotypes. Chemical fractionation uses sequential leaching to determine the fraction of each inorganic element present in ion-exchangeable form, as acid-soluble minerals such as carbonates or oxides, and as insoluble minerals such as clays. The study of inorganic associations with individual lithotypes should provide a greater understanding of the relationships between the organic substance of the coal and the incorporated inorganic species. Although this work is still in a preliminary stage, results obtained so far suggest that in general the highest relative proportions of acid-soluble elements occur in durain, or attrital coal, and the highest proportions of ion-exchangeable elements (i.e., associated with organic functional groups) occur in fusain, which has been derived from plant components.

Physical Properties and Moisture

- Studies continued on the application of the differential heats of wetting calorimeter to examining the porous structure of low-rank coals. A series of tests was run with Yampa (CO) subbituminous coal at 16, 30, 60, and -60 mesh without observing significant variation in results. These results suggest that the internal pore structure is the predominant contribution to the total surface area of the material, and that (by analogy with the behavior of other, well-characterized samples) the pores are very small. A significant difference in behavior was observed for subbituminous versus lignite samples, in that the heat of wetting was liberated almost instantaneously for lignite but that heat output occurred over several hours for the subbituminous. This suggests a difference in the nature of the pore structure for the two coals.
- The thermal and mechanical friabilities of separated lithotypes were measured. The results are consistent with general concepts of coalification. Specifically, vitrain, which formed in place with little disturbance of the plant structures, has lower thermal and mechanical friability than durain, which is an accumulation of once-unconsolidated materials. Fusain is a result of bog or forest fires during early stages of coalification, and is less subject to thermal degradation than the other two lithotypes.

Supercritical Solvent Extraction

- An issue in supercritical water extraction is whether the water plays any role other than serving as a vehicle to sweep pyrolysis products, which would have formed anyway, out of the extraction vessel. In other words, is supercritical water extraction merely "aqueous pyrolysis"? To test this question two runs were made in which the conditions of supercritical water extraction were duplicated, except that nitrogen was used instead of water. The conversions (calculated as percent of the original material removed) were 27% and 20%, whereas conversions for supercritical water extraction are typically 42-45%. Pyrolysis of the same coal in the Small Pyrolysis Reactor with a comparable temperature profile but under helium at 1 atmosphere produced at 25% conversion. These results suggest that the supercritical water does interact with the coal.

Pyrolysis and Devolatilization

- Tests with Indian Head (ND) lignite in the Small Pyrolysis Reactor indicate that heating rate has a significant effect on the concentrations of water-soluble phenolics in the condensate liquor. An increase in heating rate from 4 to 45°C/min, which roughly represent the extremes which might be encountered in the UNDERC slagging fixed-bed gasifier, results in a 21% decrease in phenol concentration and 35-50% decreases in concentrations of the cresols. On the other hand, methanol formation increases at the higher heating rate. Ethanol, acetone, acetonitrile, and 2-butanone are relatively unaffected.

2. GASIFICATION WASTEWATER TREATMENT AND REUSE

Project Nos.: 7102, 7103

B&R Nos.: AA8540000
AA8545050

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2.1 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 operations at UNDERC are designed to yield scalable 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 reuse in a cooling tower of: 1) solvent-extracted, ammonia-stripped gas liquor (SGL); 2) biotreated and granular activated carbon (GAC) treated SGL; and 3) repeat of 2 with addition of corrosion inhibitors. As soon as representative SGL is available from GPGA, the first test and the second or third will be repeated in the UNDERC cooling tower with GPGA SGL as makeup. Another objective is to test alternative treatments that would be necessary to allow discharge, rather than reuse, of the wastewater.

To accomplish these objectives, the major activities in the gasification wastewater treatment and reuse program during the second year of the Cooperative Agreement are:

1. Phase II cooling tower assessment using SGL treated by single-stage activated sludge (AS) processing followed by granular carbon adsorption (GAC) as makeup.

2. Phase III cooling tower assessment using AS/GAC treated SGL with a corrosion inhibitor as makeup.
3. Phase IV cooling tower assessment using GPGA SGL as makeup.
4. Assessment of alternative treatment methods, including nitrification, powdered activated carbon (PAC) addition to AS and rotating biological contactor treatment.
5. Characterization of the organic contaminants in lignite-derived wastewater, before and after each stage of treatment.
6. Development of models in conjunction with Radian Corp. for inorganic fouling of the cooling tower and (for the first time) the effects of key organics in the cooling tower.

2.2 ACCOMPLISHMENTS

2.2.1 SUMMARY OF OPERATIONS

Two attempts were made to operate the slagging, fixed-bed gasifier but both were terminated by the inability to maintain slag flow. No further attempt was made at gasifier operation. The activated sludge reactor processing of the solvent extracted, ammonia stripped wastewater from previous gasifier tests was continued. Phase II cooling tower testing was completed and Phase III testing was begun during the quarter.

2.2.1.1 Gasification

Two attempts were made at UND-11 operation but were terminated by difficulties in starting and maintaining slag flow. In the first attempt it was speculated that replacement of the broken thermocouple in the 3-ft section dislodged some refractory that eventually settled in the taphole area and caused plugging. In the second attempt slag flow started on schedule but could not be sustained. It was subsequently determined that an air dryer for the compressed air was not operating properly and water had collected in the process control lines. This could have led to erroneous flow readings and contributed to the slag flow problems.

After the second startup attempt, a reassessment was made of the available wastewater on hand for cooling tower studies, and a decision was made not to attempt further gasifier operation. Instead, as time and manpower allowed, mothballing of the gasifier was initiated.

2.2.2 COOLING TOWER TESTING

The cooling tower was started January 25 for Phase II testing. SGL that had been processed through an activated sludge reactor, multimedia filtration, and GAC adsorption was used as feed for this test. The test was scheduled for 50 day's duration; however, due to extreme fouling and corrosion, the test was terminated after 17 days for further evaluation of the program. The cooling tower was restarted March 22 under the original Phase II test plan and a 41 day test was completed. Results from the two tests (referred to as Phase II-a

and Phase II-b) are discussed and compared to data from the Phase I test. Table 2-1 presents the treatment steps used to treat the water used in each of the tests.

TABLE 2-1
UNDERC WASTEWATER TREATMENT STEPS

	Phase I	Phase II
Roughing Filter	Yes	Yes
Solvent Extraction	Yes	Yes
Steam Stripping	Yes	Yes
Activated Sludge	No	Yes
Granular Activated Carbon	No	Yes
Dual Media Filtration	No	Yes
Cooling Tower	Yes	Yes

The cooling tower and associated test equipment were configured and operated in the same manner as in the Phase I test. This equipment is described in detail by Willson et. al. (1). The operating parameters of the cooling tower are given in Table 2-2 with the conditions of the test heat exchangers listed in Table 2-3.

2.2.2.1 Corrosion

Makeup and blowdown streams from the Phase II test have been characterized. These data are presented in Table 2-4 along with similar data from the Phase I test. A comparison of the data shows that the Phase II water is very low in organics, with a makeup TOC level ranging from 30 to 60 mg/l. The TOC level of the makeup for the Phase I test was ~2500 mg/l. Other notable differences between the two tests were in the alkalinity, pH, sulfate, and conductivity levels. The alkalinity in the circulating water was 6 to 10 times lower in the Phase II than in the Phase I test. The pH was approximately 0.5 units lower in the Phase II test, and the sulfate level was 20 to 30 times higher than during the Phase I test due to biological oxidation of the thiocyanate and other sulfur-containing organics. The conductivity of the circulating water used during the Phase II test was approximately 3 times higher than that for the Phase I test. All four of these factors indicate that a higher corrosion rate than that noted in the Phase I test would be expected during the Phase II test. These factors are summarized in Table 2-5.

There are several methods used for predicting the corrosiveness of water from chemical analysis. Several of these have been computed for both the Phase I and Phase II tests and are presented in Table 2-5. A Langelier index of 0 or below and Ryznar index of 6 or above indicate a tendency toward corrosion rather than scaling. Both indices indicate that the Phase II water is more

TABLE 2-2
COOLING TOWER OPERATING PARAMETERS

Parameter	Average Value
Circulation Water Rate	6.5 gpm
Makeup Water Rate	
Treated Gas Liquor	0.205 gpm
Steam Condensate	0.016 gpm
Blowdown Rate (Including Drift)	0.018 gpm
Cycles of Concentration	9.7
Air Rate	1100 scfm
Inlet Air Dry Bulb	70°F
Inlet Water Temperature	120°F
Basin Water Temperature	82°F

TABLE 2-3
HEAT EXCHANGER OPERATING CONDITIONS

	Heat Exchanger 1	Heat Exchanger 2
Tube Type		
Tube 1	304 L SS	Carbon Steel
Tube 2	Carbon Steel	Carbon Steel
Tube 3	316 SS	Carbon Steel
Tube 4	304 L SS	304 L SS
Tube Velocity (fps)		
Tube 1	3	3
Tube 2	3	3
Tube 3	5	5
Tube 4	5	5
Shell-side Water Temp., °F	140	100
Heat Flux, Btu/hr-ft ²	20,000	8,000

TABLE 2-4
ANALYSIS RESULTS FROM THE UNDERC COOLING TOWER

Chemical/Physical Constituent	Ave PH 1 Makeup	Ave PH 1 Blowdown	Ave PH 1 Cycles	Ave PH 2 Makeup	Ave PH 2 Blowdown	Ave PH 2 Cycles
Total Suspended Solids	37	890	24.1	16	50	3.1
Total Volatile SS	24	720	30.0	9	28	3.1
Total Dissolved Solids	3500	30000	8.6	744	6980	9.4
Total Volatile Dis. S.	3100	23000	7.4	484	4688	9.7
TOC	2500	17000	6.8	43	240	5.6
COD	6300	45000	7.1	160	922	5.8
Dissolved Oxygen	0.52	6.4	12.3	--	6	--
Phenol	140	150	1.1	ND	ND	
o-Cresol	7.3	1.1	0.2	ND	ND	
m-,p-Cresols	22	18	0.8	ND	ND	
5,5-Dimethyl Hydantoin	1800	15000	8.3	11	20	1.8
5-Ethyl 5-Methyl Hydan.	460	3900	8.5	5	2	0.4
Methanol	190	57	0.3	ND	ND	
pH	9.1	8	--	8.5	7.5	
Conductivity	2700	8100	8.0	3472	23100	6.7
Alkalinity	1500	2600	1.7	1063	243	0.2
Ammonia	550	1200	2.2	544	1635	3.0
Nitrate	ND	ND		11	130	11.8
Sulfate	19	170	8.9	445	5348	12.0
Chloride	25	220	8.8	29	261	9.0
Total Cyanide	31	280	9.0	12	56	4.7
Thiocyanate	200	1700	8.5	54	140	2.6
Acetate	180	1100	6.1	0	0	
Formate	40	35	0.9	0	0	
Propionate	65	513	7.9	0	0	
Calcium	2	27	11.7	2	32	16.0
Sodium	180	1600	8.9	66	528	8.0
Silicon	4	25	6.4	3	12	4.0
Magnesium	2	17	7.7	1.2	11	11.0
Iron	15	130	8.7	11	42	3.8
Zinc	0.3	8	29.6	0.3	6	20.0

TABLE 2-5
FACTORS INFLUENCING CORROSION

	Phase I	Phase II
Chemical Characteristics		
pH	8	7.5
Alkalinity (mg/l)	2600	240
Conductivity (u MHO/cm)	8100	23,100
Sulfate-Makeup (mg/l)	19	445
Corrosion Indices		
Langelier Saturation Index	1.32	0.44
Ryznar Stability Index	5.36	6.92
Corrosion Index	0.80	230

corrosive than the Phase I water. Neither index indicates an extremely high corrosion potential. The "corrosion index" which is obtained from the chloride plus sulfate content divided by the alkalinity, all expressed in equivalents per million, has been proposed to define the corrosiveness of uninhibited water (2). This comparison indicates that the water from the Phase II test is much more corrosive than the Phase I water, due to lower alkalinity and an increased sulfate content. Although the corrosion index is generally used for comparison purposes, the high values shown here for the Phase II test indicate that the water would be very aggressive to metal surfaces.

Corrosion rates measured during the Phase II test showed that SGL further treated by AS and GAC is unacceptable as feed to a cooling tower without the addition of corrosion inhibitors. As summarized in Table 2-6, corrosion rates of 19 to 65 mpy for carbon steel were measured during the test. These rates are much higher than those observed during the Phase I test (8 to 18 mpy). The effect of the corrosion can be seen in Figure 2-1 which shows two Corrator tips that were corroded during the test. Corrosion rates for stainless steel were less than 0.1 mpy for all locations in the system.

An evaluation of heat exchanger tubes after the test indicated that general corrosion has occurred in the heat exchanger tubes and that the amount of pitting was minimal. Pit depths were generally less than one mil deep. Figure 2-2 shows a picture of the surface of a heat exchanger tube after the Phase II test.

Concrete test cylinders were exposed to the cooling water during the Phase II test. The cylinders were Type V concrete, the same as the concrete used in the GPGA cooling towers. An evaluation of these test specimens after the test showed no visible structural changes in the concrete. Strength analysis also indicated no changes in the strength of the sample tested.

TABLE 2-6

CORROSION RATES FROM PHASE II.b COOLING TOWER TEST

Metallurgy	Location	Temp. (°F)	Velocity (fps)	Corrosion (mpy)
1010 Carbon Steel	Cooling Tower Inlet	120	0.6	62.3
1010 Carbon Steel	HE-2 Outlet	86	1.2	19.6
1010 Carbon Steel	HE-2 Inlet	82	1.2	19.1
1010 Carbon Steel	DDM	82	2.4	18.6
1010 Carbon Steel	Cooling Tower Basin	82	<0.01	21.4
304 SS	Cooling Tower Inlet	120	0.6	0.01
304 SS	Cooling Tower Basin	82	<0.01	0.01
90/10 Copper/Nickel	Cooling Tower Basin	82	<0.01	1.0
Copper	Cooling Tower Basin	82	<0.01	1.4

FIGURE 2-1. Corrator probes used during Phase II-a testing. Middle probe is unused; outer probes in service for 10 days.

FIGURE 2-2. Photomicrograph of carbon steel heat exchange tube cross section after Phase II-a test.

2.2.2.2 Fouling

Immediately after startup of the Phase II test, fouling of the test heat exchangers was noted. Problems with plugging of the small diameter tubing and flow regulators were noted. Pressure drops across the carbon steel tubes began increasing and heat transfer coefficients began decreasing within a few hours of startup. Figure 2-3 shows the heat transfer coefficient and pressure drop for a low velocity carbon steel tube from the low temperature heat exchanger. The trends noted here are common to all carbon steel tubes used during this test, and indicate a high rate of fouling. These trends were verified after the test by determining the actual deposit accumulations during the run. Table 2-7 summarizes these results. Deposit accumulations of up to 47.6 grams/square meter/day were noted on the carbon steel tubes. These rates are approximately double those noted during the Phase I test. Visual observation of the tubes also verified the high fouling rates. Figure 2-4 shows the extent of fouling in a small section of carbon steel tubing removed from the low temperature exchanger. Fouling of the stainless steel tubes was minimal and changes in heat transfer coefficients and pressure drops were small. Only slight accumulation was noted on the stainless steel tube surfaces after the run.

Analysis of the deposits from the heat exchanger tubes indicated that the deposits were mostly inorganic corrosion products, mainly iron oxides. The only identifiable species in the deposits via x-ray diffraction were magnetite (Fe_3O_4) and hematite (Fe_2O_3).

FIGURE 2-3. Summary of data from tube 1, heat exchanger 2. Carbon steel tube with 3 ft/sec flow.

FIGURE 2-4. Photograph of cross section of carbon steel heat exchanger tube with fouling deposits in situ.

TABLE 2-7

SUMMARY OF FOULING ACCUMULATION IN TEST HEAT EXCHANGER TUBES

Tube ID # HF-Tube	Material	Velocity (Ft/Sec)	Exposure Time (Days)	Deposit Wt (g)	Deposit Wt (g/m ²)	Deposit Accumulation Rate (g/m ² /day)
Phase II-a						
1-1	304 L	3	16	1.8	61	3.79
1-2A	CS	3	7	--	--	--
1-2B	CS	3	9	8.2	276	30.70
1-3	304 L	5	16	0.5	17	1.05
1-4	316	5	16	0.4	13	0.84
2-1A	SC	3	7	--	--	--
2-1B	CS	3	9	9.5	320	35.56
2-2A	CS	3	7	5.8	195	27.92
2-2B	CS	3	9	9.6	323	35.94
2-3A	CS	5	7	--	--	--
2-3B	CS	5	9	8.8	296	32.94
2-4	304 L	5	16	0.3	10	0.63
Phase II-b						
1-1	304 L	3	41	0.3	10	0.20
1-2	CS	3	21	29.7	1000	47.62
1-4	304 L	5	41	2.3	77	1.52
2-1A	CS	3	21	24.7	832	29.61
2-1B	CS	3	20	9.4	317	15.84
2-3	CS	5	21	15.7	528	25.16

After the run, deposits were also found on the cooling tower packing. These deposits, along with sludge from the basin and deposits from the coupon rack, were analyzed. A sample of basin water was also evaporated and the residue analyzed for comparative purposes. The results are summarized in Tables 2-8 and 2-9. This analysis shows that there is over 20% carbon in the deposit from the packing and in the basin sludge in comparison to the corrosion products found on the coupons and the residue in the circulating water. The deposits from the packing and the basin sludge were analyzed to determine the nature of this carbonaceous material. Preliminary analysis indicated that the material is organic in nature. Further analysis is in progress to fully characterize these deposits. The presence of these organics in the deposits indicates that there was some coprecipitation of organic and inorganic fractions occurring in the cooling tower.

TABLE 2-8
ANALYSIS OF DEPOSITS FROM COOLING TOWER

	C	H	N	S	O	Ash
Evaporated Basin Water	3.3	3.9	13.7	19.5	21.6	38
Basin Sludge	23.4	3.3	6.5	2.7	15.0	49
Packing Deposits	29.9	4.1	6.1	3.4	15.1	41
Coupon Deposits	4.1	1.5	1.7	1.3	10.5	81

X-ray fluorescence analysis was performed on several of these deposits. This analysis indicates that there is a significant quantity of insoluble iron (iron oxides) in the circulating cooling water. The percentage of iron found in deposits at various locations in the system is much higher than that in the basin water. This indicates that corrosion is occurring in the system, causing the formation of insoluble iron oxides. These oxides are being sloughed off the system piping, and are being deposited at other locations such as the cooling tower packing and the bottom of the cooling tower basin.

Data collected from the Dynamic Deposit Monitors (DDM) also indicated that fouling of the heat transfer surfaces was occurring. Figure 2-5 shows the decrease in the heat transfer coefficient as the run progressed. A total decrease of 23% in the heat transfer coefficient was noted over the 41 days of the test.

TABLE 2-9

ASH ANALYSIS OF DEPOSITS FROM COOLING TOWER

Oxide, %	Evaporated Basin Water	Basin Sludge	Packing Deposits	Coupon Deposits
Na ₂ O	11.5	4.5	2.3	0.0
Al ₂ O ₃	0.6	1.1	1.1	0.2
SiO ₂	1.7	3.2	2.7	1.6
P ₂ O ₅	1.8	8.9	6.8	2.2
SO ₃	57.2	10.3	14.3	4.0
CaO	0.7	2.2	1.9	0.5
K ₂ O	3.5	0.4	0.5	0.0
TiO ₂	0.0	0.2	0.2	0.2
Fe ₂ O ₃	<u>1.0</u>	<u>42.3</u>	<u>46.3</u>	<u>91.2</u>
TOTAL	78.0	73.1	76.1	100.0

FIGURE 2-5. Dynamic deposit monitors.

2.2.2.3 Air Monitoring

Air samples were collected in and near the pilot-scale cooling tower at UNDERC to investigate the emission of organic compounds from the treated wastewater during the Phase II test. To collect volatile species in the water-saturated cooling tower exhaust, air samples were drawn through two types of capillary tube sorbent traps, Tenax-GC and charcoal. The samples collected were analyzed by thermally desorbing the sample species, cryogenically trapping them on a chromatographic column, and analyzing by GC/MS.

Results from this air sampling campaign indicated that the wastewater used during the Phase II test contributed no detectable organic contamination to the atmosphere. The only quantifiable compound emitted from the cooling tower during the test was ammonia. Material balances indicated that approximately 65% of the ammonia in the influent was being stripped into the atmosphere.

2.2.2.4 Biological

Throughout the Phase II test, total heterotrophic aerobic counts were performed on the makeup and basin water. The results are summarized in Table 2-10. There was no evidence of biomass cycle up in the cooling tower as the counts in the circulating water were approximately equal to those in the makeup water. This indicates that although there was a substantial level of biological activity entering the tower in the makeup, these bacteria did not

TABLE 2-10
TOTAL HETEROTROPHIC AEROBIC COUNTS

Date	Bacterial Counts/ml	
	Makeup	Blowdown
03-26-84	7.0×10^6	5.6×10^6
03-29-84	7.5×10^6	4.5×10^6
04-02-84	9.7×10^6	5.9×10^6
04-05-84	4.3×10^6	4.4×10^6
04-09-84	1.4×10^7	8.9×10^6
04-12-84	2.2×10^7	8.2×10^6
04-16-84	1.0×10^7	1.0×10^7
04-19-84	5.0×10^6	7.5×10^6

thrive in the cooling tower circulation water. Oxygen uptakes for both the makeup and recirculating water during the Phase II test were zero, also indicating that there was very little biological activity occurring during the test.

Identification of the microorganisms in the tower is in progress. Preliminary identifications are negative for sulfate reducers and oxidizers, and positive for nitrifiers.

2.2.2.5 Conclusions

Results from the Phase II test showed that aqueous gasifier effluent treated by solvent extraction, steam stripping, AS processing, GAC adsorption, and multimedia filtration was not suitable as feed to a cooling tower operated at 10 cycles of concentration. This water was highly corrosive to carbon steel, with corrosion rates of 19 to 65 mpy measured during this test. This water caused severe fouling of carbon steel, resulting in large pressure drop increases and decreases in heat transfer coefficients for carbon steel heat exchanger tubes. These results indicate that for this water to be used successfully as makeup to a cooling tower, the addition of chemicals for the control of corrosion and the associated fouling will be necessary, or substitution of stainless steel or some other corrosion resistant material for all carbon steel will be required.

This water did not appear to support any substantial level of biological activity. Exhaust air from the tower was free from organics, but a substantial amount of ammonia was stripped from in the tower (65% of the influent quantities).

2.3 GRANULAR ACTIVATED CARBON ADSORPTION

2.3.1 ISOTHERM TESTS

Adsorption isotherm studies have been completed for the biologically treated and dual-media filtered SGL to determine the feasibility of using GAC to adsorb nonbiodegradable substances, such as hydantoins. A batch kinetic experiment was performed to determine the equilibrium time. As shown in Table 2-11, the required contact time to reach an equilibrium condition would be less than 24 hours for the adsorption of either 5,5-dimethyl hydantoin or 5-methyl, 5-ethyl hydantoin. However, to ensure sufficient time for the system to reach equilibrium, 24 hours was chosen as the contact time for this isotherm test. The experimental conditions of the isotherm study were:

Carbon	Calgon Filtrasorb 400 (F-400)
Sample Volume	100 ml
Temperature	Ambient (23°C)
Contact Time	24 hours
pH	7.0

TABLE 2-11

ADSORPTION OF PURE HYDANTOINS (F-400 - ACTIVATED CARBON)

Time (hr)	5,5-Dimethyl Hydantoin (mg/l)	5-Methyl, 5-Ethyl Hydantoin (mg/l)
0	750	200
24	7	5
48	20	<5
72	20	<5
96	8	<5
120	5	<5

The isotherm data for the adsorption of Total Organic Carbon (TOC), 5,5-dimethyl hydantoin, and 5-methyl, 5-ethyl hydantoin are listed in Table 2-12, and the isotherm plots are shown in Figures 2-6 through 2-8. From the isotherm plots, it can be seen that the adsorption of TOC follows the Freundlich isotherm, the exponential equation, while those of the two hydantoins appear to have a maximum uptake. The theoretical carbon requirement per 1,000 gal of wastewater treated to reach different TOC removal efficiencies is listed in Table 2-13. However, in the column system the carbon dosage will be greater than this, since the carbon removed from the system is not saturated.

TABLE 2-12

ADSORPTION ISOTHERM DATA OF FILTERED CLARIFIER EFFLUENT
WITH F-400 ACTIVATED CARBON

Dosage (gram)	TOC (mg/l)	5,5-Dimethyl Hydantoin (mg/l)	5-Methyl, 5-Ethyl Hydantoin (mg/l)
0.0	870	700	290
0.10	740	--	--
0.20	620	640	240
0.35	500	580	190
0.50	470	470	120
1.00	240	290	40
2.50	90	70	10
5.00	60	10	<5

FIGURE 2-6. Adsorption isotherm, total organic carbon.

FIGURE 2-7. Adsorption isotherm, 5,5-dimethyl hydantoin.

FIGURE 2-8. Adsorption isotherm, 5-methyl, 5-ethyl hydantoin.

TABLE 2-13
THEORETICAL CARBON DOSAGE (F-400 ACTIVATED CARBON)

	1b Carbon/1,000 gal liquid
100% Removal of TOC at 870 mg/l	48.40
90% Removal of TOC at 870 mg/l	20.38

2.4 GRANULAR ACTIVATED CARBON SYSTEM PERFORMANCE

2.4.1 PROCESS DESCRIPTION

Overflow from the clarifier was gravity fed into a 30-gallon sump. This liquor was then pumped into a 500-gallon holding tank until there was sufficient volume to run the filtration and the adsorption systems efficiently. The filtration system consisted of two dual-media filters, plexiglass columns, 5 inches in diameter by 6 feet in height. These filters were designed as two independent parallel systems with valving to allow backflushing of one system while the other remained on line. The adsorption system consisted of six GAC columns, 8 inches in diameter by 6 feet in height, mounted vertically and connected in series, as shown in Figure 2-9. Each column had a sampling valve at its outlet and backwash capability. The dual-media filter packing consisted of 0.5 feet of pea gravel, 0.5 feet of garnet, 9 inches of 30-40 U.S. mesh silica sand, and 22 inches of 4-14 U.S. mesh anthracite. The activated carbon columns were filled with Calgon Filtrasorb 400 granular activated carbon.

The pilot system operating parameters used (per column) were those recommended by Calgon Corporation for F-400 activated carbon, as follows:

Contact Time	30 minutes
Carbon Bed Depth	4 feet
Hydraulic Loading	1.0 gpm/sq ft
Carbon Dosage (100% Removal of COD at 1320 ppm)	70 lb/1,000 gal

2.4.2 MONITORING AND SAMPLING/ANALYSIS

Flow rates of the activated carbon column effluent were measured hourly and pressure drops across each column every other hour.

TOC analysis of the effluents from the dual-media filter and from each column were performed as required to determine breakthrough conditions. Complete physical and chemical analysis of activated carbon column system effluent were performed twice a week.

FIGURE 2-9. GAC adsorption system.

2.4.3 MASS BALANCE/REMOVAL OF KEY COMPONENTS

The mass balance around the GAC bed is as follows:

$$\text{Mass-Influent} - \text{Mass-Effluent} = \text{Mass-Adsorbed}$$

The percentage removal of the substances is calculated by

$$\% \text{ Removal} = \frac{\text{Influent} - \text{Effluent}}{\text{Influent}} \times 100$$

The mean wastewater characteristics for the GAC system operated during the period of 08/30/83 through 12/12/83 are listed in Table 2-14. Removal of 90% for both TOC and COD (Chemical Oxygen Demand), 99% for 5,5-dimethyl hydantoin, and 97% for 5-methyl, 5-ethyl hydantoin were obtained.

The relatively low removal of BOD (Biological Oxygen Demand), 46%, may be due to the fact that most biodegradable organic compounds were removed in the activated sludge system. The remaining BOD would then be largely due to "inorganic" compounds, such as thiocyanate.

The removals of most inorganic compounds, as shown in Table 2-14, were not significant. The exceptions were 31% removal of cyanide, 32% of phosphate, and 96% of nitrate.

Data for nineteen trace elements were obtained during the period of 03/20/84 through 03/26/84. Significant concentration decreases through the filter and the carbon columns were noted only for Fe, Cu, Mn, and Zn. The removals of these four elements by the dual-media filter were 19%, 72%, 56%, and 96%, respectively. The removal efficiencies by activated carbon are listed in Table 2-14.

2.4.4 PRESSURE DROP VERSUS TIME

The pressure variation for the columns during the processing period was not significant. Table 2-15 presents a typical record of pressure readings in each column as a function of time. There is little pressure difference after a service time of 132 hours, which is indicative of low solid loadings to the carbon columns.

2.5 BREAKTHROUGH DATA

Complete sets of breakthrough data were obtained for the period of 03/20/84 - 03/26/84. Breakthrough curves for TOC, 5,5-dimethyl hydantoin, and 5-methyl, 5-ethyl hydantoin with breakpoint values of 100 mg/l, 85 mg/l, and 30 mg/l, respectively, are presented in Figure 2-10 through 2-12. In these figures, TK represents dual-media filter, and C1 - C6 represents the effluent from the six carbon columns.

The column test flow rate was controlled at 0.3250 gallons per minute, and the carbon bed depth of the six columns were 4.54 ft, 4.50 ft, 4.54 ft, 4.54 ft, 4.33 ft, and 4.5 ft. From each breakthrough curve, the mass transfer zone (MTZ) and the operating conditions, as shown in Table 2-16, were obtained. Contact time is defined as the time required, at a given flow rate, to

TABLE 2-14
REMOVAL EFFICIENCY OF GAC ADSORPTION SYSTEM

Analysis	Influent (mg/l)	Effluent (mg/l)	Removal, %
Oxygen Demand:			
COD	2586.0	263.0	90.0
BOD	103.0	55.0	46.0
Organic Compounds:			
TOC	1047.0	108.0	90.0
Phenol	2.3	0.0	100.0
Cresols	0.5	0.0	100.0
Acetone	3.6	0.0	100.0
Methanol	2.8	0.0	100.0
5,5-Dimethyl Hydantoin	758.0	9.0	99.0
5-Methyl, 5-Ethyl Hydantoin	197.0	5.0	97.0
Inorganic Compounds:			
Alkalinity	1456.0	1351.0	7.0
Ammonia	637.0	580.0	9.0
Cyanide	23.0	16.0	31.0
Thiocyanate	64.0	57.0	10.0
Phosphate	19.0	13.0	32.0
Nitrate	4.0	0.1	96.0
Sulfate	428.0	450.0	--
Trace Elements:			
Iron	7.6	2.8	63.0
Copper	0.046	0.008	82.0
Manganese	0.044	0.014	67.0
Zinc	0.182	0.095	48.0

TABLE 2-15
PRESSURE DROP VERSUS SERVICE TIME

Service Time (hour)	PLC1] (psi)	PLC2] (psi)	PLC3] (psi)	PLC4] (psi)	PLC5] (psi)	PLC6] (psi)
0	4.0	2.0	1.0	0	0	0
12	4.0	2.0	1.0	0	0	0
24	4.0	2.0	1.0	0	0	0
36	4.0	2.0	1.0	0	0	0
48	4.0	2.0	1.0	0	0	0
60	4.0	2.4	1.2	0	0	0
72	4.0	2.2	1.1	0	0	0
84	4.0	2.2	1.0	0	0	0
96	4.0	2.2	1.0	0	0	0
108	4.0	2.4	1.1	0	0	0
120	4.0	2.5	1.2	0	0	0
132	4.5	3.3	1.8	0	0	0

Where C1 - C6 equal the column number.

displace a volume equal to the empty bed volume in the column. Service time is defined as the time a carbon column could remain in service before the effluent reaches the breakthrough point. The amount of water treated is obtained by multiplying flow rate by the service time. Carbon dosage is defined as the amount of carbon needed for every 1,000 gallons of water treated. A bed expansion factor of 10% due to backwash, and a carbon density of 28 lb/cu ft have been reported by Calgon. Operation curves based on the data listed in Table 2-16 are presented in Figures 2-13 and 2-14. From these curves the optimum contact time and carbon dosage were found, as shown in Table 2-17. The results obtained for TOC and for 5,5-dimethyl hydantoin are surprisingly similar, given the dissimilarity of their isotherm plots.

The optimum operating conditions obtained from this column test are listed in Table 2-18. Based on these data one could design an optimized GAC column system for the treatment of biotreated SGL.

FIGURE 2-10. Breakthrough curve, 5,5-dimethyl hydantoin.

5-METHYL, 5-ETHYL HYDANTOIN
(MG/L)

LEGEND: COLUMN

 + + + C1
 △ △ △ C5

 × × × C2
 ⊠ ⊠ ⊠ C6

 □ □ □ C3
 ◇ ◇ ◇ DF

 ○ ○ ○ C4
 ⊕ ⊕ ⊕ TK

FIGURE 2-11. Breakthrough curve, 5-methyl, 5-ethyl hydantoin.

FIGURE 2-12. Breakthrough curve, total organic carbon.

TABLE 2-16
OPERATING CONDITIONS

	C1	C2	C3	C4	C5	C6
Contact Time (min)	36.5	72.6	109.1	145.6	180.4	216.6
Total Organic Carbon:						
Service Time (hr)	19.2	55.0	85.5	119.0	--	--
Water Treated (gal)	374.4	1072.5	1667.3	2320.5	--	--
Carbon Dosage (1b C/1,000 gal)	107.7	74.9	72.7	69.4	--	--
5-5-Dimethyl Hydantoin:						
Service Time (hr)	19.5	54.5	87.5	120.5	--	--
Water Treated (gal)	380.3	1062.8	1706.3	2349.8	--	--
Carbon Dosage (1b C/1,000 gal)	106.1	75.6	70.7	67.7	--	--
5-Dimethyl, 5-Ethyl Hydantoin:						
Service Time (hr)	33.5	101.0	--	--	--	--
Water Treated (gal)	653.3	1969.5	--	--	--	--
Carbon Dosage (1b C/1,000 gal)	61.8	40.8	--	--	--	--

TABLE 2-17
OPTIMIZED CONTACT TIME AND CARBON DOSAGE

	TOC	5,5-Dimethyl Hydantoin
Contact Time (min)	75	73.5
Carbon Dosage (1b C/1,000 gal)	75	74.3

FIGURE 2-13. Operating curve, total organic carbon.

FIGURE 2-14. Operating curve, 5,5-dimethyl hydantoin.

TABLE 2-18

OPTIMIZED OPERATION CONDITIONS

Hydraulic Loading (gpm/sq ft)	0.93
Mass Transfer Zone (ft)	2.5
Contact Time (min)	75.0
Carbon Dosage (lb C/1,000 gal)	75.0
Service Time (hr/MTZ)	15.2

3. HYDROGEN PRODUCTION FROM LOW-RANK COALS

Project No.: 7108

B&R No.: AA8545050

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Prepared by: R.C. Ellman, Senior Research Associate

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3.1 GOALS AND OBJECTIVES

The goal of the Hydrogen Production project is to establish the feasibility of utilizing low-rank coal gasification to produce hydrogen. Catalysts will be used to supplement the inherent reactivity of these coals to achieve satisfactory gasification rates at temperature and pressure conditions which maximize hydrogen production. An additional goal of the project is to expand the data base on the contributions of inherent mineral matter and added catalysts to gasification of low-rank coals. Initial test work will be performed in a large TGA-type apparatus designed to operate at elevated pressure and temperature.

3.2 ACCOMPLISHMENTS

3.2.1 LITERATURE SURVEY

Survey of the literature relating to catalytic steam gasification of coal is a continuing effort by which project direction can be facilitated and candidate catalysts for testing are selected. Three areas of particular interest are: 1) the catalytic enhancement of the water-gas shift reaction; 2) the catalytic enhancement of the carbon-steam reaction; and 3) the reported process considerations directed to coal gasification in which a major product is hydrogen.

A bibliography of 155 references pertaining to the catalysis of the water-gas shift reaction has been completed. This summary was organized according to heterogeneous and homogeneous catalysis and includes types of catalysts, kinetic and structural studies, photocatalytic systems, and catalyst deactivation studies.

A total of 128 references on the catalytic gasification of coal, coal char, and model carbons such as graphite and activated carbon, have been reviewed. These studies include gasification in hydrogen, carbon dioxide, and water vapor atmospheres with indigenous mineral matter, alkali, alkaline earth, and transition metals and their salts. This bibliography is in the final stages of completion.

A particular objective is to identify a catalyst or type of catalyst which may be effective in both the carbon conversion reaction and in the associated water-gas shift reaction. There is evidence that H_2S , which is produced in

gasification of coal, has a catalytic effect on the shift reaction. In coal or char gasification, the alkaline metal salts display a greater activity than alkaline earths toward steam and carbon dioxide gasification of coal. The carbonates are the most effective of these. Pretreatment, such as by oxygen, which increases the number of acid sites, improves catalytic gasification.

A variety of coal and carbon sources were tested in the referenced studies. Low-rank coals, whether tested with their natural mineral matter or in the demineralized form, demonstrate reactivities that are many times greater than other coals. In addition, the same coal may exhibit different reactivities, depending upon pyrolysis conditions.

In a commercial process, use of a catalyst has limitations of cost effectiveness, which includes considerations such as technique and method of application, its recovery for further use, and its amenability to reactivation. Although potassium carbonate is indicated to be effective, calcium carbonate is less expensive. The naturally occurring alkaline constituents of low-rank coal ash suggest also that recycled ash is a low-cost, disposable catalyst that must be considered.

3.2.2 TUBING BOMB TESTS--CATALYZED WATER-GAS SHIFT REACTION

Results of a series of tubing bomb tests were reported in the previous quarterly report. In these tests, the effects of temperature and excess steam on the water-gas shift reaction were compared without and in the presence of a commercial high-temperature catalyst and H_2S . It was indicated that equilibrium was not reached and that both the commercial catalyst and H_2S produced significantly higher and comparable conversion compared to the uncatalyzed reaction. In addition, the temperature increase on conversion did not produce the reduction in conversion as expected. These results did not therefore conform to thermodynamic predictions. The procedure and analytical techniques were then subjected to critical evaluation to establish the validity of the results. It was eventually established that a good possibility exists for error to be introduced in the gas component analysis procedure due to contamination of the gas samples with air. As a result, these tests will have to be repeated to confirm or correct the previous data. These tests have not as yet been performed due to higher priority use of required equipment.

3.2.3 COMPUTER PROGRAM STUDIES

The equilibrium modeling program is a progressive developmental effort for the purpose of providing guidance to establishing the optimum conditions and system parameters for producing hydrogen. Efforts were directed to provide the capability to establish carbon conversions as well as the influence of excess steam on the shift reaction. The modifications made now give the model the capability to predict equilibrium gas compositions exiting each of two stages in steam gasification of coal. The gaseous species considered in the model are H_2 , H_2O , CO , CO_2 , and CH_4 .

The first stage is the steam-gasification of coal in which solid carbon contacts steam at a specific molar steam/carbon ratio at a specified temperature and pressure. The gas composition in equilibrium at those conditions is computed. The reactions involved are:

Carbon conversion is also computed in this calculation. The approach to complete conversion of the feed carbon indicates the maximum steam/carbon ratio at which the existing gas stream composition is in equilibrium with the solid phase.

The second stage of the model involves the gaseous products produced in the first stage. It is an entirely gas phase reaction sequence as follows:

In the second stage, the effect of excess steam is determined over and above that needed to convert the carbon. The production of hydrogen by steam is then calculated. The effect of excess steam over a range of 500° to 700°C at atmospheric pressure is illustrated in Figure 3-1. The fraction of hydrogen produced (on a CO₂- and H₂O-free basis) is higher for greater H₂O/C ratios.

At H₂O/C ratios of slightly less than 2.0, carbon conversion is complete as indicated in data plotted in Figure 3-2. Below that ratio, gas composition is constant and the gas composition is independent of excess steam. When the ratio exceeds the point where all carbon is converted, hydrogen concentration increases and the CO and CH₄ fractions decrease.

Figure 3-3 illustrates the effect of temperature on the CO₂-H₂O-free gas composition at a steam/carbon ratio of 3.0. The hydrogen fraction passes through a maximum at approximately 600°C, but does not vary appreciably within the temperature range shown. The quantities of carbon monoxide and methane, however, are particularly sensitive to temperature. Without significantly affecting the fraction of hydrogen in the equilibrium product, the CO concentration can vary from 10% to 20% on a CO₂-H₂O-free basis while, at the same time, the CH₄ fraction decreases from 10% down to less than 1%.

A comprehensive data set has been compiled for the steam/carbon system over a wide range of temperatures and steam/carbon ratios at atmospheric pressure. Two more program runs will be performed to obtain data over the same temperature and ratio ranges at 25 and at 50 psia. These data can be used for comparative purposes; however, from previous work it has been shown that optimum hydrogen production is obtained at lower pressure.

FIGURE 3-1. Hydrogen production comparison at atmospheric pressure (CO₂-H₂O free).

FIGURE 3-2. Equilibrium gas composition as a function of steam/carbon ratio.

FIGURE 3-3. Product gas composition at $H_2O/C = 3.0$ at atmospheric pressure (CO_2-H_2O free).

Future work will include the addition of enthalpy balances around the gasification reactor. In the first step, the heat balance data will be used to compute the quantity of steam superheat necessary to carry out the reactions. Secondly, the heat balances will be used in conjunction with the addition of a combustion reaction to the system. In this manner the amount of oxygen that would have to be supplied to the system to maintain the reaction temperature can be computed.

3.2.4 TEST APPARATUS

The large sample (1 pound) reactor system was operated successfully in shakedown tests performed for the purpose of establishing the capabilities and limitations of the system. Initially, char (recovered from the slagging gasifier at its shutdown) was used as initial feedstock to eliminate tar and oil production and collection problems. Development of operating procedures and techniques progressed to the use of as-received lignite through pyrolysis and steam gasification in the last test performed in this reporting period.

The continuous weighing feature, consisting of an internal load cell, could not be modified, either by operational changes or hardware, to produce acceptable performance. As a result, an alternate method of determining gasification rate by gas production rate is being utilized. Incremental gas

production for each 10-minute interval is used to establish gas production rate. Gas samples are collected periodically during the course of the test to establish composition at a specific set of conditions.

During the pyrolysis stage, i.e., during heat-up of the lignite to gasification temperature, nitrogen is used as sweep gas. All vapors produced are condensed and collected for material balance and analysis. When the fuel bed reaches the desired reaction temperature, the nitrogen is replaced by steam and gasification begins. The gas produced is metered after excess steam and other condensable vapors are removed, sampled, and vented.

The first five tests were performed on lignite char. Gasification proceeded at 675°C in the first test (CG-1) and 700°C in the second (CG-2). In the third test, an air leak into the system during preheat permitted oxidation of the char. One observed effect in CG-3 was a significant reduction in the rate of gasification in the gasification period. The gas production rate during test CG-4 is plotted versus elapsed time in Figure 3-4. After five hours at 700°C, the bed temperature increase was followed by an increase in gas production. The gas production data for CG-5 was found to be invalid due to air leakage into the product gas line.

The gas compositions on a nitrogen- and oxygen-free basis for the limited samples collected during the five tests performed on char are given in Table 3-1. Of significance is the high H_2 content of the gas, and the low CH_4 and CO contents.

FIGURE 3-4. Product gas rate during CG-4.

TABLE 3-1

PRODUCT GAS ANALYSES FROM CATALYTIC GASIFICATION OPERATION
(Mole Percent)

Run Number Operating Temp., °C	CG-1 675	CG-2 700	CG-3 700	CG-4 700	CG-5 675	CG-7 850
Component ¹						
H ₂	62.4	61.0	61.5	61.7	62.5	62.3
CO ₂	33.9	35.8	37.4	37.1	35.8	30.5
H ₂ S	0.3	0.1	0.4	0.2	0.0	0.0
CH ₄	0.0	0.0	0.0	0.0	0.0	0.2
CO	3.4	3.1	0.7	1.0	1.7	7.0

¹All analyses calculated to nitrogen- and oxygen-free basis.

Test CG-6 was for the purpose of establishing the capabilities of the system during pyrolysis. Liquid products produced in pyrolysis were collected for analysis. In test CG-7, Indian Head lignite was pyrolyzed in nitrogen, and steam gasification proceeded to carbon depletion. Gasification was carried out at 675°C for 2.3 hours, followed by a 1.7-hour period at 850°C. Product gas flow rates are plotted versus elapsed time of steam gasification for test CG-7 in Figure 3-5. Again the increased gas production rate due to temperature increase is significant. Gas analysis for Run CG-7 is given also in Table 3-1 at the higher temperature. Compared to gas compositions from other tests, CO₂ is lower, CO higher, and the H₂ is constant, as expected at the higher reaction temperature.

Data reduction methods are being applied to observed values with the objective of smoothing data points and evaluating test results. An objective is to develop a standardized test procedure by which the rate of gasification can be compared.

Efforts are in progress to improve temperature control of the fuel bed and surmount the other vagaries of the system. Progressively, deficiencies have been and will be corrected.

FIGURE 3-5. Product gas rate during Run CG-7.

4. COAL-WATER SLURRY PREPARATION

Project No.: 7105

B&R No.: AA0520000
AA2530100
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 to be 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 is 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 reabsorbs only a minimum amount of water. Further, evidence exists that this process will reduce sodium, 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 from the coal in drying may be used for slurrying the solids, resulting in reduced surface or groundwater usage 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: 1) perform autoclave tests on several different coals to expand the low-rank coal hot-water drying data base, 2) investigate, to the extent permitted by the current funding, alternate methods of slurry concentration, such as hydroclones, centrifugal filters, etc., with the end objective to incorporate a plausible system into the hot-water coal drying pilot plant, 3) investigate the effects of fine coal cleaning on the rheology and stability of hot-water-dried coal-water slurry, and 4) operate the hot-water coal drying process development unit (PDU) to demonstrate continuous operation and to identify and address process-related problems as they become apparent. The unit will also be operated to produce suitable slurries for direct firing in coordination with the coal slurry combustion program.

Near-term objectives of the project for the period April through June 1984 were:

1. Continue construction of the hot-water coal drying PDU.
2. Continue pilot plant instrumentation.
3. Begin shakedown and pressure testing of the PDU.
4. Modify the liquefaction continuous process unit (CPU) for hot-water coal drying to produce 200 pounds of dried Wyoming subbituminous coal for shipment to Brigham Young University.
5. Produce 200 pounds of hot-water-dried slurry with Indian Head lignite using the modified CPU for laboratory studies with vendors of slurry concentrating devices.
6. Perform batch autoclave tests to study the effects of residence time in hot-water drying and determine the effects of residence time on slurry rheology.
7. Continue moisture reabsorption and aging studies for hot-water-dried coals stored in air.
8. Continue rheological studies on raw and dried Indian Head lignite as a function of particle size distribution, solids loading, temperature, and residence time.
9. Assemble a student task force and begin the preliminary economic evaluation study on the hot-water/coal drying process.

4.2 ACCOMPLISHMENTS

4.2.1 HOT-WATER/COAL DRYING PROCESS DEVELOPMENT UNIT

Construction of the hot-water/coal drying process development unit (HWD-PDU) was continued during the quarter. Achievements included installation and insulation of the 14 electrical resistance wire jacket heaters for process equipment heating and completion of the product slurry storage tank

mezzanine. The connection of 277-volt electrical service to the heaters on the coal drying reactor was also completed. The 3000-gallon slurry storage tank was received in May and was installed on the tank mezzanine floor. Also installed on the tank mezzanine floor was the 600-gallon makeup water tank. A photograph of both tanks is shown in Figure 4-1. All of the process and steam piping has been completed. Testing and insulating of process steam lines was initiated during the quarter and is continuing along with the piece-by-piece testing of process equipment. Work was continued on both the electrical and pneumatic instrument control loops and with connecting 115-volt power to the instrument panel.

FIGURE 4-1. Photograph of 3000-gallon product slurry storage tank and 600-gallon makeup water tank.

An overall estimate would place pilot plant construction at about 90% to 95% complete; however, a good deal of insulating remains to be done after the unit has been pressure tested. Also, the three repeat cycle timers, which are required for completion of the valve sequencers used to control the main slurry pressure letdown station and the lockhoppers below the slurry flash concentrators, have not yet been received from the vendor.

4.2.2 CONTINUOUS HOT-WATER/COAL DRYING STUDIES

The liquefaction CPU was modified and the process piping reconfigured to permit continuous hot-water coal drying similar to previous CPU testing (see Quarterly Technical Progress Report - January to March 1984). The CPU was modified so that approximately 200 pounds of finely ground Wyodak subbituminous coal (mass mean diameter = 45 μ m) could be hot-water dried and the resultant coal-water slurry shipped to Brigham Young University (BYU) for concentration and for use in atomization and combustion studies. Also, the CPU was used to hot-water dry approximately 100 pounds of Indian Head lignite (mass mean diameter = 48 μ m) to produce slurry for use in the laboratory

concentration studies and for shipment to vendors of slurry concentrating devices. The CPU was operated day and night for a total of 72 hours, during which time approximately 300 pounds of coal were hot-water dried. The test conditions were 300° and 330°C for the subbituminous coal and 330°C for the lignite, with operating pressure set 100-200 psig higher than the saturated steam pressure at each temperature. Actual operating conditions are summarized in Table 4-1 for both coals tested. The feed slurry in all tests consisted of 50 wt % "as-received" coal and 50 wt % deionized water. The resultant hot-water-dried subbituminous coal slurries were not stable and exhibited rapid settling in the product receiver, but settled solids were easily resuspended upon mechanical mixing. The resultant hot-water-dried lignite slurry was stable towards settling, similar to previous hot-water-dried lignite slurry produced in the CPU, but was dilute at only about 35 wt % bone-dry solids. The slurries produced for the BYU studies were shipped as dilute slurries (35 wt % bone-dry solids) for concentration by BYU personnel. The lignite slurry produced for the concentration studies will also be shipped to vendors as a dilute slurry.

TABLE 4-1

AVERAGE OPERATING CONDITIONS FOR CONTINUOUS HOT-WATER DRYING
OF WYODAK SUBBITUMINOUS COAL AND INDIAN HEAD LIGNITE

Run Period	Coal Type	Mass Mean Diameter, μm of Feed Coal	Drying Temp., $^{\circ}\text{C}$	Drying Press., psig
1	Subbituminous	45	295	1310
2	Subbituminous	45	327	1960
3	Lignite	48	324	1880

4.2.3 HOT-CHARGE AUTOCLAVE HOT-WATER DRYING TESTS

Detailed component-by-component material balances were completed for the six hot-charge, hot-water drying autoclave tests made previously on two Indian Head lignite samples having different particle size distributions and different mass mean diameters (48 μm versus 225 μm) (see Quarterly Technical Progress Report - January to March 1984). A summary of the results is shown in Table 4-2. The net yields shown in Table 4-2 were obtained from the adjusted material balances and are expressed as a weight percent of the moisture and ash-free (maf) coal originally used in the test. The adjusted material balances were determined by calculating the liquid and gas yield by difference and by forcing the carbon to balance by calculating the moisture content of the HWD coal filter cake. This concentrated all material balance errors into the yield of product gases and liquids where the most uncertainties in measurement lie. The results show increased decarboxylation,

TABLE 4-2

SUMMARY OF MATERIAL BALANCE RESULTS FOR
HOT-CHARGE HOT-WATER DRYING AUTOCLAVE TESTS

Coal:	IH0883	IH0883	IH0883	IH0883	IH0883	IH0883
Mass Mean Diameter, μm	48	48	48	225	225	225
Temp., $^{\circ}\text{C}$	275	300	335	279	307	326
Press., psig	900	1400	2290	1000	1475	1850
<hr/>						
Net Yields, wt % maf Coal fed						
H ₂	0.00	0.01	0.02	0.00	0.01	0.01
CO + CO ₂ + H ₂ O	2.91	7.75	15.38	2.58	6.97	15.63
C ₁ - C ₄	0.02	0.17	0.22	0.00	0.12	0.16
H ₂ S	0.00	0.13	0.15	0.00	0.20	0.07
NH ₃	0.01	0.01	0.08	0.00	0.04	0.01
Phenol	0.00	0.00	0.03	0.00	0.01	0.03
Cresols	0.00	0.00	0.00	0.00	0.01	0.00
Methanol	0.02	0.07	0.27	0.05	0.14	0.28
Acetone	0.00	0.00	0.03	0.00	0.01	0.02
MEK	0.00	0.00	0.00	0.00	0.00	0.00
Dried maf Coal	99.38	94.60	86.99	100.42	94.76	88.07
HHV Btu/lb dry coal	10,500	10,700	11,000	10,500	10,600	11,000
Ash Loss as Wt % of Starting Ash	12.7	14.9	17.2	16.5	12.2	23.3
Equil. Moist. of Dried Coal, Wt %	18.4	14.6	11.2	19.1	15.2	12.1

IH0883 Indian Head lignite procured in August 1983.

dehydration, and pyrolysis with increasing hot-water drying temperature for both particle size distributions.

Figure 4-2 shows the net yield of carbon oxides and water versus hot-water drying temperature. A linear increase in CO₂ + H₂O yield was observed as the HWD temperature increased. Increases ranged from 2.9 wt % of the maf coal to 15.4 wt % of the dried maf coal for the 48 μm MMD sample and from 2.6 wt % of the maf coal to 15.6 wt % of the maf coal for the 225 μm MMD sample. The net yield of dried maf coal versus hot-water drying temperature is shown in Figure 4-3. The net yield of residual maf coal decreased as the hot-water drying temperature increased going from about 99 wt % for HWD at 270 $^{\circ}\text{C}$ to about 87 wt % for HWD at 330 $^{\circ}\text{C}$. Particle size distribution of the coal had only a

FIGURE 4-2. Net yield of carbon oxides plus water versus hot-water drying temperature for 48 and 225 μ m MMD hot-water-dried Indian Head lignite.

FIGURE 4-3. Net yield of dried maf coal versus hot-water-dried coal versus hot-water drying temperature for 48 and 225 μ m MMD Indian Head lignite.

slight affect on the yield of dried coal with the finer distribution showing a slightly greater loss of dried coal product because of decarboxylation and pyrolysis. The majority of the weight loss can be attributed to the release of carbon dioxide. With the rejection of oxygen from the coal as carbon dioxide, the heating value of the product increased, with the increase being linear with increasing drying temperature (Figure 4-4). The heating value of the coal went from 10,100 Btu/lb on a dry basis for the raw coal to 10,500 Btu/lb for HWD at 270°C to 11,000 Btu/lb for HWD at 330°C. This was an increase in heating value of approximately 9% due to hot-water drying at 330°C. Energy balances, based on the weight percent of the raw coal recovered as dried product, indicate that up to 95% of the energy content of the raw coal was retained in the dewatered product.

FIGURE 4-4. Higher heating value of hot-water-dried coal versus hot-water drying temperature for 48 and 225 μ m MMD Indian Head lignite.

Some removal of inorganics occurred during hot-water drying, as can be seen by Figure 4-5, which is a plot of the ash loss versus hot-water drying temperature. Ash losses versus hot-water drying temperatures were as high as 17.2 wt % for the 48 μ m MMD coal sample and 23.3 wt % for the 225 μ m MMD coal sample. The removal of the inorganics from the coal occurs by both chemical and physical means. Some of the sulfur in the coal was converted to hydrogen sulfide and some water-soluble inorganics (such as sodium, calcium, and potassium) were extracted into the drying medium.

FIGURE 4-5. Ash loss versus hot-water drying temperature for 48 and 225 µm MMD hot-water-dried Indian Head lignite.

Comparing the results obtained by hot-water drying two coal samples of different particle size distributions, it appeared that no significant differences occurred due to the particle sizes used for the hot-charge, hot-water drying autoclave tests. This would indicate that in both cases the center of the coal particles had reached the temperature of the drying medium.

To study the effects of residence time in hot-water drying, three hot-water drying tests were performed with the hot-charge autoclave using residence times of 15, 60, and 240 minutes. All three tests were made at 300°C using Indian Head lignite with a particle size distribution having a MMD of 225 µm. The results of the residence time runs are shown in Table 4-3. The results show that the equilibrium moisture content of the coal decreased slightly with increased residence times, ranging from 15.2 wt % for the coal dried for 15 minutes to 13.3 wt % for the coal dried for 240 minutes. The primary constituent in the product gas was carbon dioxide, ranging from 97% mol % to 95 mol % and decreased with increasing residence time due to dilution by other pyrolysis products. Other gas components included ethane, hydrogen, methane, carbon monoxide, hydrogen sulfide, and ammonia. Hydrogen sulfide concentrations in the off gas decreased with increasing residence time, which may be due to the hydrogen sulfide reacting with the process water to form sulfuric acid or with the reactor walls.

The proximate, ultimate, and ash analyses for the hot-water-dried coal samples obtained in the residence time studies are shown in Tables 4-4, 4-5, and 4-6, respectively. The proximate analysis indicates that an increase in fixed carbon, and a decrease in ash and volatile matter occurred due to hot-water

TABLE 4-3

EFFECTS OF RESIDENCE TIME FOR HOT-CHARGE/HOT-WATER
DRYING OF 225 μ m MMD INDIAN HEAD LIGNITE AT 300°C

	Original Coal	Residence Time, Min.		
		15	60	240
Equilibrium Moisture, %	33.0	15.2	14.6	13.3
Product Gas Analysis (Air-Free, mol %)				
CO ₂	--	97.94	96.80	95.26
C ₂ H ₆	--	0.00	0.11	0.15
C ₃ H ₈	--	0.00	0.00	0.00
H ₂	--	0.00	0.78	1.41
CH ₄	--	0.31	1.02	1.32
CO	--	0.00	0.57	1.23
H ₂ S	--	1.75	0.28	0.00
NH ₃	--	0.00	0.44	0.63

TABLE 4-4

PROXIMATE ANALYSIS FOR INDIAN HEAD HOT-WATER DRIED
AT 300°C IN THE HOT-CHARGE AUTOCLAVE FOR VARIOUS DRYING TIMES

	Original Coal	Residence Time, Min.		
		15	60	240
Ash, %	15.6	14.6	13.7	13.9
Volatile Matter, %	47.4	37.4	39.3	37.3
Fixed Carbon, % (by diff.)	37.0	48.0	47.0	48.8

*Moisture-free basis.

TABLE 4-5

ULTIMATE ANALYSIS FOR INDIAN HEAD LIGNITE HOT-WATER DRIED
AT 300°C IN THE HOT-CHARGE AUTOCLAVE FOR VARIOUS DRYING TIMES

	Original Coal	Residence Time, Min.		
		15	60	240
Ash, %	15.6	14.6	13.7	13.9
Carbon, %	61.0	61.7	65.1	67.3
Hydrogen, %	3.7	3.7	3.9	3.9
Nitrogen, %	1.3	0.9	1.1	1.1
Sulfur, %	1.0	0.4**	0.7	0.9
Oxygen, % (by diff.)	17.4	18.7	15.5	12.9
Heating Value, Btu/lb	10,100	10,600	10,860	11,100

*Moisture-free basis.

**Number appears low.

TABLE 4-6

X-RAY FLUORESCENCE ANALYSIS OF INDIAN HEAD LIGNITE ASH BEFORE AND AFTER
HOT-WATER DRYING AT 300°C AND AT DIFFERENT RESIDENCE TIMES
IN THE HOT-CHARGE AUTOCLAVE

Ash From:	Raw Coal	Dried Coal		
		15 Min.	60 Min.	240 Min.
		Raw Filter Cake	Raw Filter Cake	Raw Filter Cake
Wt % of Ash:				
SiO ₂	35.1	39.2	36.3	35.9
Al ₂ O ₃	14.3	15.8	15.3	14.9
Fe ₂ O ₃	7.8	7.2	7.8	8.5
TiO ₂	0.9	1.0	0.9	0.9
P ₂ O ₅	0.7	0.5	0.6	0.6
CaO	13.9	15.0	15.6	15.9
MgO	5.2	5.4	5.3	5.6
Na ₂ O	5.0	3.1	2.8	2.2
K ₂ O	1.6	1.8	1.6	1.6
SO ₃	15.5	11.1*	13.8	13.9
Coal Ash, Wt % Moisture-Free Basis	15.6	14.2	13.6	13.9

*Number appears low.

drying but did not change significantly due to residence time. The ultimate analysis shows an increase in carbon content, from 61.7 wt % to 67.3 wt %, and a decrease in oxygen content, from 18.7 wt % to 12.9 wt % of the coal occurred with increasing residence time. The loss of oxygen from the coal in the form of carbon dioxide during hot-water drying, is the main cause for the increase in heating value observed for the hot-water-dried coal as residence time increased. The increase in heating value of the dried coals ranged from 10,600 Btu/lb for the 60-minute test to 11,100 Btu/lb for the 240-minutes test which was 5% to 9% higher than the heating value for the original lignite (10,100 Btu/lb) on a dry basis. The ash analysis primarily showed a decrease in sodium content and slight decrease in silica and alumina contents of the coal with increasing residence time. Decreases in sodium content of the dried coals range from 3.1 wt % to 2.2 wt % of the ash as Na_2O which was a 38% to 56% reduction in sodium content compared to the original coal (5.0 wt % of the ash as Na_2O).

As hot-water coal drying residence time increased, the pH of the process water became less basic, and the sulfate concentration increased (Table 4-7). Total phenolics, methanol, acetone, and methyl ethyl ketone concentrations in the process water increased 3 to 6 times with increased residence time. The ICAP elemental analysis (Table 4-8) indicated that concentrations of sodium, calcium, and silica in the process water also increased as residence time increased. Comparison of the water analysis for the 15-minute and 240-minute residence time runs shows that the sodium concentrations doubled and calcium concentrations increased by a factor of five for the 240-minute run.

The particle size distribution curves for the dried coals were determined by wet screening and Coulter Counter methods and the results are shown in Table 4-9. The size distribution curves indicate that particle size was not affected by residence time.

Detailed component-by-component material balances were completed on the three residence time runs. A summary of the results is listed in Table 4-10. The net yields shown were obtained from the adjusted material balances and are expressed as a weight percent of the original maf coal used in the tests. The results show that increased decarboxylation, dehydration, and pyrolysis occurred with increasing residence time during hot-water drying. Figure 4-6 is the net yield of carbon oxides and water versus hot-water drying residence time. The yield of $\text{CO}_2 + \text{H}_2\text{O}$ increased rapidly up to approximately 20 minutes followed thereafter by a moderate increase. Similarly, the net yield of dried maf coal versus residence time (Figure 4-7) decreased rapidly up to 20 minutes followed thereafter by a moderate decrease. The higher heating value of the hot-water-dried coal versus residence time is shown in Figure 4-8. The heating value of dried coal increased rapidly up to 40 minutes with a gradual increase in heating value with increasing residence time after that. The ash loss versus residence time (Figure 4-9) appears to level off after approximately 20 minutes, indicating that after that amount of drying time, very little additional water-soluble inorganics were leached into the process water and that only a minute amount of additional sulfur was converted to hydrogen sulfide.

TABLE 4-7

EFFECT OF RESIDENCE TIME ON PROCESS WATER COMPOSITION FOR 225 μ m MMD
INDIAN HEAD LIGNITE HOT-CHARGE/HOT-WATER DRIED AT 300°C

	Residence Time, Min.		
	15	60	240
pH	8.0	8.2	7.6
Alkalinity*	2410	3110	3180
Ammonia	90	40	60
Sulfate	420	1020	1030
Cyanide	Trace	--	--
Total Carbon	5100	5250	6440
TOC	1820	5010	6320
COD	12400	--	--
BOD	1270	4900	8000
Phenol	40	50	120
o-Cresol	ND	ND	10
m,p-Cresol	10	5	10
Total Phenolics	50	55	140
Methanol	670	1720	2770
Acetone	40	160	230
Methylethyl- ketone	Trace	10	20
All units in mg/l			
trace = <1 mg/l			
ND = Not Detected			

*Alkalinity of water is a measure of the quantitative capacity of the sample to neutralize a strong acid (HCl) to a designated pH of 4.5.

Alkalinity to pH 4.5 is expressed as mg/l CaCO_3 .

TABLE 4-8

EFFECT OF RESIDENCE TIME ON PROCESS WATER ELEMENTAL COMPOSITION FOR
225 μ m MMD INDIAN HEAD LIGNITE HOT-CHARGE/HOT-WATER DRIED AT 300°C

Residence Time, Min.	Al	Ca	Fe	K	Mg	Na	Si
Washed Original Coal Filtrate*	1.8	9.3	0.7	4.5	1.5	196	5.0
15 Process Water Wash*	1.3 0.4	70 9.9	2.3 0.6	23.8 6.0	13.3 2.1	1150 302	117 23.0
60 Process Water Wash*	0.4 0.2	305 43	1.4 0.5	43.0 11.0	12.0 2.3	2100 390	175 33
240 Filtrate Wash*	0.1 0.2	366 62	0.7 0.5	38.0 18.0	5.4 1.1	2480 427	180 36

*Hot-water-dried coal was washed with distilled water after first filtering to remove process water.

4.2.4 RHEOLOGY

Rheological data was determined on the Haake RV100 Rotovisco rheometer for coal-water slurries formulated using Indian Head lignite hot-water dried in the hot-charge autoclave for comparison to the slurries produced in the CPU. The effect on slurry viscosity caused by increased temperature was further investigated, and the data base now includes slurries produced in the CPU.

The CWS prepared using the 48 μ m MMD Indian Head HC-HWD coals exhibited non-Newtonian pseudoplastic and yield pseudoplastic flow behavior and were significantly thixotropic following periods of high shear. The Indian Head 225 μ m MMD slurries using coal from the HC-HWD autoclave were pseudoplastic and yield pseudoplastic. Apparent viscosity versus solids loading showing the 330°C HC-HWD data for the 48 μ m and 225 μ m MMD Indian Head lignite, along with the results obtained for the Indian Head coal dried by several other techniques, are plotted in Figure 4-10 and 4-11. The maximum pourable bone-dry solids loadings for the CWS made with HC-HWD Indian Head lignite are listed in Table 4-11.

TABLE 4-9

RESIDENCE TIME EFFECTS ON PARTICLE SIZE DISTRIBUTION FOR 225 μm MMD
INDIAN HEAD LIGNITE HOT-CHARGE/HOT-WATER DRIED AT 300°C

Residence Time, Min.	Raw Coal				
	15 60 240				
Mesh	μm	Cumulative Wt % > Screen Size			
60	250	50.6	31.2	28.9	30.0
100	150	66.6	49.7	49.0	47.1
170	90	76.6	60.5	60.2	59.0
200	75	77.8	63.4	63.0	62.1
270	53	81.0	68.1	67.2	67.6
325	45	82.0	69.5	68.2	68.5
	40	83.5	72.0	71.4	71.7
	32	86.5	75.3	74.3	74.3
	25	89.1	78.3	77.3	77.8
	20	91.4	80.9	80.2	80.7
	16	93.2	83.6	83.0	83.8
	13	94.6	86.3	85.7	86.6
	10	95.7	89.1	88.3	89.3
	8	96.5	91.7	90.9	92.0
	6	97.0	94.2	93.4	94.4
	5	97.3	96.6	95.7	96.7
	4	97.5	98.8	97.9	98.8
	3	97.7	100.0	97.9	98.8

TABLE 4-10

SUMMARY OF MATERIAL BALANCE RESULTS FOR THE HOT-CHARGE/HOT-WATER
DRYING AUTOCLAVE RESIDENCE TIME TESTS

Coal:	IH0883	IH0883	IH0883
Mass Mean Diameter, μm :	225	225	225
Temp., $^{\circ}\text{C}$	307	300	300
Press., psig:	1475	1300	1300
Residence Time, Min.:	15	60	240
Net Yields - Wt % of maf Coal Fed			
H ₂	0.01	0.02	0.01
CO + CO ₂ + H ₂ O	7.03	10.83	17.74
C ₁ - C ₄	0.12	0.04	0.10
H ₂ S	0.20	0.02	0.00
NH ₃	0.04	0.02	0.05
Phenol	0.01	0.01	0.02
Cresols	0.01	0.00	0.00
Methanol	0.14	0.28	0.47
Acetone	0.01	0.03	0.04
MEK	0.00	0.00	0.00
Dried maf Coal	94.55	91.86	86.26
HHV Btu/lb Dry Coal	10,600	10,860	11,100
Ash Loss as Wt % of Starting Ash	11.4	20.9	24.6
Equilibrium Moisture of Dried Coal, Wt %	15.2	14.6	13.3

IH0883 Indian Head lignite procured August 1983.

FIGURE 4-6. Net yield of carbon oxides plus water versus hot-water drying residence time at 300°C for 225 μ m MMD Indian Head lignite.

FIGURE 4-7. Net yield of dried maf coal versus hot-water drying residence time at 300°C for 225 μ m MMD Indian Head lignite.

FIGURE 4-8. Higher heating value of hot-water-dried coal versus hot-water drying residence time at 300°C for 225 μ m MMD Indian Head lignite.

FIGURE 4-9. Ash loss versus hot-water drying residence time at 300°C for 225 μ m MMD Indian Head lignite.

FIGURE 4-10. Apparent viscosity at 410 sec^{-1} and 28°C versus solids loading for coal-water slurries formulated with $225 \mu\text{m}$ and $48 \mu\text{m}$ MMD Indian Head lignite dried by different methods.

FIGURE 4-11. Apparent viscosity at 410 sec^{-1} and 28°C versus solids loading for coal-water slurries formulated with $225 \mu\text{m}$ MMD Indian Head lignite hot-water dried at 270° , 300° , and 330°C .

TABLE 4-11
MAXIMUM BONE-DRY SOLIDS LOADINGS FOR
POURABLE COAL-WATER SLURRIES MADE WITH INDIAN HEAD LIGNITE

Coal Type	Percent Bone-Dry Solids Loading			
	48 μ m MMD		225 μ m MMD	
	% BDS	cps	% BDS	cps
"As-received" Indian Head lignite	40.4	345	39.8	208
Conventionally-dried Indian Head lignite	42.6	261	NA	--
Indian Head lignite CPU hot-water-dried				
at 270°C	48.5	718	53.3	858
at 300°C	52.1	835	56.0	1030
at 330°C	58.0	1082	58.3	1080
Hot-charge/hot-water-dried				
Indian Head lignite				
at 270°C	50.8	1106	52.1	473
at 300°C	52.4	1007	53.5	492
at 330°C	53.8	735	56.6	725
4-Hour residence time	at 300°C	NA	--	51.5 370
1-Hour residence time	at 300°C	NA	--	51.2 386

NA = Not Available.

In addition to determining the effects of hot-water drying temperature on coal-water slurry rheology, the effects of drying time on slurry rheology were also investigated. Three hot-water drying tests were involved in the study, the normal test of a 15-minute residence time and two others of 1 and 4 hours. All three tests were made at 300°C in the hot-charge autoclave using 225 μ m MMD Indian Head lignite. The maximum solids loading achieved for a pourable slurry for the coal dried at the 4-hour residence time was 51.5% bone-dry solids (μ = 370 cps) and for the 1-hour drying time was 51.2% bone-dry solids (μ = 386 cps), which are both slightly less than the 53.5% bone-dry solids loading achieved with the coal that was dried at the 15-minute residence time. Figure 4-12 illustrates the rheogram for the 4-hour residence time CWS which depicts a Bingham plastic flow behavior. This is in contrast to the pseudoplastic flow behavior observed for the HC-HWD and CPU-HWD coal-water slurries (300°C, 15 minutes). An example of a rheogram for CPU-HWD Indian Head CWS is given for comparison in Figure 4-13.

FIGURE 4-12. Rheogram illustrating Bingham plastic flow behavior for coal-water slurry formulated with 225 μm MMD Indian Head lignite which was hot-water dried for four hours in the hot-charge autoclave.

FIGURE 4-13. Rheogram illustrating yield pseudoplastic and thixotropic flow behavior for CWS made using 48 μm MMD Indian Head lignite which was HWD for 15 minutes in the CPU.

An additional representation of the pseudoplastic flow behavior of the CPU HWD Indian Head CWS is given in Figure 4-14 where absolute viscosity is plotted versus shear rate for two coal-water slurries having different particle size distributions, one with a MMD of 48 μm and the other with a MMD of 225 μm . A pronounced reduction in viscosity with increased shear rate was again evident. For this figure, apparent viscosities taken directly from the Haake RV100 viscometer have been corrected to absolute viscosities using a computer program to determine shear rate corrections for non-Newtonian fluids based on the theories presented in "Advances in Chemical Engineering," I, 77 (1956), by A.B. Metzner, eds. by T.B. Drew and J.W. Hoopes, Jr., Acad. Press Inc., New York.

FIGURE 4-14. Absolute viscosity versus shear rate for Indian Head lignite-water slurries hot-water dried at 330°C.

Apparent viscosity versus temperature was determined for CWS made from CPU-HWD, 48 μm and 225 μm MMD Indian Head lignite. The slurries tested were at the maximum pourable solids content. The effects of temperature on viscosity for these slurries are illustrated in Figure 4-15. Increasing the temperature from 27.8° to 79.4°C reduced the apparent viscosity, measured at a shear rate of 410 sec^{-1} , from 871 cps to 405 cps for the 225 μm MMD HWD Indian Head CWS and from 845 cps to 330 cps for the 48 μm MMD HWD Indian Head CWS. This is a significant reduction when compared to the viscosity reduction seen for the conventionally dried and "as-received" Indian Head CWS.

FIGURE 4-15. Apparent viscosity at 410 sec^{-1} versus temperature for coal-water slurries formulated with 225 μm and 48 μm MMD Indian Head lignite dried by different methods.

In summary, the hot-water drying process has proven to be an effective method of forming a highly-loaded coal-water slurry fuel with the potential for gasification or combustion utilization. The slurry produced shows no evidence of significant moisture reabsorption or instability, thus making HWD CWS superior to CWS formulated with conventionally-dried or raw lignite. Also, the viscosity reduction realized with increased slurry temperature for the HWD CWS illustrates the opportunity to lower viscosities which may otherwise be considered excessive (approximately 800 to 1000 cps for a 60% BDS Indian Head lignite HWD CWS at room temperature) to more acceptable levels (300 to 500 cps at approximately 80°C).

4.2.5 AGING AND MOISTURE REABSORPTION

The aging studies using steam- and hot-water-dried Indian Head lignite previously reported (see Quarterly Technical Progress Report - January to March 1984) were completed with the 60- and 90-day exposure tests. Results, listed in Table 4-12, show that exposure of the dried coal or filter cake to air or water at 30°C for up to 90 days did not significantly affect the moisture reabsorption properties as indicated by equilibrium moisture content. The equilibrium moisture values of the 60-day air exposure may be high due to spontaneous combustion of some of the samples resulting from an unnoticed elevated temperature in the drying oven (150°C). Partial combustion of the samples would result in an erroneous measurement of the dry weight of coal, which in turn would make the equilibrated sample appear to contain more moisture than it actually did.

4.2.6 HOT-WATER/COAL DRYING ECONOMIC STUDY

A preliminary economic study of the hot-water coal drying process to determine the incremental costs added to the selling price of lignite as a result of the drying process was started. The study is aimed at sizing and costing a commercial-scale plant for hot-water drying North Dakota lignite. Two seniors and one graduate chemical engineering student were hired to assist in performing the study. A nominal plant capacity of 200 tons per hour of as-mined coal to produce a 60 wt % bone-dry coal-water slurry fuel was chosen as a design basis. The plant is being designed to utilize raw lignite from the Zap, North Dakota, mining region.

A block flow diagram of the hot-water coal drying plant (Figure 4-16) was constructed, and a mass balance over each section was performed. The plant consists of ten main areas: coal receiving and storage, coal crushing, slurry preparation, slurry drying, gas-slurry separation, slurry concentration, wet milling, fuel slurry storage, gas processing, and water recovery and treatment. The coal receiving and storage section of the plant (Area 01) will be designed to receive 2" x 0" size coal by railcar for storage. Storage capacity for the as-mined coal will be for a 10-day supply or 58,000 tons. The 2" x 0" coal will be sent to the coal crushing area (Area 02) of the plant where it will be reduced to 1/8" x 0" prior to slurry preparation. The slurry preparation step (Area 03) involves blending the coal with water in a 50/50 wt % mixture for slurry drying. Slurry drying will take place in four parallel trains (Area 04) with the slurry being dried at 340°C and 2200 psig using a 10- to 15-minute residence time. Gases produced from the hot-water drying process will be separated from the slurry in Area 05 and sent to a processing

TABLE 4-12

EQUILIBRIUM MOISTURE OF DEWATERED COAL SOAKED IN WATER AND STORED
IN AIR FOR 4, 30, 60, AND 90 DAYS(ALSO INCLUDED ARE THE ORIGINAL EQUILIBRIUM MOISTURE CONTENTS
OF THE COAL MEASURED IMMEDIATELY AFTER DEWATERING)

Coal Type	Original	Equilibrium Moisture, % ¹						
		Soaked 4 Days	Soaked 30 Days	Soaked 60 Days	Soaked 90 Days	Exposed 30 Days	Exposed* 60 Days	Exposed 90 Days
Indian Head steam dried at 300°C	11.0	13.1	12.3	13.3	13.3	12.9	16.7	13.9
Indian Head HWD 310°C no depress	11.3	12.4	12.5	14.0	13.2	15.0	16.0	14.3
Indian Head HWD 300°C depress	14.4	14.0	14.4	15.1	14.2	15.1	18.1	15.4
Indian Head HWD 270°C no depress	20.1	20.0	--	20.5	19.0	--	20.4	18.9

*Numbers may be in error due to spontaneous combustion of samples in drying oven.

¹The equilibrium moisture test involves soaking the sample in water for 3 hours, filtering, and then placing in a constant temperature humidity chamber of 98-99% relative humidity for 72 hours. Afterward the coal moisture is determined by oven drying at 105°C for 1 hour.

step (Area 09). The dilute product slurry will be sent to a concentration step (Area 06). The slurry will be concentrated from 35 wt % bone-dry solids to 60 wt % bone-dry solids and then sent to a wet ball mill (Area 07) where the particle size distribution of the slurry will be reduced to 70% less than 75 μ m. The resulting fuel slurry will be held in a product storage area (Area 08) until ready for shipment. The water removed during the slurry concentration step will be sent through a treatment step (Area 10) to remove the inorganics and organics dissolved in the process water during hot-water drying. A single water treatment plant will be utilized to treat both the recycled and makeup water that is used in the slurry preparation step.

FIGURE 4-16. Blow flow diagram for 200-ton-per-hour hot-water coal drying plant.

Several methods for coal receiving and storage, coal preparation, slurry concentration, gas processing, and recycle water treatment have been investigated. Equipment pricing from vendors and investigations into the remaining sections of the plant continues. The economic study is expected to be completed by the end of the summer.

5. LOW-RANK COAL LIQUEFACTION

Project No.: 7106

B&R Nos.: 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: 1) catalytic liquefaction, with increased attention on understanding the effects of adding H_2S , particularly in the presence of iron-containing materials; b) staged liquefaction, with emphasis on low-temperature first-stage reactions using CO as the reductant 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 how start-up solvent composition influences lined-out product) and continued characterization of liquefaction products.

5.2 CPU PRODUCT SLURRY RECYCLE

Three "long" runs have been made on the continuous process unit (CPU) with the primary objectives being to determine how the product slate was influenced by the startup solvent and the feed coal. Run 101 used A04 (anthracene oil) as the the startup solvent, while recycle solvent from Project Lignite's process development unit (PDU) was used to start Run 103. Zap lignite (from North American Coal Company) was used in both runs as well as in the PDU run from which the recycle solvent was taken (for Run 103). The nominal run conditions were: 440°C reaction temperature, 4000 psig, 95 mole percent hydrogen (with carbon monoxide as the balance), and hydrogen sulfide addition at a rate of five weight percent of the maf coal feed. In Run 106, Wyodak coal was fed, the solvent was A04, and the other conditions remained nominally the same.

Analyses of the solvents and of the feed coals may be found in previous quarterly reports. The objective of this report is to show the viscosity of the product slurry through the course of the CPU run, and to indicate the effect of "blowing down" the reactor during operation.

Figures 5-1, 5-2, and 5-3 show the viscosity of the product slurries at various run periods for Runs 101, 103, and 106, respectively. Viscosities were measured using a Wells-Brookfield Cone-and-Plate Type viscometer (Model HBT). Shear rates ranged from 1.9 sec^{-1} to 383 sec^{-1} with apparent viscosities normally being measured at three different shear rates. The mean of those determinations was taken as the "viscosity" of the slurry. The temperature was held constant at 70°C using a circulating constant-temperature water bath. Sample sizes were in the 2-3 ml range.

The A04 solvent was found to be a Newtonian fluid (i.e., the viscosity did not vary with shear rate or with time). As operating time increased, the product slurries demonstrated both pseudoplastic and thixotropic behavior.

Time-dependent behavior (i.e., the apparent viscosity decreased with increasing time but constant shear rate, in the viscometer) was noted but not quantified; the apparent viscosity was measured when it no longer changed with time. Variation in apparent viscosity with changing shear rate was also noted, but the apparent viscosity for the slurry was taken as the mean of (usually) three determinations. It was observed that as the apparent viscosity increased, the variation in apparent viscosity with shear rate also

FIGURE 5-1. Run 101 average viscosity at 70°C.

FIGURE 5-2. Run 103 average viscosity at 70°C.

FIGURE 5-3. Run 106 average viscosity at 70°C.

increased. Rheological characterization of coal liquefaction product slurries will require more detailed analysis of the shear-rate and time dependent effects. Our objective here was to obtain a measure of the ease of handling product slurry (and recycle slurry) as a liquefaction run progressed. This measure was taken to be "average apparent viscosity" (hereafter viscosity).

The abscissa of Figures 5-1, 5-2, and 5-3 is designated "run period". A run period is nominally four hours in length. Although the liquefaction unit operates continuously, the product collection, feed slurry preparation, and the feed to the reactor are batch operations. Startup solvent is fed to the CPU for the first two run periods; product slurry is collected during the first run period, and a batch feed slurry is prepared using the collected product and fresh coal during the second run period. The prepared feed slurry is fed during the third run period, while product from the second run period is used to prepare feed slurry for run period four.

Figure 5-1, showing product viscosity as a function of run period, is characteristic of the data that were obtained for many of the CPU runs up to that time. The product viscosity gradually increased with run period until, at about run period 18, the viscosity increased dramatically. At that point feed slurry preparation was difficult and feeding the viscous slurry became impossible. From Figure 5-1 it can be seen that the product viscosity reached nearly 3500 cps during run period 25 and further operation was to be suspended. Before terminating the run the reactor was "blown down" (i.e., the reactor was flushed). It was noted by the operators that almost immediately after blow down, the product slurry was much less viscous. At that point it

was decided that operation would continue. It can be seen that the product viscosity again began to increase as the CPU operation continued until it was necessary to terminate shortly after run period 40.

Based on the experience gained, it was decided to incorporate periodic reactor blow down as standard operating procedure in Run 103. The reactor was blown down following run periods 12, 24, and 36. As Figure 5-2 indicates, the product viscosity decreased after each reactor blow down, but there did appear to be a continuing increase in viscosity as the run progressed. However, the viscosity never exceeded 350 cps at any time and high viscosity did not cause termination.

Periodic reactor blow down was again practiced in Run 106 and confirmed that it is possible to control product viscosity using that operating technique. As indicated in Figure 5-3, the maximum viscosity was about 210 cps with usual values ranging from about 100 to 160 cps.

It was observed that the product slurry obtained just prior to reactor blow down contained relatively more suspended particulate matter; that material was not present after blow down. Tar balls and other "solid" material were removed from the reactor during blow down. This leads to the conclusion that materials build up in the reactor during operation, thereby decreasing the effective reactor volume and decreasing the residence time of the reacting materials. This decreases the overall conversion and causes a build up in solids in the product slurry, which is reflected in the increased viscosity. Blowing down the reactor removes the accumulated "solids", thereby increasing reactor volume, residence time, and conversion. The solids loading in the product is reduced, as is its viscosity.

Based on the experience from Runs 101, 103, and 106, it is concluded that periodically blowing down the liquefaction reactor in the CPU allows long-term operation of the unit. This technique may be useful in the operation of larger scale continuous liquefaction reactors.

5.2.1 PRODUCT SLURRY CHARACTERIZATION

The product slurries from several passes in liquefaction Runs 101 and 106 (both of which had been carried out in the continuous process unit under the same experimental conditions except for the coal used) were separated into three fractions per pass by solvent extraction (1). The coals used were Zap 2 and Wyodak in Runs 101 and 106, respectively.

Product slurry samples from Run 106 passes 7, 19, 30, 40, 45, 50, and 58 and start-up solvent A04 were separated by extraction under mild conditions using the method previously described for Runs 101 and 103 (1). Table 5-1 shows the wt % of the fraction recovered from each pass and Figure 5-4 compares the fractions from corresponding passes in Runs 101 and 106. After seven passes the oil content of the products from two runs was approximately the same. However, after nineteen passes and through the fortieth pass the quantity of oil from Run 106 was greater than that of Run 101. The oil content of the slurry from Run 106 leveled out after pass 40. The quantity of soluble heavy ends changed little in Run 106 over the course of the run and was not substantially different from that of Run 101 through 40 passes. There was

TABLE 5-1
SEPARATION OF PRODUCT SLURRIES FROM CPU RUNS 101 AND 106

Pass No.	Run 106						
	7	19	30	40	45	50	58
Extraction (wt %)							
PSHE ^a	68.0	61.4	56.8	57.2	52.7	56.3	55.7
PiHE ^b	16.7	16.6	18.4	19.3	19.2	19.2	20.7
IHE ^c	<u>13.4</u>	<u>19.3</u>	<u>20.5</u>	<u>21.9</u>	<u>22.8</u>	<u>22.0</u>	<u>22.5</u>
Total	98.1	97.3	95.7	98.4	94.7	97.5	98.9

Pass No.	Run 101			
	7	19	30	40
Extraction (Wt %)				
PSHE	70.9	50.2	54.7	48.4
PiHE	14.3	19.9	16.4	16.1
IHE	<u>8.6</u>	<u>19.1</u>	<u>27.6</u>	<u>29.8</u>
Total Recovery	93.8	89.2	98.7	94.3

^aPentane-soluble oils.

^bPentane-insoluble, methylene chloride-soluble heavy ends.

^cMethylene chloride-insoluble heavy ends, contains mineral matter.

less of the insoluble heavy ends (IHE) in Run 106 than there was in Run 101. The IHE in Run 106 remained relatively constant after approximately forty passes.

5.2.2 ANALYSIS OF ASTM D-1160 DISTILLATES

5.2.2.1 Column Chromatography

Reviewing our silica gel open-column chromatographic method indicated that for the determination of the 90 principal hydrocarbon components, the 12 fractions that had been collected could be reduced to five fractions. The first four fractions contain hydrocarbons and are the fractions used for capillary GC hydrocarbon analysis. The relative sizes of these fractions is a measure of the distribution of compound types. The first fraction "A" contains most of

FIGURE 5-4. Comparison of fractions from corresponding passes in Runs 101 and 106.

the alkanes, "B" contains the light aromatic hydrocarbons, while "C" and "D" have the heavier (more condensed) aromatic hydrocarbons. The fifth fraction contains polar materials. This fraction may be analyzed for phenols and bases, however, major components (phenol and the cresols) are lost by irreversible adsorption on the silica gel. Therefore, the phenols are base-extracted as previously reported (2) and determined from the fraction recovered after neutralization. Table 5-2 shows the distribution of the five fractions for CPU Runs 101 and 103. It should be noted that when silica gel

TABLE 5-2

FRACTIONS RECOVERED FROM OPEN COLUMN CHROMATOGRAPHY
SEPARATIONS OF DISTILLATION RUNS 101 AND 103

Run 101					
A04	0.83%	9.12%	41.7%	31.3%	13.3%
PB1	0.87	13.0	39.5	32.4	14.0
PB5	0.86	17.6	37.0	17.7	23.7
PB7	1.79	4.41	23.7	47.3	24.6
PB9	5.89	19.1	32.9	21.9	21.4
PB13	0.96	14.8	26.6	23.0	32.0
PB17	2.12	15.9	22.9	22.3	33.7
PB19	2.11	4.85	18.1	39.1	38.2
PB21	2.63	4.84	18.7	38.5	35.7
PB24	2.84	11.9	24.2	19.7	41.1
PB27	2.34	26.8	21.6	14.0	40.3
PB30	2.31	4.60	17.1	29.1	43.4
PB33	2.76	4.09	17.7	27.1	45.3
PB35	1.67	6.91	20.6	21.9	47.1
PB38	1.82	4.88	2.95	38.6	47.7
PB40	4.52	2.38	15.8	23.8	50.0
PB43	1.94	5.45	9.91	29.0	50.1
Run 103					
PDU Recycle	5.15%	15.2%	35.2%	23.7%	21.2%
PB1	9.04	19.7	33.8	18.2	17.0
PB4	4.77	19.4	29.7	19.6	22.8
PB7	*7.10	4.26	0.12	44.5	42.6
PB10	5.17	15.2	26.9	19.5	32.2
PB13	5.29	16.2	23.1	16.1	35.3
PB16	4.50	17.6	27.3	12.7	36.1
PB19	*9.95	1.96	0.09	39.4	48.2
PB22	*10.2	1.94	0.43	35.4	52.4
PB25	3.56	8.34	17.9	23.7	45.7
PB28	5.62	12.6	17.5	19.9	44.7
PB31	4.09	11.4	19.0	21.0	45.9
PB34	1.22	11.5	18.7	20.4	44.9
PB37	2.95	11.8	15.3	20.9	44.8
PB40	0.42	10.8	16.8	20.8	47.0

*Percentages may vary because different lot of silica gel was used.

column separation is used, fraction sizes are comparable only when the same lot of silica gel is used. Because overlapping capillary GC determinations are used the quantitative hydrocarbon determination is not affected.

5.2.3 AUTOMATED GC ANALYSIS

Development of an improved quantitative gas chromatographic method for the analysis of lignite liquefaction distillate fractions has continued. The internal standard method of quantitation was chosen with 2-methylpentadecane being selected as the internal standard for hydrocarbon fractions and phenyl ether being selected as the internal standard for the phenolic fraction resulting from the solvent extraction. A 3-level calibration bracketing the sample size is used. Appropriate samples from the silica gel adsorption columns and from the solvent extraction are diluted in the range of 200-1000 ppm and chromatographed under the conditions summarized in Table 5-3. Instruments used include a Hewlett-Packard model 5880A gas chromatograph and a Varian model 5880A gas chromatograph, both accomodating an autosampler, cryogenic cooling, and multi-level temperature programming. The gas chromatographic scheme developed allows for excellent resolution of 86 hydrocarbons and 22 phenols. Identification of sample components is done by retention indices and confirmation is by gas chromatography/mass spectroscopy. The temperature programs developed are summarized in Tables 5-4 through 5-8. A sample chromatogram is shown in Figure 5-5. Work is continuing to develop methods for better resolution of phenols and the quantitation of nitrogen- and sulfur-containing compounds.

TABLE 5-3

GC CONDITIONS FOR LIGNITE LIQUEFACTION DISTILLATE FRACTION ANALYSIS

Carrier Gas:	Hydrogen
Split Ratio:	75:1 Hydrocarbons 100:1 Phenols
Column:	J and W DB5-60N (0.25 μ m) Fused Silica
Detector:	Flame Ionization with Nitrogen Make-up
Injector Temperature:	250°C
Detector Temperature:	350°C

5.2.4 PHENOL DETERMINATION

The quantitation of 20 different phenolic compounds present in three additional Run 101 passes and in fifteen Run 103 passes is given in Table 5-9. The values for Run 101 may be inserted in Table 5-22 on page 5-32 of the Low-Rank Coal Research Quarterly Technical Progress Report, DOE/FE/50181-17 for April-June 1983.

TABLE 5-4
FRACTION "A" GC PROGRAM

Calibrated Components:

C-9 to C-30 Alkanes
Pristane
Phytane

All of the data show that concentrations of all of the phenols measured continue to increase at least through run period 40 for both CPU runs. Figure 5-6 shows that the total phenol content in the distillate product does not reach a constant value through run period 40 for both Runs 101 and 103. This indicates that "line-out" has not been reached.

TABLE 5-5
FRACTION "B" GC PROGRAM

CALIBRATED COMPONENTS:

5-Methylindan	5,8-Dimethyltetralin
Tetralin	2,7-Dimethyltetralin
Naphthalene	1-Ethyl-naphthalene
Indan	2-Ethyl-naphthalene
<u>m</u> -Diethylbenzene	1,3-Dimethylnaphthalene
<u>o</u> -Diethylbenzene	1,2-Dimethylnaphthalene
<u>6</u> -Methyltetralin	Acenaphthene
5-Methyltetralin	Tetrahydroacenaphthene
1-Methylnaphthalene	4-Methylbiphenyl
2-Methylnaphthalene	Dibenzofuran
2,6-Dimethylnaphthalene	Octahydrophenanthrene
2,7-Dimethylnaphthalene	Phenanthrene
2,6-Dimethyltetralin	<u>p</u> -Diethylbenzene
5,7-Dimethyltetralin	

TABLE 5-6
FRACTION "C" GC PROGRAM

Calibrated Components:

2-Methylnaphthalene	3-Methylphenanthrene
1-Methylnaphthalene	2-Methylphenanthrene
Biphenyl	2-Methylanthracene
2-Methylbiphenyl	4,5-Methylenephenanthrene
Acenaphthene	1-Methylphenanthrene
3-Methylbiphenyl	9-Methylanthracene
4-Methylbiphenyl	1,2,3,4-Tetrahydrofluoranthene
Dibenzofuran	4,5,9,10-Tetrahydropyrene
Fluorene	3,6-Dimethylphenanthrene
9-Ethylfluorene	2-Ethylanthracene
9,10-Dihydrophenanthrene	Fluoranthene
2-Methylfluorene	Pyrene
1-Methylfluorene	Benzonaphthafuran
Dibenzothlophene	Retene
Phenanthrene	1-Methylpyrene

TABLE 5-7
FRACTION "D" GC PROGRAM

325°C
2°C/Min. 132 Min. Run Time
60°C

Calibrated Components:

2,3-Benzofluorene
1-Methylpyrene
Benz(a)anthracene
Dibenz(a,h)anthracene
Benzo(e)pyrene
1-Phenylnaphthalene
2-Phenylnaphthalene
Chrysene
Pyrene
1-Phenyltetralin
Phenylether

TABLE 5-8
PHENOL GC PROGRAM

Calibrated Components:

Phenol
o-Cresol
m-Cresol
p-Cresol
2-Ethylphenol
2,4-Dimethylphenol
2,5-Dimethylphenol
4-Ethylphenol
3-Ethylphenol
3,5-Dimethylphenol
3,4-Dimethylphenol
2-Isopropylphenol
2-n-Propylphenol
4-Isopropylphenol
3-Ethyl-5-methylphenol
4-tert-butylphenyl
4-Indanol
5-Indanol
2-Phenylphenol
1-Naphthol

FIGURE 5-5. Sample chromatogram of hydrocarbon fraction from CPU Run 101.

TABLE 5-9

EXTRACTED PHENOLS FROM PRODUCT SLURRY DISTILLATE--RUNS 101 AND 103

	101 PB 19	101 PB 35	101 PB 43	PDU R.S.	103 PB 1	103 PB 4	103 PB 7
Phenol	0.956	1.573	1.585	0.255	0.487	0.638	0.813
o-Cresol	0.523	1.088	0.929	0.151	0.361	0.415	0.476
m-Cresol	0.844	1.401	1.363	0.210	0.539	0.639	0.721
p-Cresol	0.977	1.430	1.798	0.260	0.592	0.690	0.795
2-Ethylphenol	0.201	0.334	0.314	0.0503	0.130	0.147	0.175
2,4-Dimethylphenol	0.377	0.884	0.748	0.123	0.352	0.366	0.378
2,5-Dimethylphenol	0.207	0.446	0.427	0.0682	0.178	0.187	0.199
4-Ethylphenol	0.498	0.673	0.858	0.132	0.300	0.369	0.418
3-Ethylphenol	0.179	0.284	0.367	0.0550	0.125	0.138	0.153
3,5-Dimethylphenol	0.452	0.547	0.876	0.124	0.249	0.294	0.337
3,4-Dimethylphenol	0.148	0.335	0.308	0.0504	0.149	0.149	0.150
2-Isopropylphenol	0.0165	0.0226	0.0244	0.0376	0.00897	0.0150	0.0126
2-n-Propylphenol	0.108	0.163	0.179	0.0279	0.0698	0.0797	0.0919
4-Isopropylphenol	0.160	0.281	0.282	0.0456	0.122	0.133	0.146
4-n-Propylphenol	0.294	0.326	0.543	0.0843	0.153	0.197	0.227
3-ethyl, 5-Methylphenol	0.591	0.577	1.128	0.168	0.284	0.347	0.408
4-Tertbutylphenol	--	--	--	--	--	--	--
4-Indanol	0.286	0.219	0.488	0.0727	0.115	0.160	0.192
5-Indanol	0.577	0.437	0.943	0.135	0.239	0.348	0.419
2-Phenylphenol and 1-Naphthol	0.124	0.0175	0.151	0.0202	0.0206	0.0218	0.0339

TABLE 5-9 (Continued)

	103 PB 10	103 PB 13	103 PB 16	103 PB 19	103 PB 22	103 PB 25	103 PB 28	103 PB 31	103 PB 34	103 PB 37	103 PB 40
Phenol	0.795	1.082	1.022	1.276	1.255	1.394	1.457	1.433	1.395	1.616	1.470
o-Cresol	0.450	0.595	0.524	0.628	0.627	0.672	0.680	0.677	0.678	0.811	0.721
m-Cresol	0.746	0.581	0.851	0.984	0.893	0.988	1.022	1.019	1.082	1.263	1.130
p-Cresol	0.803	0.692	0.938	1.073	1.195	1.333	1.312	1.220	1.291	1.464	1.306
2-Ethylphenol	0.179	0.225	0.206	0.231	0.234	0.257	0.260	0.247	0.258	0.290	0.260
2,4-Dimethylphenol	0.370	0.474	0.397	0.422	0.425	0.521	0.467	0.431	0.499	0.554	0.506
2,5-Dimethylphenol	0.198	0.256	0.221	0.242	0.243	0.269	0.269	0.256	0.282	0.324	0.292
4-Ethylphenol	0.460	0.596	0.518	0.567	0.573	0.648	0.644	0.594	0.673	0.761	0.689
3-Ethylphenol	0.168	0.210	0.186	0.209	0.206	0.238	0.244	0.223	0.254	0.285	0.250
3,5-Dimethylphenol	0.375	0.499	0.452	0.507	0.525	0.597	0.631	0.566	0.634	0.715	0.642
3,4-Dimethylphenol	0.154	0.193	0.164	0.170	0.170	0.187	0.187	0.170	0.197	0.221	0.207
2-Isopropylphenol	0.0132	0.0269	0.0166	0.0155	0.0181	0.0175	0.0142	0.0243	0.0205	0.0231	0.0203
2-n-Propylphenol	0.0943	0.120	0.110	0.115	0.119	0.126	0.128	0.119	0.133	0.151	0.139
4-Isopropylphenol	0.150	0.194	0.165	0.169	0.172	0.186	0.180	0.169	0.194	0.217	0.199
4-n-Propylphenol	0.258	0.341	0.305	0.321	0.334	0.372	0.391	0.350	0.403	0.448	0.423
3-Ethyl, 5-Methylphenol	0.471	0.633	0.594	0.645	0.684	0.780	0.850	0.758	0.861	0.945	0.882
4-Tertbutylphenol	--	--	--	--	--	--	--	--	--	--	--
4-Indanol	0.223	0.303	0.289	0.304	0.317	0.348	0.389	0.343	0.392	0.416	0.399
5-Indanol	0.496	0.653	0.610	0.646	0.649	0.729	0.788	0.688	0.785	0.822	0.810
2-Phenylphenol and 1-Naphthol	0.0403	0.0503	0.0477	0.0508	0.0250	0.0746	0.0670	0.0513	0.0728	0.0612	0.0654

FIGURE 5-6. Total distillate phenol content versus run period for CPU Runs 101 and 103.

5.2.4.1 Improved Resolution in o-, m-, and p-Cresol Determination Using Silylation

Gas chromatography (GC) is a facile method for the separation of organic mixtures. The advent of capillary columns has enabled the separation of increasingly complex mixtures such as those from coal-derived liquids. Despite the higher resolution that is readily obtained with capillary columns, some peaks of interest co-elute. Co-elution is undesirable because it is difficult to quantify each component in the combined peak.

The phenolic fraction of the distillate product from liquefaction contains all three isomers of cresol: o-, m-, and p-cresol. o-Cresol is readily separated from m- and p-cresol, but the latter two isomers co-elute in GC analysis. Trimethylsilylation of phenols has been used to achieve separation of all three cresol isomers.

Heating o-, m-, and p-cresol with trimethylsilylchloride (TMSCl) and hexamethyldisilazane (HMDS) in the presence of pyridine converts the phenol to the corresponding trimethylsilyl ether. The capillary gas chromatogram shown in Figure 5-7 shows that baseline resolution of the three cresol isomers is readily obtained.

FIGURE 5-7. Capillary gas chromatogram of 3 cresol isomers.

Trimethylsilylation of low-rank coal-derived materials appears to be a valuable addition to our present methods of phenol identification, and we are continuing to develop the technique.

5.2.5 APPLICATION OF DEUTEROMETHANOL CHEMICAL IONIZATION TECHNIQUES

An analysis scheme using deuterium-labeled chemical ionization reagents has been developed to aid in the identification of alkyl benzenes. Identifying alkyl benzenes containing more than three additional carbons is difficult for a number of reasons. Electron impact (EI) spectra of these types of compounds are very similar and do not provide definitive identification. Also, as the number of substituted carbons increases, so does the number of possible isomeric compounds, many of which are not available as reference compounds.

Using D_2O , CH_3OD , and CH_3CH_2OD provides the basis for a method to determine the number of substituted positions on the aromatic ring. Under appropriate Chemical Ionization (CI) conditions the hydrogens attached to the aromatic ring of an alkyl benzene undergo exchange with deuterium in the reagent gas. The number of exchanges that occur corresponds to the number of unsubstituted positions on the ring. Figure 5-8 shows the molecular ion region of CH_3OD CI spectra obtained from the analysis of C_1 - to C_6 -substituted methyl benzenes. The $M + 2$ ion is the ionized species, resulting from the addition of D^+ ; it does not represent any exchange. In the case of toluene, the $M + 2$ is at $m/e = 94$. Toluene, being a mono-substituted benzene, has five hydrogens attached to the ring which should be available for exchange. This exchange is shown under the toluene structure in Figure 6. Pentaomethyl and hexamethyl have one and no exchangeable hydrogen, respectively, with only an $M + 2$ peak, the ionized species, for hexamethylbenzene.

FIGURE 5-8. The CH_3OD chemical ionization spectra of C_1 - to C_6 -substituted methyl benzenes.

The number of alkyl carbons on a benzene ring can be obtained for EI spectra (i.e., the molecular weight) while deuterium CI enables one to differentiate four isomers of C_6 -substituted benzenes. Each isomer exhibits ions corresponding to their molecular ion ($m/e = 162$) and the $M + 2$ ionized species ($m/e = 164$). *n*-Hexylbenzene shows the exchange of all five of the ring hydrogens, *m*-diisopropyl benzene shows the exchange of four, 1,3,5-triethylbenzene shows three exchanges and hexamethyl benzene does not produce any exchanges.

This technique has been applied to a sample of liquefaction light oil. The hydrocarbon fraction of 41HLO-18 was analyzed using CD_3OD CI. Figure 5-9 shows a four-minute portion of the total ion chromatogram obtained from the sample. This portion of the chromatogram contains the C_3 alkyl benzenes. Electron impact mass spectroscopy was used to identify the occurrences of C_3 benzenes in a comparable analysis of the same sample. This analysis verified that all eight of the possible isomers of C_3 alkyl benzenes were present in the sample, but the EI spectra were similar enough that it was impossible to distinguish between the trimethyl and the methylethyl substituted benzenes. Figure 5-10 shows the assignments made based on the CI spectra. The spectrum labeled A shows a molecular ion at $m/e = 120$, the ionized species at $m/e = 122$ and four exchanges corresponding to $m/e = 123, 124, 125,$ and 126 . This compound was assigned a methylethyl structure. Spectrum B again shows $m/e = 120$ and 122 but indicates only three exchanges corresponding to a trimethyl substituted benzene. No method has been reported in the literature which allows the determination of alkyl substitution on a benzene ring without the extensive use of standard compounds and the study of fragmentation patterns. Standard compounds are generally unavailable for larger molecular weight alkyl benzenes (i.e., >4 alkyl carbon atoms). Using fragmentation patterns is very difficult when the samples contain complex mixtures of hydrocarbon species that are not completely resolved by gas chromatography. The method that has been developed requires no standard compounds, and yields identifiable proton-exchange mass spectra even when studying extremely complex hydrocarbon samples.

Buchanan (3) reported using CH_3OH and CD_3OD chemical ionization to characterize oxygen-containing compounds. This procedure can be used to distinguish between classes of compounds containing heteroatoms. Compounds such as substituted phenols that contain an acidic proton undergo ionization as well as proton exchange, whereas compounds such as aromatic ethers only undergo ionization. Thus, species that are often indistinguishable by their EI (e.g., phenols and methoxy benzenes, 1° , 2° , and 3° aromatic amines) can easily be identified by CI with deuterated reagents. Figure 5-11 shows some of the compound types for which this method can be used. Several trials on polar fractions of liquefaction products have been run and more work is planned.

5.3 REPRODUCIBILITY OF TUBING BOMB EXPERIMENTS

Three tubing bomb runs (T-048, T-099, and T-100) were made at nominally identical conditions to: 1) determine reproducibility between separate bombs in the same run and 2) to examine reproducibility between different runs. The nominal run conditions were: 1.5 grams of Zap I lignite (from the North American Coal Company), AO4 solvent, 360°C and 20 minute reaction time. Twelve bombs were used for each run; they are designated by letter beginning with A and running through L. Bombs A through F contained pure hydrogen feed gas with an initial pressure of 1400 psig, while bombs G through L were fed an equimolar mixture of hydrogen and carbon monoxide at the same initial pressure (1400 psig) at room temperature. Additionally bombs A and L contained hydrogen sulfide (H_2S) at an initial partial pressure of 100 psig.

FIGURE 5-9. CD₃OD ionization spectra of hydrocarbon fraction from CPU Run 41 light oil.

FIGURE 5-10. CI spectra peak assignment in liquefaction light oils.

Aromatic Alcohols Vs Aromatic Ethers

Primary Vs Secondary Vs Tertiary Amines

FIGURE 5-11. Compound types suitable for determination by chemical ionization methods.

Figure 5-12 shows the reactor temperatures for the three tubing bomb runs as a function of time. It will be noted that the sand bath heater was preheated to 700°F prior to introducing the twelve tubing bombs. The sand bath temperature then dropped suddenly and leveled off at 359°C. Figure 5-12 shows that the bath temperature was fairly close to 400°C for some time prior to introducing the tubing bombs in Run T-098. In Run T-099 the bath temperature was decreasing from a higher temperature shortly before the run started, and the temperature was noticeably cycling about 400°C in Run T-100. In every case, however, the temperature appeared to be stable at 400°C before the tubing bombs were inserted. The figure also shows that when the bombs were inserted the temperature response was slightly different in each case. In T-098, the bath temperature dropped suddenly to a level slightly below the desired final temperature before leveling off at 360°C. In Run T-099, there was a "spiked" temperature rise of about 10°-12°C upon insertion of the bombs; then the temperature dropped suddenly before leveling off at 360°C.

In Run T-100, there were problems inserting the bombs, and there was a more gradual drop in temperature. The bath temperature again leveled off at 360°C, but the "run time" was somewhat longer in this case than for the other two runs. All of this points out that tubing bomb runs are not routine, and some small differences can occur during operations.

FIGURE 5-12. Reactor temperature profiles for tubing bomb Runs T-198, T-099, and T-100

Table 5-10 shows conversion for the twelve bombs in each of the three tubing bomb runs that were made.

Statistical analysis of the conversion data indicated that for the pure hydrogen tests there were no significant differences in conversion between bombs within a single run nor were there significant differences between runs. For the syngas (equimolar mixture of hydrogen and carbon monoxide) tests, there were significant differences between bombs and between runs. Analysis also indicated that when H_2S was added to the reaction mixture, the overall conversion was significantly different for both gases (i.e., both pure H_2 and syngas).

More detailed statistical analysis is continuing, but there are indications that the temperature "spike" in Run T-099 caused the reaction mixture to "see" a somewhat higher temperature than was intended. The 10-12°C rise apparently was sufficient to significantly affect the overall conversion.

Difficulties encountered when inserting the tube bundle in Run T-100 may have contributed to the generally lower conversion in that run. It is clear that at the lower liquefaction temperatures where conversion and product distribution are relatively more sensitive to changes in temperature, more attention must be paid to the operation of the system if meaningful results are to be expected.

TABLE 5-10
OVERALL CONVERSION IN TUBING BOMB TESTS

Feed Gas	Bomb/Run	T-098	T-099	T-100
H ₂	B	29.1	29.7	28.5
H ₂	C	31.8	27.5	27.7
H ₂	D	22.8	--	14.8
H ₂	E	30.1	32.6	28.0
H ₂	F	19.7	29.6	30.1
H ₂ /CO	G	33.1	41.6	35.9
H ₂ /CO	H	38.8	42.0	44.1
H ₂ /CO	I	37.8	43.2	39.1
H ₂ /CO	J	39.8	48.6	41.1
H ₂ /CO	K	39.4	51.4	49.1
H ₂ /H ₂ S	A	51.0	69.7	58.2
H ₂ /CO/H ₂ S	L	65.6	71.9	63.9

6.4 REFERENCES

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6. 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 NO_x reduction step in conjunction with the high-temperature baghouse provides for simultaneous control of SO_x/NO_x emissions.

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

1. Investigate the effects of low-rank coal ash on the conversion of SO₂ to SO₃.
2. Evaluate NO_x emissions control using an ammonia injection/throwaway catalyst system on the 130-scfm propane-fired combustor/high-temperature baghouse system.
3. Evaluate enhanced sorbents (pressure hydrated lime/additive sorbents identified from bench-scale screening tests) on the 130-scfm propane-fired combustor/high-temperature baghouse system.
4. Investigate simultaneous SO_x/NO_x emissions control on the 130-scfm propane-fired combustor/high-temperature baghouse system, using techniques evaluated in 2 and 3 above.
5. Investigate simultaneous particulate/SO_x/NO_x control on a pc-fired system using the technique evaluated in 4 above.

6. Investigate pressure hydrated lime injection for retrofit SO_2 control evaluating effects on boiler fouling and ESP performance.
7. Conduct an engineering/economic evaluation of a dry process for simultaneous particulate/ SO_x/NO_x control.

The planned activities in the first quarter of the second year of the Cooperative Agreement included the following:

1. Complete preliminary bench-scale screening of potentially enhanced pressure hydrated lime/additive sorbents.
2. Complete evaluation of data from simultaneous particulate/ SO_x/NO_x control testing on the pc-fired combustor/high-temperature baghouse system.
3. Complete evaluation of commercial dolomitic hydrated lime and limestone injection tests on the pc-fired combustor/high-temperature baghouse system.
4. Resume bench-scale evaluation of potential throwaway NO_x reduction agents, focusing on hematite (Fe_2O_3) and NO_x reduction as a function of surface area.
5. Complete preparation of a paper entitled "Pilot-Scale Studies of Simultaneous Control of SO_x/NO_x Emissions Derived From the Combustion of Low-Rank Coal," for submission to the Pittsburgh Coal Technology Conference.
6. Complete the engineering/economic evaluation of a simultaneous particulate/ SO_x/NO_x control technique.

6.2 ACCOMPLISHMENTS

6.2.1 BENCH-SCALE SCREENING OF POTENTIALLY ENHANCED PRESSURE HYDRATED LIME/ADDITIVE SORBENTS

In the Quarterly Technical Progress Report for January through March 1984, a fixed-bed reactor was described and four hydrated lime/additive screening tests were reported to have been completed. This section details results of these tests, as well as three other tests in which the reactor was used to evaluate the SO_2 retention capabilities of hydrated lime/additive sorbents produced in the bench-scale pressure hydrator.

To conduct a test, 4.0 g of sample were placed into a sample bucket. Because most of the samples consisted of finely-sized calcium hydroxide formed by pressure hydration, kaowool was used to pack the sample into the sample bucket such that sorbent was not entrained into the gas stream. In later tests, circular pads cut from ceramic fabric filter cloth (Nextel, manufactured by the 3M Corporation) were substituted for the kaowool.

The sample bucket was placed in the reactor, all couplings were tightened and a leak-check ensued. When minimal or no leakage was detected, the furnace was heated until the bed temperature reached 1440° to 1600°F, after which the temperature was maintained by an electrical resistance heating element.

A gas mixture consisting of N₂, CO₂, O₂, and SO₂ was introduced into a manifold and subsequently through the reactor bypass loop to measure and adjust gas concentrations and flow rates. Table 6-1 lists typical gas concentrations employed during a run. After stable conditions were achieved through the bypass loop and the bed temperature held roughly constant for a period of ten minutes or more, the gas mixture was passed through the reactor.

TABLE 6-1
TYPICAL GAS INLET CONCENTRATIONS

N ₂	82%
CO ₂	14%
O ₂	4%
SO ₂	900 ppm

Outlet gas concentrations were monitored during the course of an experiment, with readings taken automatically at two-minute intervals by a Kaye Data Logger. Figure 6-1 illustrates the relationship between run duration and SO₂ concentration for Run PBR II.8. Typically during the initial stage of an experiment, an induction period occurs; CO₂ and O₂ concentrations remain at levels observed through the bypass loop, while SO₂ concentrations (as measured by DuPont Model 400 Photometric Analyzers) parallel bypass concentrations for about two minutes, then drop sharply. The estimated residence time from the reactor inlet to the analyzers is 45 s, and it is postulated that the induction curve results from relatively low gas velocities through the system coupled with uneven gas mixing in the reactor when the gas mixture is first introduced.

Starting materials consisted of quicklime (CaO) hydrated at a pressure of 100 psig at 350°F to produce pressure hydrated lime (Ca(OH)₂)

The highly-exothermic reaction produces a fully hydrated, submicron size material with a surface area of about 7 m²/g. In the reactor, decomposition of Ca(OH)₂ occurs at about 850°F

FIGURE 6-1. Sulfur dioxide concentration versus time for fixed-bed reactor screening tests.

Reaction of quicklime ensues with the flow of simulated flue gas through the bed:

Above 1350°F and in the presence of sufficient oxygen, Reaction [4] predominates and Reaction [3] does not occur to any measureable extent.

Recarbonation occurs according to Reaction [5]

Calcite has been identified in some, but not all of the reacted hydrate materials. Since CaCO_3 decomposes to CaO and CO_2 at 1517°F, it is believed that recarbonation occurs after the experiment is complete. Unreacted CaO scavenges atmospheric CO_2 (or CO_2 remaining in the reactor after completion of the run) to form CaCO_3 ; evidence to support this derives from the fact that samples which were not submitted for analysis immediately after a given run were the ones in which CaCO_3 was a major phase in x-ray diffraction scans.

Additives were incorporated in the solution in which the quicklime was hydrated. The report of the previous quarter described the process used. Furthermore, it was noted that the form of additive association was not discernible in the x-ray diffraction patterns generated, though CaCl_2 was identified in one sample which included a chloride additive.

Data and experimental conditions from seven tests are presented in Table 6-2. The heading Rdn_{60} in the table refers to the measured reduction of $[\text{SO}_2]$ through the reactor after 60 minutes. This value provides a relative measure of steady-state reactivity. The induction period, measured in seconds, refers to the time between introduction of the gas stream and the beginning of the exponential curve relating $[\text{SO}_2]$ and time.

TABLE 6-2
REACTOR CONDITIONS AND TEST RESULTS

Run	Sample	Bed Temp., °F	Flow Rate scfh	SO_2 Inlet ppm	Induction, S	RDN_{60}
PBR11.7	Salime	1470	15.6	1167	106	34
PBR11.8	Linwood	1545	11.4	787	283	48
PBR11.9	Salime	1475	13.6	770	106	31
PBR11.10	Salime 3% Na_2CO_3	1484	12.4	846	191	20
PBR11.11	Salime 10% Na_2CO_3	1441	12.6	837	899	51
PBR11.12	Salime 3% MnCl_2	1536	11.2	917	235	29
PBR11.13	Salime 10% MnCl_2	1505	13.2	866	184	27

With respect to reactivity measurement, the post-induction curve was used to derive kinetic parameters. Equation [6]

$$\ln [\text{SO}_2] = a \ln \left(\frac{1}{t} \right) + b \quad [6]$$

where t is the time in seconds, and a and b are constants, was found to provide a best fit for most of the data; Run PBR II.7 was not included in the reactivity measurements since a leak developed in the reactor later in the run. Equation [7]

$$\ln [SO_2] = a \left(\frac{1}{t}\right) + b \quad [7]$$

was applied to a portion of the data for Run PBR II.11. Table 6-3 lists regression coefficients and the number of data points used to generate the mathematical correlations.

TABLE 6-3
CORRELATION COEFFICIENTS

Test	N (Data Points)	r
PBR II.8	13	0.957
PBR II.9	12	0.995
PBR II.10	9	0.994
PBR II.11	5	0.991
PBR II.11	5	0.987
PBR II.12	15	0.973
PBR II.13	14	0.995

First order reaction mechanisms have been reported elsewhere to describe the reaction of calcium-based sorbents with SO_2 ; Davis and Keener (1) observed the sulfation of $Ca(OH)_2$ to proceed according to Equation [7], whereas Equation [6] was representative of the sulfation of CaO . As explained previously, decomposition of $Ca(OH)_2$ occurs at 850°F, and thus, agreement between the data and Equation [7] is anomalous. A possible explanation is that a high reactor pressure during heat-up may have made the decomposition of the hydrated lime thermodynamically unfavorable; upon introduction of flow through the reactor, the pressure decreased, allowing simultaneous dehydration and sulfation.

Agreement of data with values reported by Davis and Keener are equivocal, since the reaction temperatures were 1000°F lower in their study. Their investigation provided evidence that the reaction is chemically rate limited, both for CaO and $Ca(OH)_2$ at the lower temperature. It is not known whether sulfation of sorbents in this study is chemically rate controlled; a method described by Borgwardt (2) may be used in the future to ascertain the rate limiting mechanism.

Table 6-4 lists sorbent utilization values for select tests obtained by calculating ratios of SO_3 to CaO as determined using XRF techniques. For PBR II.9 and PBR II.10, values appear to be low. These low values may have occurred because of the recarbonation of CaO ; future samples shall be calcined prior to pellet formation to compare the utilization values obtained for the carbonate-free samples.

TABLE 6-4
SORBENT UTILIZATION

Run	Length of Run (hr)	Utilization, %
PBR II.8	2.0	22.3
PBR II.9	2.3	9.2
PBR II.10	1.5	3.3
PBR II.11	1.4	17.1

Samples submitted for XRD were observed to include lime (CaO), anhydrite (CaSO_4), and calcite (CaCO_3). Although the presence of additives is confirmed for the reacted materials, to date, x-ray diffraction scans do not indicate a phase representing chemical reaction between SO_2 and the additive. Further results are awaited to confirm this observation.

Surface area is considered to be a critical feature of the sorbents. Previously, a distinction was made between the surface areas of hydrated limes produced using Salime or Linwood lime (3); the former provides a pressure hydrated product with a surface area of $6.5 \text{ m}^2/\text{g}$, the latter yielding a product with a surface area of $14.0 \text{ m}^2/\text{g}$. As evidenced in Table 6-2, the material with a higher initial surface area proved more effective in capturing SO_2 . In dry sorbent studies conducted by EPRI (4), results suggest that a higher initial surface area does not necessarily correlate with higher sulfur capture, though sorbent samples subjected to furnace injection and collected by a probe were reported to undergo increasing sulfation with increasing particle surface area.

Thus far, only one reacted hydrated lime sample has been submitted for surface area determination. The material was produced using a hydration solution of 3% NaHCO_3 . The sulfated product resulted in a surface area of less than $1 \text{ m}^2/\text{g}$; low surface areas for many of the reacted hydrated lime samples are expected due to sulfation reactions and possibly particle sintering.

Tests have been completed in which additive-enhanced pressure hydrated limes were reacted with simulated flue gas, with salts of Na, Fe, Cu, and Mn as dopants. Analyses for these tests will be completed and reported, along with reactivity data. Based upon results obtained in this study, as well as evidence reported by others (5), a discussion of the effect of additives and the possible mechanisms by which dopants enhance sorbent utilization will be

reported. Additionally, changes being made in the reactor configuration will permit the use of a moist simulated flue gas. Some tests involving sulfation of hydrated lime at lower temperatures ($<1200^{\circ}\text{F}$) are under consideration. Finally, sintering characteristics of sodium-enhanced hydrated limes shall be evaluated.

Upon completion of tests to identify materials which enact significant reduction of SO_2 or NO_x , and based upon previous work, the fixed-bed reactor shall be employed in a matrix of tests aimed at simultaneous SO_2 and NO_x control. It is expected that an additive-enhanced hydrated lime may be incorporated in this aspect of the study.

6.2.2 SIMULTANEOUS PARTICULATE/ SO_x / NO_x CONTROL ON THE PC-FIRED AF COMBUSTOR/HIGH-TEMPERATURE BAGHOUSE SYSTEM

Data evaluation has been completed for a test performed in March on the pc-fired combustor/high-temperature baghouse system. The purpose of the test was to demonstrate simultaneous particulate/ SO_x / NO_x control. Resultant SO_x / NO_x control levels were less than 80%. Mechanical problems with a feeder/scale system were responsible for poor SO_2 control. Ash deposits plugging the SCR reactor caused poor NO_x control. Inadequate cleaning of piping upstream of the SCR reactor caused the plugging.

A similar test was performed in June of this past quarter. Sulfur dioxide reduction of 80% was achieved using calcitic pressure hydrated lime. The Ca/S ratio was 1.67 resulting in a utilization value of 48%. The injection point temperature and inlet SO_2 concentration were 1900°F and 700 ppm, respectively. Utilization of sorbent in the high-temperature baghouse, operated at about 950°F and an A/C ratio of 3.0 ft/min, was less than 10%.

Only a 70% reduction of NO_x emissions was observed during the test with the NH_3 /SCR system. Reactor temperature, NO_x concentration, and NH_3 / NO ratio were 735°F , 700 ppm, and 1.0, respectively. Previous tests at these conditions have always resulted in NO_x reduction of $>80\%$. The reduced performance of the SCR reactor may have been an artifact of the previous test during which ash plugging of the reactor was a problem. Additional testing with the NH_3 /SCR reactor is not planned at this time. Future simultaneous SO_x / NO_x testing will combine calcitic pressure hydrated lime injection for SO_2 control and a throwaway technique for NO_x control.

6.2.3 CALCIUM-BASED SORBENT INJECTION FOR SO_2 CONTROL ON THE PC-FIRED COMBUSTOR/HIGH-TEMPERATURE BAGHOUSE SYSTEM

Data presented in the January-March quarterly report showed SO_2 reduction and sorbent utilization values as high as 55% for calcitic pressure hydrated lime injection tests performed on the AF combustor/high-temperature baghouse system. Injection temperature, Ca/S ratio, and SO_2 concentration were 1900°F , 1.0, and 700 ppm, respectively. Figure 6-2 presents the SO_2 reduction data as a function of injection point temperature. Sulfur dioxide reduction in the baghouse never exceeded 7% for the six tests performed. Low SO_2 reduction in the baghouse is consistent with previous results. Operation of a baghouse at temperatures ranging from 800° to 1000°F may not increase utilization of

FIGURE 6-2. Sulfur dioxide reduction versus injection temperature for the pc-fired combustor/high-temperature baghouse system.

calcium-based sorbents enough to warrant use of a high-temperature baghouse only for SO₂ control. But in combination with a NO_x control technique, the 5% to 10% increase in sorbent utilization must be considered significant.

Lower SO₂ reduction at injection temperatures below 1900°F was probably a result of insufficient residence time in the flue gas temperature region where SO₂-CaO reaction kinetics are most favorable. As injection temperature increased from 1900°F, SO₂ reduction again decreased. This decrease may have been caused by sintering of the sorbent particles (reduced surface area development) or some interaction with the fly ash. Although fly ash interference is possible, injection tests performed at UNDERC have not shown fly ash interference to be a problem. Figure 6-3 presents SO₂ reduction as a function of injection temperature for the natural gas-fired injection tests. Although the curve is similar to that in Figure 6-2, actual SO₂ reduction is slightly lower for tests performed during natural gas-firing.

Test results from the pc- and natural gas-fired system were different from those obtained from the propane-fired system in that maximum SO₂ reduction and hydrated lime utilization were observed when injecting the hydrated lime into a temperature regime of about 1900°F rather than 2800°F. This would indicate the overall time/temperature profile of the pc-/natural gas-fired combustion system was more favorable at lower flue gas temperatures than those reported for the propane-fired system. Hydrated lime utilization values of 40% to 55% have been achieved in both cases for Ca/S ratios ranging from 0.8 to 2.0.

FIGURE 6-3. Sulfur dioxide reduction versus injection temperature for natural gas-fired injection tests.

Two injection tests were performed at Ca/S ratios of 1.0 but at SO₂ levels of 1300 and 3000 ppm. Results from these tests, presented in Table 6-5, showed SO₂ reduction remained in the 45% to 50% range for the higher SO₂ levels. Injection tests have not yet been performed at Ca/S ratios exceeding 1.0 for SO₂ levels greater than 700 ppm.

A single injection test was also performed using a commercial dolomitic hydrated lime. The specific sample used for this test was collected from a commercial hydration facility prior to ball milling. Test conditions and SO₂ reduction data are presented in Table 6-6 (Test No. 0484.9). The resulting SO₂ reduction for this test was about 40%, as compared to the 55% value obtained with the calcitic pressure hydrated lime produced in the bench-scale pressure hydrator. Without further testing, it is not clear whether this difference is due to the composition of the dolomitic hydrate (presence of MgO), or to the differences in pressure hydration equipment used.

Table 6-6 presents some physical property data for both the UNDERC calcitic pressure hydrate and the commercial dolomitic pressure hydrate. The table does not identify any significant differences other than the presence of MgO in the dolomitic material. The particle size distribution data is believed to be erroneous. Commercial manufacturers of pressure hydrated lime claim an average particle size of ~0.4 μm prior to ball milling. In addition, SEM micrographs of calcitic hydrated lime produced in the bench-scale pressure hydrator have shown an average particle size of <1.0 μm. Recent measurements

TABLE 6-5

PRESSURE HYDRATED LIME SO₂ REDUCTION DATA

Test ^a No.	Total SO ₂ Reduction, %	SO ₂ Conc. ppm	Ca/S ^{b,c}	Sorbent Utilization, %
0584.1	55 725	1.0	55	
0584.5	45 1320	1.0	45	
0584.7	48 3000	1.0	48	
0484.9	40 740	1.0	40	

^aInjection temperature, baghouse temperature, and air-to-cloth ratio were nominally 1900°F, 940°F, and 3.0 ft/min), respectively.

^bThe sorbent used in tests 0584.1, 0584.5, and 0584.7 was a calcitic pressure hydrated lime (75% CaO) produced in the bench-scale pressure hydrator.

^cThe sorbent used in test 0484.9 was a commercial dolomitic pressure hydrate (40% CaO and 30% MgO).

TABLE 6-6

PHYSICAL PROPERTIES OF PRESSURE HYDRATED LIME
USED IN DIRECT INJECTION TESTS

<u>UNDERC</u> Type:	<u>Commercial</u> Calcitic:	Dolomitic:
Surface area ^a	13-15 m ² /g	18 m ² /g
Particle size distribution ^b	80% < 4.0 μm	80% < 6.5 μm
Wt. % CaO ^c	75%	40%
Wt. % MgO ^c	--	30%
Density (139 lb/ft ³)	2.23 g/cm ³ (137 lb/ft ³)	2.20 g/cm ³

^aSurface area determined using BET Monosorb technique.

^bParticle size distribution determined using Coulter Counter.

^cWt. % CaO and MgO determined from XRF.

^dDensity determined using Helium-Air Pycnometer.

using a TSI Model 3300 Aerodynamic Particle Sizer indicated that the mean particle diameter for a dry sample of hydrated Linwood lime was about 2.0 μm , while the same sample introduced as an aerosol through a TSI Model 3460 Tri-jet Aerosol Generator measured a mean particle diameter of about 0.7 μm . The TSI instruments appear to provide a more precise tool for the measurement of very finely sized particles (6).

This information indicates that coulter counter analysis is not a good quantitative technique for determining the particle size distribution of pressure hydrated lime, since the lime particles readily stick together, creating a dispersion problem when attempting to perform coulter counter analysis. Despite this problem and the relative insensitivity of coulter counter to particles less than 2 μm , data can be used qualitatively to compare samples of pressure hydrated lime.

6.2.4 PACKED-BED EVALUATION OF POTENTIAL THROWAWAY NO_x REDUCTION AGENTS

Bench-scale fixed-bed testing of potential throwaway NO_x reduction agents was resumed the last week of the quarter. Initial test plans for the second quarter include the following:

1. One series of tests will be conducted to verify previously reported data involving the catalytic activity of a lignite fly ash in the reduction of NO_x .
2. A sample of $\delta\text{-Fe}_2\text{O}_3$ will be tested in the fixed-bed reactor to evaluate NO_x reduction.
3. A limited number of tests will be conducted evaluating NO_x reduction as a function of surface area.

Work conducted by Pence et al (7) with synthetic mordenite supports NO_x reduction results reported previously by UNDERC (8). Subsequent work failed to identify other zeolites capable of promoting NO_x reduction. Therefore tests evaluating NO_x reduction as a function of surface area are not expected to show significant NO_x reduction.

6.2.5 REPORT ON SIMULTANEOUS SO_x/NO_x CONTROL

Preparation of a report entitled "Pilot-Scale Studies of Simultaneous Control of SO_x/NO_x Emissions Derived From The Combustion of Low-Rank Coal" has been completed. An abstract of the paper was submitted and has been accepted for presentation at the Pittsburgh Coal Technology Conference to be held September 17-21, 1984. The paper is currently being reviewed prior to being submitted for publication in the proceedings of the Pittsburgh Coal Technology Conference.

6.2.6 ENGINEERING/ECONOMIC EVALUATION OF A SIMULTANEOUS PARTICULATE/ SO_x/NO_x CONTROL TECHNIQUE

Preparation of an engineering/economic evaluation of a simultaneous particulate/ SO_x/NO_x control technique is about 20% complete. The control technique to be evaluated proposes a high-temperature baghouse and ceramic filters for particulate control, furnace injection of pressure hydrated lime

for SO₂ control, and selective catalytic reduction (SCR) for NO_x control. Recent discussions with members of the Senior Technical Committee have raised questions concerning the focus of the evaluation. Specific questions included:

- 1) Is it reasonable to evaluate selective catalytic reduction (SCR) for NO_x control in light of economic information currently available?
2. Is it reasonable to evaluate a throwaway catalytic NO_x reduction technique when a specific throwaway catalyst capable of 80% NO_x control has not been identified?
3. Is it reasonable to include the high temperature baghouse concept since the apparent advantage with respect to sorbent utilization is relatively small (5% to 10%)?

Work on the evaluation will be delayed until these questions are resolved in discussions with members of the Grand Forks Project Office.

6.3 REFERENCES

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7. PARTICULATE CHARACTERIZATION

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, 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 provide data which may be used to assess environmental effects of emissions and of new or revised emissions standards, which may relate to respirability, ultrafine particle emissions, or metal content.

7.2 ACCOMPLISHMENTS

7.2.1 THE INFLUENCE OF FLY ASH PROPERTIES ON BAGHOUSE EMISSIONS

Experimental data generated to date show that baghouse emissions are highly dependent on coal type (Table 7-1). Furthermore, there is a strong correlation between ash composition and baghouse penetration. The strongest correlation between baghouse penetration and individual elemental composition is with sodium. The correlation is inverse with higher sodium concentrations correlating with lower baghouse emissions. Other elements which appear to correlate inversely with baghouse penetration are magnesium, phosphorous, and sulfur. Previously (1) it was shown that combining magnesium and sodium gave a stronger correlation than either of these alone. Since the last quarterly report, additional data points have been added and further analysis has been completed to obtain an even better correlation between baghouse emissions and ash composition. Figures 7-1 through 7-3 are graphs of baghouse penetration versus elemental composition for Na_2O , MgO , and P_2O_5 . The graph for Na_2O (Figure 7-1) shows a strong inverse correlation even though there is some data scatter. The graph for MgO (Figure 7-2) shows a weaker inverse correlation with again a fair amount of data scatter. The graph for P_2O_5 (Figure 7-3) shows the inverse relationship but with a large amount of data spread. Figure 7-4 shows the correlation when MgO and Na_2O have been combined in the form $0.8 \text{ MgO} + \text{Na}_2\text{O}$. This relationship resulted from performing regression analysis

FIGURE 7-1. Penetration versus Na_2O for 24 shaker chamber tests.

FIGURE 7-2. Penetration versus MgO for 24 shaker chamber tests.

FIGURE 7-3. Penetration versus P_2O_5 for 24 shaker chamber tests.

with various coefficients for MgO . A coefficient of 0.8 gave the highest R^2 value. In comparing Figure 7-4 with Figures 7-1 and 7-2, it is apparent that there is much less data scatter when MgO and Na_2O are combined. In Figure 7-5 P_2O_5 has been added to see if this will give an even better curve fit. It appears that by adding 4 P_2O_5 to the $0.8 MgO + Na_2O$, the correlation is improved. At this point the coefficient for P_2O_5 has not been optimized; however, a coefficient of 4 was strategically chosen high enough to affect the overall relationship since the average P_2O_5 levels are much lower than MgO and Na_2O (see Table 7-1).

In order to statistically evaluate the correlations, regression analysis was completed to determine what mathematical model best fits the data and to determine which elements or combination of elements give the best curve fit. Initially multiple regression analysis indicated that the data best fit a curve of the form $y = ax^b$ so this was used for subsequent regression analysis. The program used will fit a set of data points (x,y) to the curve described by the equation $y = ax^b$ with regression analysis by the method of least squares. The analysis is reduced to linear regression by rewriting with natural logarithms: $\log y = \log a + b \log x$ and substitution back into the above equation with $Y_1 = \log y$, $A_1 = \log a$, $X_1 = \log x$; $Y_1 = A_1 + bX_1$. Least squares regression is then performed, and A_1 is converted back to a .

For each set of data points the program computes the geometric curve which best fits the given data along with the coefficient of determination or R^2 . The results of the regression analysis are given in Table 7-2. The analysis shows a strong correlation with sodium with an R^2 value of 0.69. When the

FIGURE 7-4. Penetration versus MgO and Na₂O for 24 shaker chamber tests.

FIGURE 7-5. Penetration versus Na₂O, MgO, and P₂O₅ for 24 shaker chamber tests.

TABLE 7-1
EFFICIENCY AND FLY ASH ANALYSIS

Name	Coal			Inlet Dust Loading grains/SCF	Baghouse Removal Efficiency, %	Baghouse Penetration, %	Fly Ash Analysis Pct Concentration as Oxides									
	Symbol	Source	Rank				SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	P ₂ O ₅	CaO	MgO	Na ₂ O	K ₂ O	SO ₃
Big Brown	BB1	Freestone Co., TX	Lignite	5.0	76.0	24.0	53.6	17.7	7.4	1.6	0	14.7	3.0	0.44	0.9	1.2
Big Brown	BB2	Freestone Co., TX	Lignite	6.4	83.5	16.5	53.0	19.7	7.7	1.6	0	13.3	3.0	0.37	1.1	0.7
Phillips "A"	PA	Panola Co., TX	Lignite	5.3	86.3	13.7	59.2	13.8	11.9	1.4	0	9.8	1.7	0.81	1.2	0.9
Choctaw (washed)	CW	Choctaw Co., AL	Lignite	2.7	89.6	10.4	25.2	12.6	19.1	1.0	0.2	26.7	2.4	0.70	0.7	11.7
Pike Co.	PK	Pike Co., AL	Lignite	3.6	90.0	10.0	34.4	18.8	6.9	1.6	0.1	27.5	1.9	0.71	0.3	8.5
WB Coal	WB	Western USA	Bituminous	2.0	91.9	8.1	62.0	22.6	4.9	1.2	0.6	3.0	1.4	1.3	2.4	0.5
Choctaw (unwashed)	CA	Choctaw Co., AL	Lignite	4.6	92.2	7.8	32.2	13.2	26.8	0.9	0.1	13.8	2.5	0.54	1.1	9.4
Naughton	NT	Lincoln Co., WY	Subbit.	1.6	93.6	6.7	56.4	15.9	8.3	0.9	0.1	7.7	3.2	0.20	1.7	0.8
Arapahoe	AR	Routt Co., CO	Subbit.	2.8	95.5	4.5	58.4	24.8	3.9	1.2	0.7	6.4	2.1	0.60	1.6	0.9
San Miguel	TL1	Atascosa Co., TX	Lignite	12.0	99.1	0.9	60.2	20.1	3.7	1.1	0.04	5.4	1.1	3.6	2.6	1.2
Antelope High Na	AN max	Wyoming	Subbit.	1.5	99.1	0.9	35.9	10.4	7.1	1.2	0.5	28.6	6.1	2.4	0.6	7.3
Beulah Low Na	BW	Mercer Co., ND	Lignite	3.2	99.3	0.7	38.2	7.4	12.1	1.7	0.2	19.3	5.2	5.8	0.2	9.7
Velva	V5	McLean Co., ND	Lignite	2.5	99.4	0.6	32.9	13.2	6.6	1.3	0.1	30.3	6.4	3.2	0.6	5.3
San Miguel	TL2	Atascosa Co., TX	Lignite	6.2	99.4	0.6	47.8	16.5	8.3	1.2	0	13.1	1.7	5.3	2.2	3.8
Antelope Low Na	AN low	Wyoming	Subbit.	2.8	99.4	0.6	47.7	19.7	4.1	2.0	1.3	17.6	4.2	1.1	0.6	1.8
Caballo/ Spring Creek	NE/SP	Cambell Co., WY	Subbit.	1.9	99.5	0.5	37.6	15.1	6.6	2.0	0.6	26.2	4.3	2.4	0.4	4.7
Velva	V3	McLean Co., ND	Lignite	1.9	99.5	0.5	18.4	10.7	6.4	0.7	0.4	42.2	9.9	3.2	0.1	8.2
Antelope Medium Na	AN med	Wyoming	Subbit.	1.7	99.5	0.5	29.7	14.0	8.8	1.4	0.7	30.9	6.3	1.3	0.4	6.5
Sarpy Creek	SC	Big Horn Co., MT	Subbit.	3.5	99.65	0.35	36.1	16.3	6.8	1.2	0.2	26.2	2.9	5.0	0.8	4.0
Wyodak	WD	Campbell Co., WY	Subbit.	2.4	99.69	0.31	36.2	15.7	7.4	1.7	0.9	27.3	5.5	1.7	0.4	3.4
Indian Head	I3	Mercer Co., ND	Lignite	2.5	99.7	0.3	29.2	12.4	11.5	1.0	0.4	20.6	5.3	10.2	1.1	8.3
Antelope/ Spring Creek	AW/SP	Wyoming	Subbit.	1.6	99.8	0.2	36.9	13.1	7.5	1.3	0.6	25.5	5.2	3.1	0.5	6.5
Velva	V4	McLean Co., ND	Lignite	2.0	99.8	0.2	14.8	9.5	7.6	0.8	0.5	41.4	9.4	4.3	0.1	11.7
Beulah High Na	BA	Mercer Co., ND	Lignite	2.1	99.8	0.2	25.5	12.3	11.2	1.1	0.5	18.1	4.3	13.7	0.6	12.9

TABLE 7-2

REGRESSION ANALYSIS FOR CORRELATIONS BETWEEN BAGHOUSE
PENETRATION AND ELEMENTAL CONCENTRATIONS FOR 24 COALS

Elemental Comparison	Mathematical Model Penetration =	Coefficient of Determination R^2
Penetration vs Na_2O	$2.86 [\text{Na}_2\text{O}]^{-1.23}$	0.69
Penetration vs MgO	$12.0 [\text{MgO}]^{-1.69}$	0.38
Penetration vs P_2O_5	$0.63 [\text{P}_2\text{O}_5]^{-.385}$	0.31
Penetration vs .8 MgO + Na_2O	$55.2 (.8[\text{MgO}] + [\text{Na}_2\text{O}])^{-2.23}$	0.80
Penetration vs 4 P_2O_5 + .8 MgO + Na_2O	$117 (4[\text{P}_2\text{O}_5] + .8[\text{MgO}] + [\text{Na}_2\text{O}])^{-2.36}$	0.86

lignites are considered by themselves the R^2 value is even higher. It is apparent from Figure 7-1 that the lignite and subbituminous coals follow separate but parallel trendlines; however, the regression analysis which resulted in an R^2 value of .69 included all 24 data points. The R^2 value for MgO was only 0.38 and the value for P_2O_5 was 0.31, which show that these correlations are weak compared to Na_2O . When Na_2O and MgO are combined the R^2 value is 0.80. When P_2O_5 is added the R^2 value increases still further to 0.86. This indicates that these three elements have a combined effect on baghouse emissions which follows the equation in Table 7-2. It should be noted that this equation is for the single combination of fabric and shaker cleaning cycle previously reported (2). The value of the model at this stage is not in describing baghouse penetration in general but rather in documenting the influence that ash composition can have on baghouse emissions. The model is certainly not complete with only three elements but it does show that adding elements can improve the correlations and suggests that additional elements such as sulfur should be considered. After learning which elements have the greatest effect on baghouse emissions, one can begin to look at the mechanism involved to gain an understanding of the cause of extreme differences in emission behavior with different coals.

Speculation as to the causes of the differences include particle size distribution (PSD), surface morphology, electrical effects, and ash cohesiveness. PSD will likely have an effect but it is not clear that a finer PSD is always more difficult to collect. Our test data continue to show that there is a broad spectrum of PSD among both the coals with easily collected ash and the coals with difficult to collect ash, indicating no clear correlation between penetration and PSD. Surface morphology will likely have an effect on the way ash builds up on a fabric layer and on the resulting ash cohesiveness. Our results show differences in surface morphology for difficult and easily collected ash which will be presented in the next

section. Studies with electrically enhanced fabric filtration have shown that electrical effects can be very important in fabric filtration (3). Recent tests with a unique felted fabric, which is a blend of glass and Teflon fibers, show that this fabric has superior filtering characteristics to fabrics constructed of either glass or teflon alone (4). It is suspected that the different triboelectric characteristics of the two fibers contribute to electrostatic effects which enhance filtration characteristics. In any case since the electrical properties of ash are composition dependent, efforts should continue to evaluate how ash chemistry affects fabric filtration. Also since the primary concern is with fine particle emissions, not only the bulk ash composition should be considered, but also composition as a function of size. Some of our data on ash composition as a function of size will be presented in a later section of this report.

The adhesive and cohesive nature of the ash is also important in fabric filtration. Initially, in starting with a new fabric, ash particles must adhere to the filter fibers and build up on the fabric in such a way that larger openings in the fabric structure (such as occur in woven glass fabrics) are bridged over resulting in reduced particle penetration through the fabric. Once a dust cake is heavy enough to cause high pressure drop the fabric must be cleaned by reverse air, pulse jet, or mechanical shaking. It is desirable, especially for woven fabrics, to operate a cleaning cycle so that enough of the dust cake is removed to lower the pressure drop, but not too much to cause a serious decrease in removal efficiency. In other words the cleaning cycle should be optimized to maintain an adequate residual dust cake which in turn is dependent on the adhesive and cohesive nature of the ash. Tests with Beulah, North Dakota lignite show that the high-removal efficiencies of 99.9+% can be achieved after only a few hours from starting with new fabric, indicating that only a very light residual dust cake is necessary for this ash. Apparently the adhesive/cohesive nature of this ash gives it excellent filtration properties. Tests of coals with difficult to collect ashes indicate that an adequate residual dust cake is not maintained with the same cleaning cycle as the Beulah tests. One longer test showed that this did not improve even after 100 hours of operation. This indicates that the adhesive/cohesive nature of this ash is very different. We have also observed that the most difficult to collect ash will not adhere well to a glass dust loading filter, indicating a lack of adhesion between the glass filter and the dust cake. One of the problems in trying to study the adhesive/cohesive properties of the ash, however, is the lack of standard measuring technique. It would be desirable to measure quantitatively the cohesiveness of fly ash in the laboratory and determine the correlation with observed differences in fine particle emissions from a fabric filter.

7.2.2 SURFACE MORPHOLOGY COMPARISONS

One of the ash characteristics that will likely have an effect on the collectability in a fabric filter is the surface morphology of the ash. Even though fly ash from pc-fired combustion consists primarily of spherical particles, there are several different aerosol formation mechanisms which contribute to a variety of particles present and to the surface morphology (5). Fisher, (6) for example, using light microscopy defined 11 major classes of coal fly ash particles. Small (7) reported 11 different morphological particle types in coal fly ash by using SEM to evaluate surface characteristics. In any case, the resulting particulate matter will depend on

the mineralogical composition of the coal as well as on combustion conditions. To gain insight on the effect of particle morphology on fabric filter emissions, we will compare the particle morphology of easily collected ash with that from difficult to collect ash. At the two ends of our penetration data are Big Brown Texas lignite which has shown the poorest collection efficiency, and Beulah and Indian Head, North Dakota lignites which have shown high collection efficiency. In this section a comparison of the surface morphology of these two ashes is made, not to make a complete morphological characterization, but rather to note any clear differences in these two ashes.

In the first comparison SEM micrographs were taken from the deposits of a University of Washington Mark 5 impactor which sampled at the outlet of the baghouse. In Figures 7-6 through 7-9 the morphology of the Indian Head outlet ash is compared with Big Brown ash. Figure 7-6 shows stage 2 particles which are in the range of 3 to 10 μm in size. In both cases the particles are mainly spherical, although close examination will reveal some irregularly shaped particles. The magnification used is 1000X with an enlarged view of 5000X for the framed in portion. The main difference that can be noted is the smooth surface of the Big Brown particles while the Indian Head particles have rough surface deposits of them. The Indian Head particles look as though they were originally formed as smooth spheres and subsequently picked up surface deposits, either by very fine particle deposition or by the condensing of volatile species on the surface of the larger particles. In looking at Figure 7-7, particles from stage 3 of the impactor, which are 2 to 3 μm in size, the difference is still apparent--Indian Head particles have surface deposits while the Big Brown particles have smooth surfaces. This same difference holds true for stages 4, 5, and 6 of the impactors; however, by stage 7 (0.5 to 1 μm particles) there appears to be a change in morphology for the Indian Head fly ash. The Big Brown particles are still predominantly smooth spheres but the Indian Head particles are a mix of spheres and cylindrical shapes with more irregularly shaped particles than spheres (Figure 7-8). There is definitely a major difference in particle morphology in this size range for the two ashes. This same particle morphology appears to hold for stages 8 through 11 of the 11-stage impactor. Figure 7-9 shows the impactor backup filters for the two ashes. A blank filter would appear as smooth glass fibers so all deposits on the fibers are very fine fly ash particles <0.3 μm . The Indian Head particles appear to be mostly spherical or egg-shaped. The irregular shapes present in impactor stages 7 through 11 do not appear here. The smallest particles for big Brown also appear to be spherical and are similar to the smallest Indian Head particles. There are a number of much larger particles on the Big Brown filter that theoretically should not be there. They are apparently there because of particle bounce or reentrainment in upper impactor stages. This is another difference that we have noted between Big Brown and Beulah or Indian Head. That is, Big Brown ash appears to be much more subject to particle bounce in an impactor. It should be noted that these impactor tests were done without any grease substrate on the plates to prevent interference of the grease in the analysis. Normally one would coat the plates with a light layer of grease to help prevent particle bounce. We have seen, however, that even when grease is used in the impactor, the Big Brown ash is still much more subject to particle bounce.

Indian Head N.D. Lignite

Big Brown TX Lignite

FIGURE 7-6. Stage 2 from outlet impactor tests.

— 2 μ m

Indiar Head N.D. Lignite

Big Brown TX Lignite

FIGURE 7-7. Stage 3 from outlet impactor tests.

— 2 μ m

Indian Head N.D. Lignite

Big Brown TX Lignite

FIGURE 7-8. Stage 7 from outlet impactor tests.

— 2 μ m

Indian Head N.D. Lignite

Big Brown TX Lignite

FIGURE 7-9. Backup filter from outlet impactor tests.

— 2 μ m

SEM comparisons were also made of size fractionated fly ash from the inlet of the baghouse collected with either 3-stage or 5-stage multicyclones. Figure 7-10 shows a SEM comparison of stage 1 ash for Beulah and Big Brown lignites with a magnification of 1000X. The samples consist of particles which have aerodynamic diameters $\geq 10 \mu\text{m}$. In both cases there are mostly spherical particles with some irregular shapes. The major difference, however, is again the large amount of surface deposits on the Beulah ash while the Big Brown particles are relatively free of surface deposits. Figure 7-11 shows backup filter samples for these two ashes at a 10,000X magnification. The particle size is $\leq 1 \mu\text{m}$. The Big Brown ash consists of spherical particles while the Beulah sample for submicron particles shows mainly nonspherical particles with many cylindrical and irregular shapes.

Results clearly show there are two major differences in particle morphology between Big Brown Texas lignite and Beulah or Indian Head North Dakota lignite. First, for larger particles in the range of 2 to 20 μm , there are surface deposits on the Indian Head and Beulah lignites which are noticeably absent in Big Brown lignite. This results in a rough surface texture for the Indian Head and Beulah, compared to a very smooth surface for Big Brown. Second, for particles in the size range of 0.3 to 1 μm , the Indian Head and Beulah ashes consist of largely nonspherical and irregular shapes while the Big Brown ash consists of spherical particles. Since the rough surface texture is noted with the ashes that are easily collected, one can speculate this makes the particles more cohesive and subsequently enhances particle collection. The smooth surface texture of the Big Brown ash, on the other hand, may inhibit agglomeration of particles on the fabric surface so that particles slide over one another and eventually work their way through the fabric contributing to high emissions. One must use caution in using these results to explain the observed differences in baghouse emissions with different coals, since the comparison is only among 3 of the 24 coals and since other factors such as particle size distributions and electrical effects may also affect emissions. It does, however, offer a plausible explanation for the observed differences of both physical and chemical characteristics since higher concentrations of more volatile constituents such as organically bound magnesium and sodium could contribute to more surface deposition on larger particles.

7.2.3 ELEMENTAL CONCENTRATION AS A FUNCTION OF PARTICLE SIZE

The correlations presented earlier relating baghouse emissions with elemental concentrations were for the bulk fly ash compositions. The SEM surface morphology results suggest there may be different elemental concentrations with decreasing particle size since there are changes in particle morphology with size. Others have shown varying degrees of elemental enrichment with decreasing particle size (5) and surface enrichment of certain elements on fly ash (8). Previous research at UNDERC (9) has shown that for Beulah, North Dakota lignite, both Na_2O and SO_3 occur in higher concentrations on the surface of larger particles. They also increase in bulk concentration with decreasing particle size.

Beulah N.D. Lignite

Big Erown TX Lignite

FIGURE 7-10. Fly ash from SASS train cyclone 1 samples at 1000X.

Beulah N.D. Lignite

Big Brown TX Lignite

FIGURE 7-11. Fly ash from multicyclone backup filters at 10,000X.

Table 7-3 gives the elemental concentrations for size fractionated samples collected with a SASS high-volume stack sampler. Stage 1 has a D_{50} cut point of 10 μm ; stage 2 has a cut point of 3 μm ; and stage 3 has a cut point of 1 μm . The SASS sampler can collect gram-size samples in all three stages which are large enough for x-ray fluorescence analysis.

The data show that for Beulah, North Dakota lignite and Sarpy Creek subbituminous coals, which showed good baghouse removal efficiencies, there is substantial enrichment of Na_2O with decreasing size. This includes Run 231 (Beulah) which had been ion exchanged to reduce the sodium level. For San Miguel Texas lignite, which also showed good removal efficiency, the sodium level did not clearly increase with decreasing particle size even though the average Na_2O level was still quite high at 3.2% to 4.9%. For Arapahoe and Big Brown coals, which showed poor baghouse removal efficiency, the sodium level remained below the 0.5% detection level of the instrument. SO_3 is greatly enriched in the fines for Beulah but there is also some enrichment for the Texas lignite. Arapahoe and Sarpy Creek data do not indicate a clear trend for SO_3 . Fe_2O_3 is substantially depleted in the fines for Sarpy Creek and Beulah while it is somewhat enriched for Arapahoe. It shows no clear trend for the Texas lignites. SiO_2 is depleted in the fines for all coals except Sarpy Creek for which there is a slight enrichment. Al_2O_3 is enriched in the fines for all coals except Beulah for which it remains fairly constant. The ion-exchanged Beulah, however, shows a depletion of Al_2O_3 with smaller fly ash particles. TiO_2 appears to increase in concentration with finer particles for Sarpy Creek, Beulah, and San Miguel while Arapahoe and Big Brown remain fairly constant. The trend for P_2O_5 in the four cases where the concentration is above the 0.1% detection level of the instrument, is higher concentrations with smaller particle size. CaO shows varying trends in that it is significantly depleted in Sarpy Creek and Beulah, is fairly constant for Arapahoe and Big Brown, and is somewhat enriched for San Miguel. MgO also shows varying trends. It is enriched in the fines for Sarpy Creek and Arapahoe, shows no clear trend for Big Brown and ion exchanged Beulah and one San Miguel sample, and is depleted for Beulah and the other San Miguel sample. Finally, K_2O is enriched in the fines for Sarpy Creek, Arapahoe, and Beulah, is somewhat depleted for the Texas lignites, and shows no clear trend for ion-exchanged Beulah. The results clearly show there is enrichment of some major elements in the fly ash with decreasing particle size but the enrichment/depletion characteristics are highly coal specific. The most general trends are the enrichment of SO_3 and the depletion of SiO_2 with decreasing particle size.

The next logical step is to use these elemental enrichment or depletion trends to explain the differences in morphology between Beulah or Indian Head North Dakota lignite and Big Brown Texas lignite (presented in the previous section). The most obvious difference in elemental enrichment is the large increase in Na_2O and SO_3 for finer particles with Beulah, which is absent with Big Brown. One can deduce that Na_2O and SO_3 must have a key role in forming the surface deposits present and in forming the irregular shapes of submicron particles. Particle size distributions of the two coals presented in a previous report (1) reveal that the Beulah ash has a much higher concentration of submicron particles than Big Brown. The implication is that higher levels of Na_2O and SO_3 are promoting a finer particle size distribution. These results show that there must be different coal specific particle formation

TABLE 7-3

X-RAY FLUORESCENCE ANALYSIS OF SIZE FRACTIONATED FLY ASH
COLLECTED WITH SASS TRAIN MULTICYCLONE

Coal	PTC Run	Cyclone Stage	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	P ₂ O ₅	CaO	MgO	Na ₂ O	K ₂ O	SO ₃
Sarpy Creek	SC-199	1	36.5	17.5	6.6	1.2	.2	26.9	2.5	3.6	.8	4.3
		2	37.3	21.1	3.6	1.3	.3	20.1	3.0	7.2	1.2	4.9
		3	38.9	22.8	3.5	2.1	.4	15.1	3.6	8.1	1.3	4.1
Arapahoe	AR-205	1	59.1	26.0	3.1	1.1	.5	5.8	1.8	<.5	1.7	.5
		2	53.0	27.7	4.8	1.5	1.2	6.7	2.6	<.5	1.8	.5
		3	50.7	28.9	5.8	1.3	1.8	5.3	3.3	<.5	2.1	.8
Arapahoe	AR-206	1	59.4	25.5	3.1	1.1	.5	6.0	2.1	<.5	1.7	.7
		2	52.8	28.4	4.7	1.5	1.1	6.7	2.5	<.5	1.8	.5
		3	51.7	30.5	4.1	1.1	1.8	5.1	3.2	<.5	1.8	.7
Big Brown	BB-209	1	53.7	17.3	7.4	1.8	<.1	15.1	2.6	<.5	1.0	1.1
		2	52.1	20.2	6.5	1.6	<.1	14.0	3.2	<.5	1.0	1.4
		3	45.4	23.0	7.7	1.9	<.1	16.6	2.7	<.5	.7	2.0
Beulah	BA-215	1	26.9	13.3	14.3	1.1	.3	20.2	4.6	11.0	.5	7.9
		2	26.0	13.8	8.7	1.2	.5	16.3	3.8	14.7	.7	14.2
		3	21.9	13.2	6.0	1.7	.8	11.2	2.8	17.9	1.2	23.5
Beulah	BA-220	1	28.1	12.7	13.8	1.1	.2	21.1	4.9	10.5	.5	6.9
		2	25.8	13.2	8.7	1.2	.5	16.3	3.9	14.6	.8	14.2
		3	21.9	12.9	5.8	1.4	.8	10.4	2.4	19.2	1.3	24.1
San Miguel	TL-226	1	62.6	19.5	3.8	1.0	<.1	5.1	1.0	3.5	2.9	.7
		2	55.6	22.1	3.6	1.5	<.1	8.4	1.4	4.2	1.9	1.2
		3	51.4	21.4	4.4	1.9	.2	11.4	1.7	3.2	1.3	3.1
San Miguel	TL-230	1	61.6	19.3	4.0	1.0	<.1	5.8	.9	3.5	3.0	.9
		2	56.1	23.8	3.1	1.4	<.1	6.2	1.2	4.9	1.9	1.5
		3	54.2	24.0	3.1	1.4	<.1	6.3	.9	4.9	1.9	3.3
Beulah (Ion Exchanged)	BI-231	1	36.2	16.1	12.4	1.0	<.1	19.0	4.6	5.5	.8	4.4
		2	28.7	17.4	9.6	1.3	<.1	21.1	5.3	9.2	.5	8.9
		3	32.5	10.2	9.4	1.8	<.1	14.8	4.1	8.4	.9	10.0

mechanisms present which produce different particle morphology, different particle size distributions, different elemental enrichment/depletion characteristics, and different collector performance. Because of the complex nature of inorganic material in coal and the rapid transformations that occur in combustion, it is difficult to explain the causes for varying chemical and physical properties of fly ash which have been noted. The results do, however, document the differences in particle characteristics that occur and the resulting dramatic effect it can have on emissions from fabric filters. The results emphasize the need for a more thorough understanding of particle formation mechanisms in coal combustion systems. This would facilitate the prediction of particulate characteristics on the basis of ash composition and ultimately enable the design of collectors which are optimized for the highest level of fine particulate control based on coal specificity.

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8. WASTE CHARACTERIZATION

Project No.: 7204

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8.1 GOALS AND OBJECTIVES

The goals of the Waste Characterization project are to 1) characterize the solid wastes derived from the direct utilization and conversion of low-rank western coals; 2) assess the extent to which deleterious major and trace elements may be mobilized into groundwater; and 3) evaluate and develop measures to mitigate undesirable environmental impacts. These measures may include coal preparation, immobilization by fireside additives, ash treatment, or improved disposal methods and siting.

8.2 ACCOMPLISHMENTS

8.2.1 ASTM LEACHING STUDIES

A previous quarterly report (1) discussed the possible use of fireside additives to immobilize deleterious elements leachable from fly ash. An alternative concept is ash treatment. Depending upon the process, this could be very awkward logistically and expensive in a large utility station. Simple processes requiring readily available, inexpensive agents, need examination.

One element which seems to display a generic tendency to leach at significant concentrations from pc-fired ashes is boron (Table 8-1). Boron is not a RCRA element (2) and currently there are no drinking water standards for the element. However, there are long- and short-term irrigation criteria (3,4). These are based on relative tolerances of plant species to boron. Generally speaking, small grains and vegetable row crops are listed (3) as semi-tolerant or tolerant to boron; fruits and nuts, not widely cultivated in northern plains coal fields, are said to be sensitive to boron. The semi-tolerant species are those which display slight to moderate injury at boron levels of 1.0 to 2.0 mg/l, and "tolerant" crops at levels of 2.0 to 4.0 mg/l. The margin between nutrient levels and harmful levels is said to be small (3), although this may depend upon soil types (4). It is possible that irrigation waters might be drawn from undrained impoundments at mined-out areas down the hydraulic gradient from ash disposal sites. For this reason, boron needs continuous surveillance since its ash leachate concentrations often exceed long-term irrigation criteria by factors of 4-140 (Table 8-1).

TABLE 8-1
BORON CONCENTRATIONS IN ASTM LEACHATE

- o Standards: RCRA--None
Primary Drinking Water--None
- o Criteria: Irrigation-0.75 mg/l long term
-2 mg/l short term
- o Selected ASTM Leach Experiments:

Fuel (State)	Technology	Leachate mg/l ⁺
High Na Beulah (ND)	AFBC PC	103 8
San Miguel (TX)	PC AFBC	87 0.5
Naughton (WY)	PC	77
Arapahoe (CO)	PC	65
75% Big Brown (TX)/ 25% High Na Beulah (ND)	PC	25
Sarpy Creek (MT)	PC	4
Velva (ND)	PC	3
Falkirk (ND)	PC (Util. Stn.)	0.8

⁺Analyses by ICAP.

UNDERC data displays a moderate negative correlation between concentrations of boron in 27 ASTM D3987-81 batch leachates and the amount of calcium in the corresponding fly ashes. In particular, leachate boron levels were lowest for ashes high in CaO (lime) as distinct from total calcium. Several studies were conducted to investigate effects of treating high-boron AFBC ash water wash liquors with calcium-bearing fly ash or lime. The AFBC ash chosen was from a high-Na test burn, FB2-BU4-0383; the water wash liquors are similar to ASTM leachates.

The procedure was to slurry 200 g AFBC ash in 800 ml distilled water. To this was added 200 ml Ca-bearing ash or lime either prior to or subsequent to a preliminary filtration. The results appear in Table 8-2. Both lime and a lime-rich Antelope Valley Station ash reduced the boron (and aluminum) levels in the AFBC ash leachate. Mixed results were obtained for other elements and for addition of lime-poor, high total Ca San Miguel ash from the PTC. The same procedure was applied to several pc-fired ash leachates (Table 8-3), with negative results. Very possibly the higher firing temperature experienced by pc-fired ash has significantly changed both ash and leachate boron chemistry. Alternative treatment procedures are being investigated, prompted in part by observed correlations between B and Al.

Additional conventional ASTM D3987-81 batch leaching tests have been performed during this reporting period (Table 8-4). These data fall into several categories, all ash being from the PTC.

- o low-Na Beulah
- o ion-exchanged Beulah
- o Big Brown with Na_2SO_4 flame side addition
- o Big Brown doped with NaOAc
- o Comparison of two mine samples (shipments) of Big Brown
- o Comparison of baghouse and cyclone ash from Big Brown
- o a commercial Texas lignite with limestone injected at flameside

Each of the Beulah and Big Brown leachates displays leachate boron concentrations in the upper range of our previous results; molybdenum, however, is low for all Beulah ashes. Instrumental problems prevented its measurement in any of the remaining ashes.

Although the ion-exchanged Beulah (5,6) ashes were not produced from the BW low-sodium shipment, it is probably significant that their ash leachates are substantially lower in boron than are ash leachates produced from unmodified coal.

In the case of the two sodium-enhanced Big Brown ashes, aside from an expected increase in leachate sodium, there is little other change. Increases of 2.3 to 3.1 in leachate aluminum may not be significant, for all of the numbers are quite small.

The PB Texas lignite is believed to be similar to Wilcox group lignites such as Big Brown. Higher leachate Ca, presumably due to the limestone injection, is apparent but may also reflect mine-to-mine variations in extraneous mineral matter in the parent coal (cf. BB1 and BB2 data). Big Brown ash was collected with such poor efficiency in the shaker baghouse that large quantities of backup cyclone ash were also available. The three baghouse ashes display large run-to-run variations for several elements in ASTM leachate. These variations are comparable to the differences between the two cyclone ashes and their corresponding "precutter" baghouse ashes. At least for Big Brown, there does not appear to be any trend which would justify significant continued effort to seek differences between baghouse and cyclone catches.

None of the ash samples discussed in this report produce leachates in violation of RCRA standards for any element measured.

TABLE 8-2

EFFECTS OF ADDING LIME OR CALCIUM-RICH FLY ASH UPON ELEMENTAL CONCENTRATIONS
IN FBC FLY ASH LEACHATE (RUN NO. FB2-BU4-0383). CONCENTRATIONS ARE mg/l.**

Coal Ash Designation Technology Run Number	San Miguel		Indian Head	High Na-Beulah				
	PTC-TL	Util-TL	AVS	AFBC	AFBC	AFBC FB2-BU4-0383	AFBC	AFBC
	PC	PC	PC					
	PTC-TL- 156,158,159,161	Utility Sta.	Utility Sta.					
Additive	--	--	--	--	PTC-TL	Util TL	AVS	Pure Lime
G. Additive Element:	--	--	--	0	200	200	200	200
Al	0.18	3.3	0.73	52	0.85*	141	0.39*	0.33*
B	87	19	1.2	103	185	120	27*	24*
Ca	1430	293	580	500	552	676	568	600
Fe	0.47	0.2	0.5	0.25	0.34	0.43	0.4	0.36
K	18	--	400	1400	>1300	>1450	>1700	1300
Mg	0.04	--	0.09	0.38	0.03*	2.6+	0.02*	0.28
Na	440	243	5400	32000	>3000	>2700	>2600	33000
Si	2.6	0.5	3.3	1.42	34+	1.8	10+	15+
As	ND	0.3	0.08	0.5	1.8	1.3	0.3	0.3
Ba	0.31	0.2	0.23	0.15	0.23	0.29	0.59	0.05*
Cr	0.25	0.05	0.37	0.06	0.27+	0.03	0.39+	0.01*
Sr	12	3.5	46	25	25	37	34	30
Mo	1.2	0.9	1.1	55	59	74	64	ND*
Mineralogy of Ash	CaSO ₄ rich CaO poor	Low Ca ash	High CaO ash	Na ₂ SO ₄ rich CaO poor				

*Significant reductions in concentration.

+Significant increase in concentration.

**Analyses by ICAP.

TABLE 8-3

EFFECTS OF ADDING LIME UPON ELEMENTAL CONCENTRATIONS IN
PC-FIRED ASHES. CONCENTRATIONS ARE mg/l.⁺

Coal Run Number g Lime	San Miguel PTC-TL-156,158,159,161		Naughton PTC-NT-246			Low-Na Beulah PTC-BW-240		Arapahoe PTC-AR-183	
	0	200	0	200	200	0	200	0	200
Element:									
Al	0.18	0.37	24	0.78*	1.7*	0.19	0.58	3.6	0.86
B	87	104	78	73	73	38	87	65	62
Ca	1430	682	500	650	460	752	777	540	450
Fe	0.47	0.56	0.40	0.70	0.56	0.39	0.85	0.32	0.50
K	18	25	20	30	36	80	95	5	25
Mg	0.04	0.02	0.1	0.04	ND*	0.02	0.27	0.07	ND
Na	440	757	15	218	255	2000	2000	29	275
Si	2.6	0.79	3	0.67*	0.66*	3.4	2.7	13	1.4
As	ND	ND	ND	ND	0.1	ND	ND	ND	ND
Ba	0.31	0.05	0.76	6	12	0.19	0.15	0.7	4
Cr	0.25	1.7	0.8	0.54	0.17	0.23	1.6	0.6	0.7
Sr	12	77	6	568	481	39	55	10	418
Mo	1.2	~1	0.70 (AA)	ND	<1	~3.3	<1	0.76 (AA)	<1
Mineralogy of Ash	CaSO ₄ rich	X	Low Ca ash	X	X	CaSO ₄ and CaO rich	X	Low Ca ash	X

*Elemental concentration in leachate significantly reduced by the addition of lime.

⁺Analyses by ICAP unless AA is indicated.

TABLE 8-4

ASTM D3987-81 LEACHATE RESULTS FOR PARTICULATE TEST COMBUSTOR ASHES.
LEACHATE CONCENTRATIONS EXPRESSED AS mg/l (ppm)⁺

Fuel Coal Code Run Number	Ion Exchange Beulah			Low-Na Beulah			Big Brown			Big Brown				TX Lig.	
	BI 231	BI 232	BUI 262	BW 238	BW 239	BW 240	BB-2 252	BB-2 258	BB-2 257	BB-1 209	BB1 210	BB1 210	BB1 211	BB1 211	PB 271
Comment:							NaOAc Doped	Na ₂ SO ₄ Inj.		BH Ash	Cycl. Ash	BH Ash	Cycl. Ash	LS Inj.	
Element:															
Al	6.0	0.4	3.1	0.1	0.1	0.2	2.3	5.4	7.2	0.4	0.2	1.2	0.2	0.6	0.1
B	4.8	5.3	20	22	24	28	10.0	11.0	12.5	9.4	2.6	13.7	7.2	6.7	12.2
Ca	290	580	1380	900	820	750	350	300	340	790	1050	520	840	620	1550
Fe	0.27	0.37	0.52	0.43	0.43	0.39	0.29	0.24	0.25	0.33	0.42	0.30	0.32	0.29	0.5
K	120	100	20	80	91	80	4	0.3	8	ND	ND	ND	0.2	ND	3
Mg	0.02	0.02	0.03	0.02	0.02	0.02	0.06	0.05	0.09	0.03	0.02	0.03	0.02	0.04	0.02
Na	1920	2000	500	1500	1500	2000	7	32	1200	10	6	9	11	9	6
Si	20	9	1	3	2	3	10	7	12	52	6	23	11	400	1
As	0.1	0.1	0.2	<0.1	ND	<0.1	0.1	0.1	0.1	ND	ND	ND	ND	ND	<0.1
Ba	0.97	1.1	0.44	0.22	0.24	0.19	0.68	0.79	0.26	1.53	1.47	1.24	2.23	1.45	0.75
Cd	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	<0.1	ND
Cr	0.3	0.36	0.18	0.09	0.14	0.23	0.92	0.46	0.61	1.04	0.42	1.59	1.27	1.13	0.18
Pb	<0.1	<0.1	<0.1	ND	<0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Sr	54	62	40	49	43	39	12	8	8	15	15	15	17	14	15
Be	0.001	0.001	0.001	<0.001	<0.001	0.001	0.001	0.002	0.005	ND	ND	0.001	ND	0.001	0.001
Cu	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	ND	<0.02	<0.02	ND	ND	ND	ND	ND	<0.02
Mo	2	1	1	3	3	3	--	--	--	--	--	--	--	--	--
Ni	<0.05	0.06	3.05	0.06	<0.05	<0.02	0.06	ND	ND	ND	ND	ND	ND	ND	ND
Zn	ND	ND	ND	ND	ND	ND	ND	<0.02	ND	ND	ND	ND	ND	ND	ND

⁺Analyses by ICAP.

In the previous Quarterly Technical Progress Report (7), a typographical error transposed concentrations in Table 8-4 for Sr and Sb (a RCRA element) for San Miguel utility station ash. Strontium (Sr) should have read 3.1 ± 0.05 ppm, and antimony (Sb) was not analyzed. Other Sr and Sb data in the table are correct. In Table 8-6 of the same report, headings of the last two columns were reversed; " $\mu\text{g/g ash}$ " and "ppm" must be transposed. Since that report was published, additional analyses have been received. In particular, 1.8 ppm Se was observed in leachate from the 75% Big Brown-25% Beulah ash leachate. The RCRA standard is 1.0 ppm Se.

8.2.2 SPECIFIC SURFACE AREA

Other factors besides elemental concentrations and solubilities affect leaching rates for various ashes. Accessibility of ash components to the leaching fluid may be rate controlling. For this reason we have measured specific surface area of a variety of coal-derived solid wastes (Table 8-5). These are collected using the BET method with helium, after outgassing at 300°C .

Presumably because specific surface area is highly sensitive to particle porosity, there is no substantial correlation between surface area and particle size distribution measured either aerodynamically or by coulter counter.

Aside from the Pike County, Alabama lignite, which differs from others we have studied in numerous ways, the pc-fired solids as a group have lower specific surface areas than the other materials by a wide margin. Almost certainly this relates in part to formation temperature and the fusion which occurs in pc-fired ash particles. Because our data are sparse, it may be premature to correlate the surface area of FBC ash particles with the demonstrated higher concentrations of some FBC ash leachate constituents.

TABLE 8-5

SPECIFIC SURFACE AREA OF COAL DERIVED SOLID WASTES
DETERMINED BY BET METHOD WITH HELIUM FOLLOWING 300°C OUTGASSING

Sample Type and Fuel	Code	Area, m ² /g
Pc-fired Fly Ashes:		
Pike Co., AL	PK	4.0
Choctaw, AL		
Washed	CW	1.5
R.O.M.	CA	1.3
High Na Beulah, ND	BA	1.2
Indian Head, ND	I3	1.1
Big Brown, TX	BB1	0.7
San Migeul, TX	TL	0.5
PC-Fired Bottom Ash		
Indian Head, ND	I3	0.7
AFBC Ash		
High-Na Beulah, ND	BA	9.5
Low-Na Beulah, ND	BW	4.4
AFBC Bed Material		
Dolomite, High-Na Beulah Burn	--	6.9
BurMin Gasifier Ash (Wellman-Gelusha)		
Indian Head	I3	9.8

8.3 REFERENCES

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2. Federal Register, 45FR33122, May 19, 1980.

3. National Technical Advisory Committee on Water Quality Criteria, Water Quality Criteria, Federal Water Pollution Control Administration, April 1968.
4. U.S. EPA, Quality Criteria for Water ("The Red Book"), EPA-440/9-76-023, July 1976.
5. Zobeck, B.J. Final Experimental Data Report for the Ion-Exchange Unit, Run No. IX-1182, EG G-TR-1382, December 1982.
6. Zobeck, B.J. Final Experimental Data Report for the Ion-Exchange Unit, Run No. IX-1282, EG G-TR-0583, January 1983.
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9. FINE COAL CLEANING

Project No.: 7225

B&R No.: AA052000

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

Prepared by: M.J. Mitchell, Research Supervisor, Fine Coal Cleaning

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9.1 GOALS AND OBJECTIVES

The goals for the Fine Coal Cleaning project are two-fold. The first is to support PETC in building 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 selected low-rank coals, with emphasis on upgrading the quality of low-rank coal/water slurries.

The Pittsburgh Energy Technology Center (PETC) is providing 156 coal samples for centrifugal float-sink analysis. The testing plan is given in Figure 3-1, Fine Size Centrifugal Float-Sink Procedure, Quarterly Progress Report, April-June 1983, this project. Splits of coal, prepared to 65, 200 and 325 mesh top size will be separated at specific gravities of 1.3, 1.4, and 1.6. Washability studies on these same coal samples in the conventional size range are being performed in other PETC-funded 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 fine coal particle sizes, while performing the float-sink cleaning studies. Specifically, identify 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. Evaluate the impact of surface and bound moisture on the fine coal cleaning procedures used in this study.
4. Determine the degree of segregation of inorganic constituents of selected low-rank coals as a function of coal source, coal moisture (after conventional or steam drying), and size fraction. In addition, identify the separation of coal components as a function of size fraction 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).

9.2 ACCOMPLISHMENTS

9.2.1 COAL SELECTION AND PRIORITIES

9.2.1.1 Coals Selection and Priorities for Coals to be Included in the Data Base

The remaining samples for the program have been received from PETC. These are listed in Table 9-1. Of the previously received samples, W-1 through W-24 are in progress and W-25 through W-86 were listed in Table 9-4 of the previous quarterly report for this project. The samples have been prioritized for the fine coal cleaning data base and the next groups of coals to be included in the data base are listed in Table 9-2.

9.2.1.2 Coals Selected for In Depth Fine Coal Cleaning Studies

The coals chosen for oil agglomeration and other studies are:

1. Martin Lake, Gulf Coast lignite
2. Beulah-Zap, North Dakota lignite
3. Navaho Mine, San Juan Basin subbituminous
4. Eagle Butte Mine, Wyoming subbituminous

These coals are in-house in sufficient quantities for the study. Preliminary coal analysis is in progress and initial crushing and wet screen studies are expected to start during the next quarter.

9.2.2 DATA ANALYSIS

The 65 mesh top size samples are complete and the data for these samples are listed in Table 9-3. In addition, preliminary data for the 200 mesh top size samples are given in Table 9-4 (for the same coals, with float-sink data at 1.30 specific gravity only). Float-sink tests on 1/3 of the samples has been done at 1.40 s.g. but analytical results are not available at this time. Based on the results of the float-sink testing noted, the following observations can be made.

On the 65 mesh top size samples at 1.30 s.g., we were able to reach ash levels of less than 1% on coal W-8 from Rogers Co., OK. This coal float was recovered at nearly 36%. The total sulfur value in the float is low and is approximately the same as the bulk value. The average ash content of this coal is between 5% and 6%. The 1.30 s.g. float on coal W-9, from Wagner Co., OK, contained less than 1% ash with a 59% recovery by weight. Sulfur was approximately 1/2 that found in the bulk coal. Coal W-1 from Arkansas had a 1.30 float with ~1% ash but the weight recovery is low. Several of the Oklahoma coals had 1.30 s.g. floats with 1% to 2% ash. The highest ash content in the 1.30 s.g. float was Wilcox Bed lignite from Titus Co., TX with 6.8% ash. This coal (W-18) has a high bulk ash content.

TABLE 9-1

NEW SAMPLES RECEIVED FROM PETC

Identification No.	Mine/Location	Comments
W-87	Savage Mine, Top Seam-Richard Co., Savage, Montana-- Knife River Mining Co.	3/8 x 0 Reserve--sampled 9-3-80
W-88	Savage Mine, Bottom Seam-Richard Co., Savage, Montana-- Knife River Mining Co.	3/8 x 0 Reserve--sampled 9-3-80
W-89	East Decker Mine, Dietz No. 1, Upper Seam-Big Horn Co., Decker, Montana	3/8 x 0 Reserve--sampled 9-17-80
W-90	East Decker Mine, Dietz No. 1, Middle Seam-Big Horn Co., Decker, Montana	3/8 x 0 Reserve--sampled 9-17-80
W-91	East Decker Mine, Dietz No. 2, Middle Seam-Big Horn Co., Decker, Montana	3/8 x 0 Reserve--sampled 9-19-80
W-92	Decker Coal Co., Dietz Nos. 1 and 2 Seams, Big Horn Co., Decker, Montana	3/8 x 0 Reserve--sampled 9-20-80
W-93	Peter Kiewit Sons, E. Seam-Big Horn Co., Decker Coal Co., Decker, Montana	3/8 x 0 Reserve--sampled 9-21-80
W-94	Northwestern Resources Co., Grass Creek Mine, Mayfield Seam-Hot Springs Co., Thermopolis, Wyoming	3/8 x 0 Reserve--sampled 9-24-80
W-95	Morrison Knudsen/Skull Point Mine, Green River Seam- Lincoln Co., Kemmerer, Wyoming	3/8 x 0 Reserve--sampled 9-27-80

TABLE 9-1 (Continued)

Identification No.	Mine/Location	Comments
W-96	Elkol Strip Mine, Kemmerer Coal Co., Adaville No. 8-Bottom Bench--Lincoln Co., Wyoming	3/8 x 0 Rawhead
W-97	Kemmerer Coal Co., Elkol Strip Mine, Adaville No. 4 Seam-Bottom Bench--Lincoln Co., Wyoming	3/8 x 0 Rawhead
W-98	Kemmerer Coal Co., Elkol Strip Mine, Adaville No. 2 Seam-Bottom Bench--Lincoln Co., Wyoming	3/8 x 0 Rawhead
W-99	Kemmerer Coal Co., Elkol Strip Mine, Adaville No. 1, Zone 1--Lincoln Co., Wyoming	3/8 x 0 Rawhead
W-100	Kemmerer Coal Co., Elkol Mine Strip, Adaville No. 1, Zone No. 2, Lincoln Co., Wyoming, Part 3	3/8 x 0 Rawhead, BuMine 4-8-81
W-101	Kemmerer Coal Co., Elkol Mine Strip, Adaville No. 1, Zone No. 3, Lincoln Co., Wyoming, Part 3	3/8 x 0 Rawhead, BuMine 4-8-81
W-102	Kemmerer Coal Co., Elkol Mine Strip, Adaville No. 1, Zone No. 4, Lincoln Co., Wyoming, Part 3	3/8 x 0 Rawhead, BuMine 4-8-81
W-103	Kemmerer Coal Co., Elkol Mine Strip, Adaville No. 3, Top Seam, Lincoln Co., Wyoming, Part 3	3/8 x 0 Rawhead, BuMine 4-8-81
W-104	Kemmerer Coal Co., Elkol Mine Strip, Adaville No. 11 Seam, Lincoln Co., Wyoming, Part 3	3/8 x 0 Rawhead, BuMine 4-9-81

TABLE 9-1 (Continued)

Identification No.	Mine/Location	Comments
W-105	Kemmerer Coal Co., Elkol Mine Strip, Adaville No. 7, Upper Seam, Lincoln Co., Wyoming, Part 3	3/8 x 0 Rawhead, BuMine 4-10-81
W-106	Palmer Coking Coal Co., King Co., Washington, Gem Seam, Rawhead	3/8 x 0--sampled 7-13-81
W-107	Palmer Cokingn Coal Co., McKay Seam, Rawhead, King Coal Co., Washington	38 x 0--sampled 7-13-81
W-108	Burlington Northern, Seam No. 1, Big Dirty Kittitas Co., Roslyn, Washington	3/8 x 0--sampled 7-13-81
W-109	Wilkeson No. 3 Seam, Gale Creek Coal Field, Wilkeson Co., Wilkeson, Washington (Mine not operating)	3/8 x 0--sampled 7-13-81
W-110	Wilkeson No. 1 Seam, New No. 5 Seam, Pierce Co., Wilkeson, Washington (Mine not operating)	3/8 x 0--sampled 7-13-81
W-111	Widco Mine, Little Dirty Seam, Thurston Co., Centralia, Washington	3/8 x 0 Rawhead 7-13-81
W-112	Consolidation Coal Co., Burnham Mine--Yellow No. 6 Seam, San Juan Co., Farmington, NM	3/8 x 0 Rawhead 7-13-81
W-113	Consolidation Coal Co., Burnham Mine--Yellow No. 4 Seam, Part No. 3, San Juan Co., Farmington, NM	3/8 x 0--sampled 7-13-81
W-114	Consolidation Coal Co., Burnham Mine--Blue No. 4 Seam, San Juan Co., Farmington, NM	3/8 x 0 BuMine 5-6-81

TABLE 9-1 (Continued)

Identification No.	Mine/Location	Comments
W-115	Consolidation Coal Co., Burnham Mine, Blue No. 3 Seam, San Juan Co., Farmington, NM	3/8 x 0 Rawhead 5-6-81
W-116	Consolidation Coal Co., Burnham Mine, Blue No. 25 Seam, San Juan Co., Farmington, NM	3/3 x 0 Rawhead 5-7-81
W-117	Southern Utah Fuel Mine No. 1, Upper Hiawatha Seam, Sevier Co., Salina, Utah	3/8 x 0 Rawhead BuMines 5-11-81
W-118	Southern Utah Fuel Mine No. 1, Upper Haiwatha Seam, Part No. 3, Sevier Co., Salina, Utah	3/8 x 0 Rawhead 5-11-81 BuMines
W-119	Coal Search Corp., Hiawatha Rie (Cretaceous) Seam, Part No. 3, Sevier Co., Salina, Utah	3/8 x 0 Rawhead BuMines 5-13-81
W-120	Utah International, Trapper Mine, G Seam, Moffat Co., Part No. 3, Craig, Colorado	3/8 x 0 BuMines 5-28-81
W-121	Utah International, Trapper Mine, G Seam, Moffat Co., Part No. 3, Craig, Colorado	3/8 x 0 BuMines 5-28-81
W-122	Utah International, Trapper Mine, R-Rider, Moffat Co., Part No. 3, Craig, Colorado	3/8 x 0 Rawhead BuMines
W-123	Utah International, Trapper Mine, I-Seam, Moffat Co., Part No. 3, Craig, Colorado	3/8 x 0 Rawhead BuMines

TABLE 9-1 (Continued)

Identification No.	Mine/Location	Comments
W-124	Northern Coal Co., Northern No. 1 Mine, F-Seam, Rio Blanco Co., Meeker, Colorado	3/8 x 0 Rawhead BuMines 6-1-81
W-125	Northern Coal Co., Renau Mine, G-Seam, Rio Blanco Co., Meeker, Colorado	3/8 x 0 Rawhead 6-2-81
W-126	Snowmass Coal Co., Thompson Creek No. 1 Mine, A-Seam, Pitkin Coal Co., Carbondale, Colorado	3/8 x 0 Rawhead BuMines 6-4-81
W-127	Snowmass Coal Co., Thompson Creek No. 1 Mine, B-Seam, Pitkin Coal Co., Carbondale, Colorado	3/8 x 0 Rawhead BuMines 6-3-81
W-128	Snowmass Coal Co., Thompson Creek No. 3 Mine, Anderson Seam, Pitkin Coal Co., Carbondale, Colorado	3/8 x 0 Rawhead BuMines 6-5-81
W-129	Empire Energy Coal Co., Eable No. 5 Mine, F-Seam, Moffat Co., Craig, Colorado	3/8 x 0 Rawhead BuMines 6-16-81
W-130	Mid-Continent Resources, No. 2 Mine, Dutch Creek Seam, Pitkin Co., Carbondale, Colorado	3/8 x 0 Rawhead BuMines 6-10-81
W-131	Mid-Continent Resources, Basin Seam No. 3 Mine, Lower Coal Seam, Pitkin Co., Carbondale, Colorado	3/8 x 0 Rawhead BuMines 6-12-81
W-132	Mid-Continent Resources, Basin Seam No. 3 Mine, Upper Coal Seam, Pitkin Co., Carbondale, Colorado	3/8 x 0 Rawhead BuMines 6-13-81
W-133	Blackrock Mining Co., Coal Basin "D" Seam, Bituminous (Deep), Glenwoods Spring, Colorado	3/8 x 0 Rawhead BuMines 6-12-81

TABLE 9-1 (Continued)

Identification No.	Mine/Location	Comments
W-134	Empire Energy Co., Eagle No. 9 Mine, "P" Seam, Moffit Co., Craig, Colorado	3/8 x 0 Rawhead BuMines 6-17-81
W-135	Yampa Mining Co., Haden Gulch Strip, Seam No. 4, Routt Co., Haden, Colorado	3/8 x 0 Rawhead BuMines 6-8-81
W-136	Yampa Mining Co., Haden Gulch Mine, No. 3 Seam, Routt Co., Haden, Colorado	3/8 x 0 Rawhead BuMines 6-23-81
W-137	Yampa Mining Co., Haden Gulch Mine, No. 2 Seam, Routt Co., Haden, Colorado	3/8 x 0 Rawhead BuMines 6-24-81
W-138	Yampa Mining Co., Haden Gulch Mine, No. 1 Seam, Routt Co., Haden, Colorado	3/8 x Rawhead BuMines 6-25-81
W-139	Yampa Mining Co., Haden Gulch Mine, No. 5 Seam, Routt Co., Haden, Colorado	3/8 x 0 Rawhead BuMines 6-26-81
W-140	Yampa Mining Co., Haden Gulch Mine, No. 1a Seam, Routt Co., Haden, Colorado	3/8 x 0 Rawhead BuMines 6-26-81
W-141	Colowyo Coal Co., Axial Mine, "X" Seam, Moffat Co., Meeker, Colorado	3/8 x 0 Rawhead BuMines 6-29-81
W-142	Colowyo Coal Co., Axial Mine, "D" Seam, Moffat Co., Meeker, Colorado	3/8 x 0 Rawhead BuMines 6-30-81

TABLE 9-1 (Continued)

Identification No.	Mine/Location	Comments
W-143	Kaiser Steel Corp., Sunnyside No. 3 Mine, Upper Sunnyside Seam, Carbon Co., Sunnyside, Utah	BuMines 7-7-81
W-144	Kaiser Steel Corp., Sunnyside No. 1 Mine, Lower Sunnyside Seam, Carbon Co., Sunnyside, Utah	BuMines 7-7-81
W-145	Price River Coal Co., Carbon Co., Part 3, Helper, Utah	BuMines 7-9-81
W-146	Price River Coal Co., Carbon Co., Part 3, Helper, Utah	BuMines 7-9-81
W-147	Plateau Mining Co., Wattis Seam, Carbon County, Part No. 3, Price, Utah	BuMines 7-11-81
W-148	Plateau Mining Co., Starpoint No. 2, Third Bed, Carbon County, Part No. 3, Price, Utah	BuMines 7-13-81
W-149	Plateau Mining Co., Starpoint No. 2, Wattis Seam, Carbon Co., Part No. 3, Price, Utah	BuMines 7-15-81
W-150	U.S. Fuel Company, King No. 4 Mine, A-Seam, Carbon County, Part 3, Hiawatha, Utah	3/8 x 0 Rawhead BuMines 7-23-81
W-151	U.S. Fuel Company, King No. 4 Mine, B-Seam, Carbon County, Part 3, Hiawatha, Utah	3/8 x 0 Rawhead BuMines 7-23-81
W-152	U.S. Fuel Company, King No. 6 Mine, Hiawatha Seam, Carbon Co., Hiawatha, Utah	3/8 x 0 Rawhead BuMines 7-24-81

TABLE 9-1 (Continued)

Identification No.	Mine/Location	Comments
W-153	Spring Creek Mine Anderson/Dietz, (Top 0-20 Test Coal Bed) Big Horn County, Part No. 3, Decker, Montana	3/8 x 0 BuMines 7-27-81
W-154	Spring Creek Mine Anderson/Dietz Coal Bed, Big Horn County, Part No. 3, Decker, Montana	3/8 x 0 BuMines 7-27-81
W-155	Spring Creek Mine, Anderson Coal Bed, Big Horn County, Decker, Montana	3/3 x 0 Rawhead BuMines
W-156	West Decker Mine, Dietz Bed (40'-46' feet level), Big H County, Part 3, Montana	3/8 x 0 Rawhead BuMines 7-30-81
W-157	West Decker Mine, Dietz Bed (46'-52' level), Big H County, Part 3, Montana	3/8 x 0 Rawhead BuMines 7-30-81

TABLE 9-2
PRIORITY OF COALS FOR COAL CLEANING DATA BASE

<u>Coals First Group</u>	
<u>Sample No.</u>	<u>Sample Description</u>
W-36	Hagel Bed Falkirk Strip Middle McLean Co., ND
W-43	Beulah Zap Beulah So. Strip Bottom Oliver Co., ND
W-50	Wyodak Black Thunder Mine Campbell Co., WY
W-53	Monarch Bed Big Horn Strip B Sheridan, WY
W-56	Rollin Bed Cloves Pt. Pit Campbell Co., Gillette, WY
W-66	Bed 78 Bottom Seminoe No. 2 Carbon Co., Hanna, WY
W-83	Rosebud McKay Seam Absoloka Mine Big Horn Co, MT
W-90	Dietz No. 1 Middle East Decker Mine Big Horn Co., MT
W-108	No. 1 Seam Big Dirty Burlington Northern Kittitas Co., WA
W-119	Hiawatha Rie Seam, Coal Search Corp. Sevier Co., UT
W-124	F. Seam Northern Coal Co. Northern No. 1 Mine Rio Blanco Co., CO
W-73	Lower Deadman Seam, Jim Bridger Mine Sweetwater Co., WY

Coals Second Group

<u>Sample No.</u>	<u>Sample Description</u>
W-39	Hagel Bed Center Mine Oliver Co., ND
W-42	Beulah Zap Beulah So. Strip Middle Oliver Co., ND
W-38	Kinnemen Creek Bed Center Mine Oliver Co., ND
W-47	Harmon B Bed Knife River Strip Gascoyne Bowman Co., ND
W-51	Badger Bed, Dave Johnson Strip Converse Co., WY
W-62	Bed 65 Upper Ferris Strip, Energy Dev. Corp. Carbon Co., WY
W-68	Hanna Bed 5 Top Seminole No. 2 Carbon Co., WY
W-69	Hanna Bed 5 Bottom Seminole No. 2 Carbon Co., WY
W-122	R-Rider Seam, Utah International Trapper Mine Moffat Co., CO
W-126	A Seam Snowmass Coal Co. Thompson Creek No. 1 mine Carbondale, CO
W-114	Blue No. 4 Seam, Consolidation Coal Co., Burnham Mine, San Juan Co., NM
W-112	Yellow No. 6 Seam, Consolidation Coal Co., Burnham Mine, San Juan Co., NM

Coal Reserve List

<u>Sample No.</u>	<u>Sample Description</u>
W-28	Fleming Bed Bills Coal Co. Ft. Scott Strip No. 3, Vernon Co., KS
W-41	Beulah Zap Top Beulah So. Strip Oliver Co., ND
W-48	Harmon C Bed Knife River Strip Gascoyne Bowman Co., ND
W-54	Dietz No. 3 Up. Monarch Big Horn Strip C Sheridan Co., WY
W-71	Bed 74 Middle Seminoe No. 2 Carbon Co., WY
W-82	Seam 2 Brophy No. 2 Mine Carbon Co., MT
W-74	Upper Deadman Seam, Jim Bridger Mine, Sweetwater Co., WY
W-95	Green River Seam Skull Point Mine Lincoln Co., WY
W-97	Adaville No. 4 Seam Elko Strip Mine Lincoln Co., WY
W-107	McKay Seam Palmer Coking Coal Co. King Co., WA
W-133	Coal Basin D Seam Blackrock Mining Co. Glenwood Springs, CO
W-135	Seam No. 4 Haden Gulch Strip Routt Co., CO
W-143	Upper Sunnyside Sunnyside No. 3 Mine Carbon Co., UT

TABLE 9-3

WASHABILITY ANALYSIS SHOWING THE EFFECTS OF PYRITE, SULFUR, AND
OTHER IMPURITIES FOR 65 X 0 COAL

	Recovery, Pct		Btu	Btu/lb	Ash	Percent	
	Product	Weight				Pyritic Sulfur	Total Sulfur
65 X 0							
83-1062	Float - 1.30	4.45	4.89	15,218	1.09	X	0.59
(W-1)	1.30 - 1.40	71.34	76.88	14,939	3.48	0.46	0.99
Paris Bed	1.40 - 1.60	14.19	13.67	13,355	11.22	3.70	4.19
Logan Co., AR	Sink - 1.60	10.02	4.56	6,308	49.75	8.10	12.37
83-1063	Float - 1.30	0	X	X	X	X	X
(W-2)	1.30 - 1.40	70.02	74.75	14,609	4.13	0.2	1.02
V. Hartshorne	1.40 - 1.60	25.66	23.30	12,428	16.59	0.88	2.12
Co., AR	Sink - 1.60	4.31	1.95	6,210	50.34	4.40	8.57
83-1064	Float - 1.30	0.69	0	X	1.23	X	0.94
(W-3)	1.30 - 1.40	70.91	78.70	14,874	3.28	1.14	1.07
Charleston Bed	1.40 - 1.60	16.26	15.55	12,817	13.92	1.00	2.20
Co., AR	Sink - 1.60	12.24	5.75	6,299	48.82	4.20	7.00
83-1065	Float - 1.30	30.96	35.18	14,723	2.19	0.40	1.28
(W-4)	1.30 - 1.40	47.21	52.57	14,427	4.87	1.14	2.82
L. McAlister	1.40 - 1.60	5.83	5.53	12,303	14.22	3.40	7.17
Bed, Latimer Co., OK	Sink - 1.60	15.99	6.72	5,441	52.90	7.30	9.21
83-1066	Float - 1.30	19.73	22.42	14,372	3.23	0.26	1.45
(W-5)	1.30 - 1.40	49.76	54.48	13,849	7.38	1.24	2.99
U. McAlister	1.40 - 1.60	18.09	17.67	12,356	15.08	3.90	7.45
Bed, Latimer Co., OK	Sink - 1.60	12.42	5.42	5,523	50.34	10.10	11.99
83-1067	Float - 1.30	19.45	18.05	13,763	1.10	0.09	0.84
(W-6)	1.30 - 1.40	64.17	58.69	13,566	2.69	0.17	1.08
Croweburg Bed	1.40 - 1.60	7.71	6.12	11,777	13.15	1.20	3.42
Okmulgee Co., OK	Sink - 1.60	8.66	2.06	3,535	55.84	7.50	10.97
83-1068	Float - 1.30	49.3	52.19	14,201	1.13	0.01	0.37
(W-7)	1.30 - 1.40	41.32	42.18	13,692	3.97	0.02	0.24
Croweburg Bed	1.40 - 1.60	6.23	5.64	12,136	14.64	0.11	0.39
Wagner Co., OK	Sink - 1.60	3.24	X	X	60.36	X	1.43

TABLE 9-3 (Continued)

	Recovery, Pct.		Btu	Btu/lb	Ash	Percent	
	Product	Weight				Pyritic Sulfur	Total Sulfur
83-1069 (W-8) Croweburg Bed Rogers Co., OK	Float - 1.30 1.30 - 1.40 1.40 - 1.60 Sink - 1.60	35.94 45.71 7.06 11.28	40.05 50.11 7.05 3.04	14,011 13,808 11,869 3,408	0.88 3.34 17.08 51.84	0.01 0.02 0.1 0.27	0.47 0.41 0.48 0.74
83-1070 (W-9) Secor Bed Wagner Co., OK	Float - 1.30 1.30 - 1.40 1.40 - 1.60 Sink - 1.60	59.35 34.45 3.26 2.93	60.76 34.82 3.17 1.25	14,357 14,174 13,640 6,004	.97 1.65 11.22 49.75	0.01 0.04 0.40 X	0.47 0.55 0.84 12.35
83-1071 (W-10) San Pedro Bed Webb Co., TX	Float - 1.30 1.30 - 1.40 1.40 - 1.60 Sink - 1.60	37.17 44.14 9.44 9.25	42.74 46.67 7.90 2.64	13,661 12,575 9,952 3,391	5.34 9.99 16.54 50.34	0.03 0.14 0.5 1.90	0.98 1.33 2.37 7.53
83-1072 (W-11) Bull Creek Bed Coleman Co., TX	Float - 1.30 1.30 - 1.40 1.40 - 1.60 Sink - 1.60	0.22 18.43 59.22 22.12	X 25.68 64.01 10.31	X 12,442 9,652 4,165	3.82 5.52 13.92 48.82	X 0.06 0.5 4.60	1.20* 1.19 1.97 8.67
83-1073 (W-12) Thurber Bed Erath Co., TX	Float - 1.30 1.30 - 1.40 1.40 - 1.60 Sink - 1.60	4.30 42.08 14.85 38.77	6.38 57.84 17.73 18.05	13,937 12,914 11,221 4,375	1.59 7.92 14.22 52.90	0.41 0.26 1.10 5.00	1.16 1.75 3.23 10.04
83-1074 (W-13) Dilco Bed McKinley Co., NM	Float - 1.30 1.30 - 1.40 1.40 - 1.60 Sink - 1.60	0.65 72.10 22.80 4.44	X 78.58 19.46 1.96	X 12,368 9,686 5,003	2.90 4.46 15.08 50.34	X 0.03 0.15 0.69	0.55 0.50 0.52 1.66
83-1075 (W-14) PQ Dilco Bed McKinley Co., NM	Float - 1.30 1.30 - 1.40 1.40 - 1.60 Sink - 1.60	8.46 62.54 26.19 2.81	9.32 66.17 22.09 .75	13,156 12,633 10,071 3,159	2.92 4.00 13.15 55.84	0.01 0.01 0.09 X	0.49 0.50 0.53 1.42
83-1076 (W-15) Sundance Bed McKinley Co., NM	Float - 1.30 1.30 - 1.40 1.40 - 1.60 Sink - 1.60	2.36 76.32 12.58 8.74	2.74 82.99 11.57 2.66	13,538 12,654 10,432 2,870	1.59 2.95 14.64 60.36	X 0.02 0.07 0.85	0.72 0.71 0.61 2.28

TABLE 9-3 (Continued)

		Recovery, Pct		Btu	Btu/lb	Ash	Percent	
		Product	Weight				Pyritic Sulfur	Total Sulfur
83-1077	Float - 1.30	1.67	2.02	13,450	3.65	X	0.52	
(W-16)	1.30 - 1.40	76.13	83.94	12,300	3.82	0.02	0.54	
Dilco Bed M	1.40 - 1.60	8.93	7.82	10,033	17.08	0.04	0.46	
Seam, McKinley Co., NM	Sink - 1.60	13.28	5.12	4,299	51.84	0.36	1.00	
83-1078	Float - 1.30	0.12	X	X	7.58*	X	0.92	
(W-17)	1.30 - 1.40	14.68	21.50	11,274	5.89	0.01	0.76	
Lignite, Wilcox	1.40 - 1.60	57.97	64.34	8,542	5.16	0.05	0.83	
Field, Titus Co., TX	Sink - 1.60	27.15	14.16	4,014	49.36	0.12	1.13	
83-1079	Float - 1.30	3.96	X	X	6.82	X	0.88	
(W-18)	1.30 - 1.40	35.51	42.13	10,076	8.66	0.02	0.89	
Lignite, Wilcox	1.40 - 1.60	50.18	51.93	8,789	17.14	0.01	0.80	
Bed, Titus Co., TX	Sink - 1.60	10.35	5.93	4,870	50.53	0.04	0.68	
83-1080	Float - 1.30	18.93	28.47	14,752	2.06	0.01	1.59	
(W-19)	1.30 - 1.40	26.01	36.33	13,702	7.72	0.53	2.33	
Rowe Coal Bed	1.40 - 1.60	12.72	16.09	12,408	14.18	1.30	3.18	
Barton Co., MO	Sink - 1.60	42.33	19.10	4,428	55.09	6.50	11.09	
83-1081	Float - 1.30	18.74	24.62	14,632	2.61	0.36	1.43	
(W-20)	1.30 - 1.40	41.40	43.11	11,598	19.24	1.13	4.57	
Kniveton Bed	1.40 - 1.60	21.96	22.83	11,578	19.27	1.60	3.95	
Barton Co., MO	Sink - 1.60	17.90	9.44	5,871	48.46	8.20	12.49	
83-1082	Float - 1.30	30.46	36.80	14,142	1.97	0.02	1.86	
(W-21)	1.30 - 1.40	40.73	45.79	13,160	2.34	0.64	3.39	
Fleming Seam	1.40 - 1.60	7.29	7.22	11,591	13.28	1.90	5.58	
Vernon Co., MO	Sink - 1.60	27.51	9.28	3,946	49.82	9.60	17.85	
83-1083	Float - 1.30	33.23	39.78	14,281	3.08	0.19	1.92	
(W-22)	1.30 - 1.40	39.55	44.15	13,321	7.56	0.62	2.67	
Fleming Seam	1.40 - 1.60	9.20	8.98	11,654	14.70	1.55	4.59	
Vernon Co., MO	Sink - 1.60	18.02	7.01	4,646	51.12	10.90	18.12	
83-1084	Float - 1.30	3.23	5.08	13,816	1.29	0.12	3.17	
(W-23)	1.30 - 1.40	41.48	60.71	12,824	4.04	0.32	4.23	
Mulberry Seam	1.40 - 1.60	15.15	19.08	11,036	13.68	0.5	4.64	
Bates Co., MO	Sink - 1.60	40.14	15.12	3,300	54.53	6.20	13.70	

TABLE 9-3 (Continued)

	Recovery, Pct		Btu	Btu/lb	Ash	Percent	
	Product	Weight				Pyritic Sulfur	Total Sulfur
83-1085	Float - 1.30	7.13	9.78	14,058	2.09	0.25	2.59
(W-24)	1.30 - 1.40	41.00	51.69	12,911	6.01	0.70	4.36
Weir Seam	1.40 - 1.60	24.38	22.07	9,271	22.88	3.35	10.90
Henry Co., MO	Sink - 1.60	27.49	16.45	6,128	37.51	9.70	18.94

*Duplicate analysis could not be performed due to small sample size.

X = Insufficient sample for analysis.

TABLE 9-4

PRELIMINARY ANALYTICAL DATA - 1.30 FLOAT-SINK PRODUCTS; 200 MESH

Grand Forks Number	Location	Description	Weight (%)	Moisture (%)	Ash (%)	Total Sulfur (%)	Pyritic Sulfur (%)	Btu/lb
83-1062 (W-1)	Paris Bed Logan County, AR	Float Sink	11.2 88.8	1.01 1.74	1.33 7.50	0.37		15,271
83-1063 (W-2)	V. Hartshorne Bed Lamar County, AR	Float Sink	0.0 100.0	X 1.70	X 9.16	X	X	X
83-1064 (W-3)	Charleston Bed Franklin County, AR	Float Sink	1.6 98.4	0.91 1.84	1.40 8.13	0.86	X	14,926*
83-1065 (W-4)	L. McAlister Bed Latimer County, OK	Float Sink	39.7 60.3	1.46 1.58	1.82 17.2	1.07		14,879
83-1066 (W-5)	U. McAlister Bed Latimer County, OK	Float Sink	24.5 75.5	1.13 1.98	3.30 17.18	1.51		14,529
83-1067 (W-6)	Croweburg Bed Okmulgee County, OK	Float Sink	54.4 45.6	4.02 4.24	1.27 10.32	0.78		13,576
83-1068 (W-7)	Croweburg Bed Wagner County, OK	Float Sink	50.8 49.2	2.54 3.13	1.04 10.02	0.26		13,941
83-1069 (W-8)	Croweburg Bed Rogers County, OK	Float Sink	37.7 62.3	2.70 3.94	0.92 8.91	0.41		13,917

TABLE 9-4 (Continued)

Grand Forks Number	Location	Description	Weight (%)	Moisture (%)	Ash (%)	Total Sulfur (%)	Pyritic Sulfur (%)	Btu/lb
83-1070 (W-9)	Secor Bed Wagner County, OK	Float Sink	60.4 39.6	1.53	0.96	0.40		14,191
83-1071 (W-10)	San Pedro Bed Webb County, TX	Float Sink	32.5 67.5	2.77	4.37	1.06		13,495
83-1072 (W-11)	Bull Creek Bed Coleman County, TX	Float Sink	0.00 100.0	X	X	X	X	X
83-1073 (W-12)	Thurber Bed Erath County, TX	Float Sink	7.9 92.1	2.22	2.08	1.32		13,660
83-1074 (W-13)	Dilco Bed McKinley County, NM	Float Sink	1.1 98.9	2.50	2.76	0.57	X	13,881
83-1075 (W-14)	PQ Dilco Bed McKinley County, NM	Float Sink	1.7 98.3	4.39	2.58	0.33	X	13,793
83-1076 (W-15)	Sundance Bed McKinley County, NM	Float Sink	1.0 99.0	4.66	1.38	0.61	X	13,478
83-1077 (W-16)	Dilco Bed M Seam McKinley County, NM	Float Sink	0.8 99.2	4.20	2.92	0.38	X	13,532
83-1078 (W-17)	Lignite, Wilcox Field Titus County, TX	Float Sink	0.0 100.0	X	X	0.76*	X	X

TABLE 9-4 (Continued)

Grand Forks Number	Location	Description	Weight (%)	Moisture (%)	Ash (%)	Total Sulfur (%)	Pyritic Sulfur (%)	Btu/lb
83-1079 (W-18)	Lignite, Wilcox Bed Titus County, TX	Float Sink	0.0 100.0	X	X	0.69*	X	X
83-1080 (W-19)	Rowe Coal Bed Barton County, MO	Float Sink	15.7 84.3	1.34	1.94	1.45		14,608
83-1081 (W-20)	Kniveton Bed Barton County, MO	Float Sink	19.4 80.6	1.76	2.22	1.23		14,470
83-1082 (W-21)	Fleming Seam Vernon County, MO	Float Sink	17.4 82.6	4.26	1.60	1.68		13,626
83-1083 (W-22)	Fleming Seam Vernon County, MO	Float Sink	35.1 64.9	2.66	2.76	1.85		13,909
83-1084 (W-23)	Mulberry Seam Bates County, MO	Float Sink	5.4 94.6	4.14	1.68	2.87		13,258
83-1085 (W-24)	Weir Seam Henry County, MO	Float Sink	4.5 95.5	3.38	2.40	2.52		13,426

*Duplicate analysis could not be performed due to small sample size.

X = Insufficient sample for analysis.

In general, 1.60 sinks contained approximately 50% ash with a high of 60.4% for W-15, Sundance Bed McKinley Co., NM, Croweburg Bed Wagner Co., OK. The low ash content in the 1.60 s.g. sink was 37.51% on coal W-24 from Henry Co., MO. This response to the float-sink test indicates that the test procedure is functional.

There is very little difference between the float response at the 1.30 s.g. for the two top sizes (65 mesh and 200 mesh). Data at 1.40 and 1.60 s.g. will be needed before any evaluation of the operation of the test procedure can be made for the different sample top sizes.

9.2.3 OIL AGGLOMERATION AND FROTH FLOTATION

9.2.3.1 Equipment

The equipment for oil agglomeration and flotation has been received, installed and tested. All equipment is functioning properly and work is proceeding at this time.

9.2.3.2 Preliminary Oil Agglomeration Test Procedure

The following preliminary test description is based on the tests at UNDERC and on published material, primarily by the National Research Council of Canada. The tests method will be further checked and modified if necessary during the next quarter.

The test will be done as follows:

1. Obtain a sample of approximately 100 gms of fine coal of known ash and moisture.
2. Add the weighed sample to 500 ml of D.I. water in a laboratory blender. Disperse coal sample in water at a minimum of 12,000 RPM for a minimum of 30 seconds.
3. Add agglomeration oil, 8% of the weight of the coal sample, to the blender. Blend coal/water/oil mixture at liquefy on the Oster blender, or low on the Waring units, for 10 minutes. If an inversion point is noted, record the time at which the phenomenon is observed. The inversion is the point where the mixture forms two visible phases, one light colored, containing the water and minerals, the other dark, enriched in coal and oil.
4. Phase separate the agglomerated sample on a 100 mesh screen or a mesh screen one standard size larger than the top size of the coal sample. Record the pH for the fluid that has passed through the screen. Wash the oil-rich material on the screen gently with 500 ml of water. Collect all the drained fluid, and filter, dry, and analyze the mineral-rich fraction as desired.

5. Physically remove the oil-rich material from the screen surface if the sample in the oil agglomerated condition is desired. If the coal is to be recovered free of oil, wash the sample with an organic solvent such as heptane or toluene and filter. This process may be repeated several times if necessary. Dry the sample, weigh, and analyze as desired.

9.2.3.3 Discussion of the Test Method

Oil agglomeration tests were done prior to 1970 at the National Research Council of Canada and tests in Canada have reached the pilot plant scale. The light agglomeration oils, such as kerosene, Stoddard solvent, and varsol give nearly identical results on a given coal. Kerosene will be the most commonly used light oil as it is representative of much of oil used in studies in the literature. A heavy motor or fuel oil will also be used. There is a general indication in the literature that eastern and high-rank coals agglomerate better with light oils and low-rank coals agglomerate better with heavier oils. The pulp density is not expected to be a large test variable and blender time is not critical after the oil has had sufficient time to contact the coal during blending. The 10-minute contact time should be sufficient for agglomeration using very heavy oils. The blender speeds are higher than those used in some studies, but the sample weight and fluid volumes are larger than the studies using lower blending RPM. The 8% oil weight is expected to give agglomerates large enough for relatively easy separation from the aqueous phase. There will be no initial attempt to control the pH.

9.2.3.4 Preliminary Oil Agglomeration Tests

Preliminary oil agglomeration tests have been made on several coals and on a coal-water slurry made with 330°C hot-water dried Indian Head. The coal size was 75% less than 90 μm . All coals agglomerated producing two distinct phases. No analytical work has been completed on these tests.

9.3 ACTIVITIES FOR THE NEXT QUARTER

Activities for the next quarter include:

1. Continuing the float-sink data base studies.
2. Preliminary analysis of the four coals for advanced cleaning and initial wet screen size tests.
3. Development and checkout of oil agglomeration methods and tests.

10. COMBUSTION RESEARCH AND ASH FOULING

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10.1 GOALS AND OBJECTIVES

The combustion research and ash fouling project has two primary objectives. The first is the development of fundamental data and correlations on the combustion reactions of low-rank coals. This information will be generated over a range of particle sizes, reaction atmospheres, and temperatures representative of the combustion process. 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 is to examine mineral matter transformations in low-rank coal combustion systems. Part of this effort will involve expansion of the technical data base at UNDERC on ash fouling and slagging in pc and cyclone furnaces burning LRCs. Additional work will deal with the mineral matter transformations occurring in combustion environments. This will include both laboratory studies and modifications to pilot-scale devices allowing for a more complete description of mineral matter as it moves through the combustion system.

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

1. Examine single particles of Beulah lignite using bench-scale combustor at UNDERC. Parametric testing will examine the effects of particle size, gas temperature, gas composition, moisture content (includes the effect of drying), and ash composition on behavior. Both physical changes and kinetic data will be examined. Testing will involve both whole coal and coal char.
2. Examine combustion kinetics of five additional low-rank coal char samples. Samples will include coal from the Gulf Coast and Powder River regions.

3. Examine low-rank coal using bench-scale sintering device. Study will focus on particle-to-particle bonding by looking at shrinkage and changes in electrical resistance. Will attempt correlation with results from pilot-scale testing.
4. Pilot-scale testing of five well-characterized lignites. Correlation of fouling behavior with petrographic analysis will be examined.
5. Preliminary studies of Raman Spectroscopy as a means of studying surface chemistry of high temperature ash material.
6. Publish the ash fouling topical report.

The planned activities for the current quarter include the following:

1. Examine single particles of low-rank coal and petroleum coke.
2. Examine ash particle metal substrate bonding.
3. Examine particle-particle bonding in ash deposits.

10.2 BENCH-SCALE COMBUSTOR

Construction of the bench-scale combustor for examination of single particles of low-rank coal has been completed. Previous quarterly reports have discussed in detail the capabilities that have been designed into the system. During this quarter, work has involved improvement and optimization of the optical pyrometer and the first of a series of experimental surface temperature measurements of single particles of petroleum coke.

10.2.1 EQUIPMENT

Calibration of the optical pyrometer has progressed to the point where reliable temperature measurements of the moving-pinhole target can be obtained. The system has been adjusted to give optimum readings in the 1000°-1500°C temperature range using 700, 800, and 850 nm lines. A new mounting rail has been fabricated for the pyrometer optics, greatly simplifying the alignment procedure. Improvements have been made to the computer programs controlling the pyrometer data acquisition and analysis routines.

The Hewlett-Packard 5880A gas chromatograph has been installed and tested. Tests of the gas chromatograph with mixtures of nitrogen, oxygen, and carbon dioxide prepared by the gas mixing system gave results within the accuracy of the mixing system. Tests of the gas sampling probe with GC analysis of the probe samples gave reasonable results for major gas components in the gas-fired combustor flame. However, minor gas components were not observed due to dilution of the extracted samples with the nitrogen quench gas. A second gas sampling probe employing indirect water cooling rather than nitrogen dilution is being designed to enable examination of combustion products present in trace amounts.

10.2.2 MEASUREMENT OF PETROLEUM COKE PARTICLE TEMPERATURES

To establish the validity of single-particle temperature measurements obtained with the bench-scale combustor and optical pyrometer, a series of experiments to obtain single-particle temperature measurements of petroleum coke at several gas temperatures and compositions is underway. The particle temperatures and kinetic rates obtained will be compared with results in the literature.

The first experiments in the test matrix resulted in particle temperatures of 75-106 micron petroleum coke particles at a gas temperature of 1000°C and gas composition of 33% oxygen and 67% nitrogen. Approximately thirty particle temperatures were obtained at each of four heights above the ignition point in the observation chimney. Distributions of the particle temperatures obtained are shown in Figures 10-1 through 10-4. Although the set of experiments and analysis of the data is not complete, the preliminary results appear consistent with the literature values under similar conditions.

10.3 COAL ASH SLAG PROBE

10.3.1 BACKGROUND

Previous investigations of the slagging potential of coals have used water wall devices in experimental furnaces with mixed results. A water wall device is simply a metal plate, similar in alloy to boiler tubing cooled to approximate boiler tube temperatures which collects ash deposits from the combustion of pulverized coal over a period of several hours to days. The accumulated slag can be weighed, sectioned, and then examined in a variety of ways to determine the apparent course of the deposition, the type of ash responsible, and by comparison of results from many coals arrive at an intercomparison of slagging potential.

Previous investigations have had one or two common deficiencies that the present apparatus should overcome. The long term test results from a water wall in an experimental furnace, usually firing from 50 to several hundred pounds of coal per hour, permit an assessment of the quantity of slag accumulation, and by sectioning the deposit, an electron probe analysis can be made of the deposit from metal surface to the last surface ash deposit. Without a device to accelerate the flow of furnace gases impinging on the water wall panel, the velocity in an experimental furnace of the gases and entrained ash is less than that in an actual boiler by an order of magnitude or more. In addition, because the water wall is usually installed for the duration of the test run, the process of deposition cannot be readily studied in short time intervals and the mechanism is inferred from the subsequent analyses of the sectioned slag deposit.

The work of Austin, Kinneman, Abbott, and others at Penn State has concerned the actual mechanism of slag deposition from inception to the build up of massive slag deposits. One of the principal tools used in this investigation has been a controlled surface temperature probe in which the furnace gases and entrained ash are accelerated through a nozzle to velocities approximating the velocities of the gases in a full scale boiler, i.e., from 50 to 100 ft/sec. In addition, the probe is designed to be inserted for relatively short periods

FIGURE 10-1. Particle temperature distribution for 75-106 μ m petroleum coke particles 65 mm above grid (gas temperature 1060°C, 33% oxygen).

FIGURE 10-2. Particle temperature distribution for 75-106 μm petroleum coke particles 75 mm above grid (gas temperature 1060°C, 33% oxygen).

FIGURE 10-3. Particle temperature distribution for 75-106 μm petroleum coke particles 85 mm above grid (gas temperature 1060°C, 33% oxygen).

FIGURE 10-4. Particle temperature distribution for 75-106 μm petroleum coke particles 95 mm above grid (gas temperature 1060°C, 33% oxygen).

while the experimental furnace is operating at steady state. This has permitted the initiation of deposition to be evaluated without the uncertainty of changes occurring after the build up of a thick slag cover.

This type of probe can also be used for longer deposition studies by incorporating a simulated soot blowing device to remove loose ash cover much like either soot blowing or the variable turbulence in a full scale boiler would do, leaving only adhered and sintered ash on the boiler tube surface.

The results of the Penn State investigations indicate that deposits of ash that are high in iron, often with significant amounts of silica are the primary means by which ash adheres to boiler tube surfaces. The iron in a partially reduced state, resulting from the incomplete oxidation of pyrite/pyrrhotite seems to flux with lesser amounts of silica, and form glassy ash when melted in a flame of sufficient temperature, generally above 1450°C. This glassy ash, which may require the presence of a certain amount of alkali, tends to pass from the flame with the cooling furnace gases and remain a supercooled, sticky, glass and is capable of impacting, wetting, and sticking to the much cooler boiler tube surfaces.

Capture of this ash by rapid quenching clearly shows these particles to be a mixture of glassy and crystalline materials, mostly magnetic with significant amounts of magnetite-like material, iron in the plus 2 state, or spinel-like structure. Subsequent reheating of the frozen ash shows it to melt considerably higher than the gas temperature at which it was collected. This clearly indicates a nonequilibrium process. The reheating causes most of the particles to crystallize. Actual furnace ash will generally form strong sinters at temperatures above 1000°C where a given coal has a history of slagging or fouling. The identity of the particles of ash that cause the greatest sintering tendency is a subject of ongoing research in a number of laboratories. It appears that the initial high iron content particles are usually larger than 3 microns, whereas the sintering species appear to be submicron in size and involve complex compounds of alkali metals, sulfates, and silica/aluminates.

10.3.2 OBJECTIVES FOR THE USE OF THE SLAG PROBE

Most North Dakota and Montana lignite coals do not cause slag problems in practice because of the lower temperatures of combustion, i.e., 1450°C or less, and the absence of large pyrite deposits or mineral concentrations in the coal matrix. The usual presence of large amounts of calcium may also prevent the occurrence of significant amounts of glassy, high iron ash particles, the calcium acting as a nucleating agent. However, certain lignite or brown coals from both Texas and Australia cause serious slag problems which appear to involve relatively low temperature melting glassy, silica dominated particles. One of the primary purposes of the probe built at Grand Forks is to study the initiation and growth mechanism of slag from these low-rank coals. The availability of this impact type of probe will also be useful for the investigation of slag from all ranks of coal.

10.3.3 APPARATUS DESCRIPTION

The slagging probe for use with the UNDERC ash fouling furnace is shown in Figures 10-5 and 10-6. Details of the various portions of the probe are described below.

Nozzle. The nozzle is made of a light weight pressure molded alumina ceramic, "Zircar" or "Sali" made by Zircar Corporation of Florida, New York. It has a density of 30 to 40 lbs/cu ft and is readily machinable on lathe or by hand with file or knife. The nozzle throat is 3/4" in diameter, an arbitrary size, and may well be larger in subsequent design modifications. Table 10-1 shows the relationship of nozzle diameter to gas velocity and the quantity of gas to be taken from the furnace through the nozzle to achieve the desired velocities of 50 to 100 ft/sec. The gas volumes are at 80°F (27°C); the assumed entering furnace gas temperature is 2500°F (1370°C).

Water Cooling Jacket. The cooling chamber and primary structure of the probe is made up of a 4" outside diameter stainless steel tubing and an inner 3" O.D. tube connected together by machined pieces. The connecting piece in the nozzle end also serves for the 8-32 threaded holes to secure the nozzle to the probe body with four, 1", 8-32 bolts. The entire rear cover is made in one piece with the necessary four tubing penetrations. Cooling water is brought to the nozzle end through two equally spaced 3/8" stainless steel tubes branched from a single 3/8" water inlet line.

Substrate Support and Cooling Block. This part and adjacent portions of the probe are shown completely dimensioned in Figure 10-6. The block is constructed of brass for better heat transfer from the substrate to the inner cooling surface as is the threaded insert which is soldered to the inner 3/4" stainless steel tube which serves as the exit for the internal cooling air/water. The substrate attachment face was machined to a flatness tolerance of 0.0001". Six equally spaced holes tapped for 4-40 bolts were put on a 1.62" diameter circle to secure the substrate and copper foil.

Air/Water Cooling Tubes. Cooling air is brought to the cooling block inner face through a 3/8" stainless steel tube with a reduced diameter outlet of 3/16" which forms the outer part of the cooling nozzle. The inner 3/16" stainless steel tube carries the water to the nozzle. The water nozzle is a 0.052" hole drilled in a bolt threaded into the end of this tube. The three "Swageloc" nuts external to the probe secure the three inner tubes using the "teflon" ferrals. This permits disassembly of the nozzle tubes from the rear, the 3/4" tube pushes forward with cooling block.

Furnace Mounting Flanges. Two ports are available for mounting the slag probe in the A.F. furnace. The two ports are located approximately 12" and 48" above the burner cone. When the probe is not in use, the 4-3/8" I.D. ports are closed with a blind flange and a loose piece of ceramic is placed in the port to keep ash from slagging on the inside of the port. The probe can be inserted while the furnace is operating at steady state or before starting up with gas. The usual precautions of operating at negative pressure are followed when inserting or removing the probe during a firing.

FIGURE 10-5. Slag probe for use with UNDERC ash fouling furnace.

TABLE 10-1

RELATIONSHIP OF NOZZLE DIAMETER, GAS VELOCITY, AND VOLUME

Inches	Velocity (ft/sec)*	Volume at 80°F in cu ft/hr
0.75	50	92.8
0.75	100	186
1.00	50	166
1.00	100	333
1.25	50	258
1.25	100	519

*The above is calculated from the following:

$$V = 0.9(D/24)^2 v (3600) T_s / T_f$$

where:

0.9 = The approximate correction for condensed water of combustion and water in fuel for low-rank coals

D = diameter of nozzle throat in inches

24 = divisor to obtain radius in ft

v = velocity of furnace gas through nozzle in ft/sec

T_s = 580°R (2500°F), standard temperature

T_f = 2980°R, assumed furnace gas temperature

3600 = factor to convert /sec to /hr

V = standard volume in cu ft/hr

FIGURE 6. Substrate support and cooling block for the UNDERC ash fouling furnace.

Substrate Preparation. The term substrate is synonymous with coupon and either term will suffice; the former is used exclusively in this report. The substrates were prepared from a piece of 3/16" thick A515 grade 70 boiler steel. This steel is extensively used in boiler construction and was chosen as representative of typical medium carbon steel similar in metallurgy to boiler tube metals. The plate was punched into 2-1/2" diameter pieces and flat ground on both sides to a nonpolished finish. Fifty-two substrates were made by Young Manufacturing Company of Grand Forks, North Dakota.

Each piece is drilled on the 1 5/8" diameter circle to match the tapped 4-40 holes in the brass cooling plate. In order to increase the amount of contact area between the substrate and brass, an interlayer of copper foil is drilled with a similar pattern. The copper is dead soft flashing, 0.019" thick. After drilling the holes, the surfaces must be carefully shaded to restore their original flatness or point contact and poor heat transfer will result.

After use, the area of maximum contact shows a different color than the area with less contact with the substrate. This system is the least desirable part of the apparatus and an improvement would be desirable. This lack of uniformity of the water/air mixture led to the use of the brass cooling block to distribute the somewhat uneven cooling of the air/water spray.

Measurement of the Substrate Temperature. The edge of the substrate is drilled 1/2" deep to receive a stainless steel clad chromel/alumel thermocouple lead in ceramic (MgO) insulation. The sheath is 1/16" diameter and 14" long. It is made by the Omega Engineering Company of Stamford, Connecticut. This lead is quite flexible and is bent around a 3/8" rod to enter the substrate with sufficient room to clear the interior of the suction chamber. The lead is secured to the rear face of the probe with a small compression fitting tapped into the rear face with a 1/8" NPT pipe head.

The temperature is indicated on a digital read out observable by the operator at the instrument control panel. There is approximately a 15 to 30 second delay for temperature changes to be observed on the substrate after a change in the air/water cooling system is made.

Control Instrumentation. The main cooling water to the outer jacket is set with a simple gate valve to a rate of one or two gallons per minute and the outlet monitored to be just warm to the touch, 90° to 120°F. The air flow to the nozzle is controlled with either a rotameter or a pressure regulator. In the first tests, the air flow through the 1/4" supply line was set between 40 and 50 psi. The water flow is the most critical control point to maintain a desired substrate temperature. When first operating with no ash cover, as much as 50 cc/minute is necessary to keep the temperature below 400°C. As the ash cover builds up, the water flow can be reduced to zero and the air flow also reduced.

The total quantity of furnace gas sucked through the probe determines the amount of nozzle air/water cooling required. In the first tests using the 3/4" ceramic nozzle, the inlet velocity was maintained at 50 ft/sec, assuming the gas temperature was 2500°F. The suction flow is regulated primarily by the amount of bypass air admitted down stream from the rotameter. The small "shop vac" used to supply suction has a capacity several times that actually needed. The control system for both cooling water and furnace gas is shown in Figure 10-7.

Based on experience with this type of probe at Penn State, a certain amount of blockage can be expected under certain combustion conditions, for example, when running with low temperature burning fuels or under reducing conditions. A vacuum gage located on the rotameter inlet line will indicate blockage as the bypass air is reduced to maintain the desired flow rate. Ceramic nozzle blockage will be encountered when the test coal is a severely slagging coal and the accumulated ash on the nozzle sinters during the test run.

Inlet Suction Gas Trap. The large amount of water of combustion and the extra water from low-rank coal combustion must be condensed and removed in the stainless steel trap to prevent fouling the rotameter. The trap is immersed in a bucket of ice water and the bottom exit line kept open to the vacuum manifold to remove the condensed water and some entrained ash and char. If the rotameter still tends to get wet or dirty, a second trap made of a one or two liter suction flask with a loose filter of glass wool is usually sufficient. The glass fiber filter in both traps should be replaced after each run.

FIGURE 10-7. Control system for cooling water and gas velocity in UNDERC slag probe.

Slag Evaluation Procedures. After most runs, a large amount of loose ash is attached to the surface with variable amount of adhesion and in some cases will have sintered to a firm well adhered slag mass. If the ash is not firmly attached, a standard removal technique is to use soft brushing of a predetermining number of strokes, this ash weighed and set aside for analysis and microscopic examination. The remaining deposit may have the property of being attached by "dry sticky forces" as well as a portion strongly bonded to the oxide surface.

Microscopic evaluation using both visual and SEM techniques will be used to obtain a three dimensional evaluation of the strongly adhered deposits. Sectioning of a well formed mass of slag often fails to clarify how the slag mass becomes attached because of two dimensionality of the section cut. For example, a number of eastern steam coals exhibit a build up of so called islands of adhesion which cover only a small portion of the surface. Between the well adhered islands, which are iron rich and made up of thousands of small ash particles, are areas of loose ash which eventually sinter over. When such a deposit is sectioned, the islands of adhesion may or may not be bisected by the section cut and the actual adherent structure is thus missed. This has led to the puzzling presence of loose ash under an apparently well adhered slag deposit.

In conclusion, a combination of observing the formation of slag deposits over short and longer intervals is probably necessary for a complete understanding of the slag mechanism and the composition of the ash which is most prone to both adhere and sinter in a significant slag build up. It is hoped that extensive use of this type of impact-suction probe will result in a series of standardized procedures which will enable a better prediction of slagging potential and the portion of ash responsible.

The development of standard impact probe slag evaluation procedures will permit testing of selective coal cleaning procedures, use of additives, coal blends, and other means of slag reducing procedures. This type of probe is also a relatively inexpensive means of looking at slag build up as the tests are generally only several hours duration.

10.4 PARTICLE-TO-PARTICLE BONDING OF LRC ASHES

Sintering tests using the bench-scale sintering furnace were conducted on additional ASTM ashes from low-rank coals using the procedures outlined in previous quarterly reports. The two ashes shown in Table 10-2, Beulah low Na and Beulah high Na, have their sinter points rated using shrinkage. Previous work has indicated that although electrical resistance may have some merit for evaluating the onset of melting of ashes, shrinkage may be a better method for rating ASTM ash sintering tendencies.

Additional tests were run on the Beulah high-Na ASTM ash. Separate sintering tests were run on two particle sizes, -60 mesh and $<10\ \mu\text{m}$, to determine what effect a reduced particle size may have on bonding (i.e., electrical resistance and shrinkage). Results are shown in Table 10-2.

TABLE 10-2
SUMMARY OF ASTM ASH SINTER POINTS

Ash	Shrinkage Sinter Point, °C
Beulah low Na	829
Beulah high Na:	
-60 mesh	884
<10 μm	867
-60 mesh heated to 850°C	--
-60 mesh heated to 910°C	896
-60 mesh heated to 1000°C	898

The Beulah high-Na (-60 mesh) ASTM ash was heated to three temperatures, one below the calculated sinter point, one very near the sinter point, and one much greater than the sinter point, 850°, 910°, and 1000°C, respectively. SEM micrographs were made to examine bonding between particles at those temperatures (see Figure 10-8a, 10-8b, and 10-8c).

A series of compounds made from pure mineral phases is another area of interest using the bench-scale sintering device. Up to this point five compounds have been made and tested. Results are shown in Table 10-3. Combinations of mineral phases were chosen based on tendency to form compounds which are significant in the fouling deposits noted in low-rank coal combustion systems. This may lead to identification of the specific phases involved in the particle-to-particle bonding noted in ash deposits.

TABLE 10-3

SUMMARY OF PURE MINERAL PHASE SINTER POINTS

Minerals	Molar Ratio	Sinter Points, °C
CaAcetate + Kaolinite $\text{CaCH}_3\text{CO}_2 + \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$	1:1	725
NaAcetate + Kaolinite $\text{NaCH}_3\text{CO}_2 + \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$	1:1	865
NaAcetate + CaAcetate + Kaolinite	1:1:1	785
NaSO_4 + Kaolinite	1:1	Heated to 1050°C with no indicated point of sintering
NaSO_4 + Kaolinite + CaAcetate	1:1:1	890 with additional displacement increase at 991°C

11. FLUIDIZED BED COMBUSTION OF LOW-RANK COALS

Project No.: 7206

B&R No.: AA3505450
AA3510100

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11.1 GOALS AND OBJECTIVES

The Fluidized Bed Combustion (FBC) project at the University of North Dakota Energy Research Center (UNDERC) has three major goals: 1) to resolve identified problems such as bed agglomeration, low turndown ratio, and enhanced utilization of SO_x sorbents; 2) to continue the development of a data base on the FBC process and systems utilizing low-rank coals; and 3) to develop advanced AFBC concepts for use with low-rank coals.

Specific objectives of the Fluidized Bed project for the second year of the Cooperative Agreement which contribute to these major goals are:

1. The evaluation of agglomeration formation, including the effects of different coal feed methods on bed material agglomeration, obtaining more representative bed samples by the use of a bed sampling probe, the performance of laboratory studies to better understand agglomeration formation, and based upon laboratory results, the demonstration of sodium forms on bed agglomeration on the 2.25 sq. ft. AFBC.
2. The design and construction of a second generation pilot scale fluid bed combustor that will beneficially utilize the characteristics of low-rank coals.
3. The determination of the radiative component of the heat transfer coefficient for in-bed heat transfer tubes.
4. The comparison of PFBC data from New York University to AFBC data on similar low-rank coals.
5. The completion of a technology base report on the performance of low-rank coal in Atmospheric Fluidized Bed Combustion.

11.2 ACCOMPLISHMENTS

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

11.2.1 AGGLOMERATION FORMATION IN AFBC OF LOW-RANK COALS

11.2.1.1 Alternate Feed System: Effect on Bed Agglomeration

Four runs using the 2.25 ft² atmospheric fluidized-bed combustor at UNDERC were performed. Modifications to the coal feed system of the 2.25 ft² unit were completed at the start of the quarter. The previous coal feed system, shown in Figure 11-1, was designed to pneumatically feed coal underbed. The recently completed coal feed system, shown in Figure 11-2, is capable of feeding coal particles up to 1-1/4 inches in size overbed and 1/4 inch coal particles underbed by either pneumatic or screw feed.

FIGURE 11-1. Previous coal feed system configuration.

Runs B51-0284 and B52-0384 were shakedown runs to test the operation of the modified coal feed system. Several problems were initially encountered with the system when operated in the underbed feed configuration. Combustion was very unstable as evidenced by wildly fluctuating flue gas O₂ concentration and bed temperatures. Some of the instability was apparently caused by uneven feeding of the coal feed auger. To correct the problem, the auger speed was

FIGURE 11-2. Modified coal feed system.

doubled, which resulted in a significant improvement in combustion stability. Another cause of unstable combustion conditions was the leakage of coal fines by a diverter valve into the overbed feed port when feeding through the underbed feed system. This leakage of coal fines was eliminated when a blank flange was installed in the overbed coal feed piping.

Run B53-0484 was the baseline test for a series of runs to determine the effects of alternate coal feeding systems on the AFBC of low-rank coals. A new shipment of lignite from Beulah, North Dakota (Knife River Coal Mining Co.) was used for the run and will be used for the entire test series. The coal was fed underbed with the pneumatic coal feed system. Other specified parameters for the run included a silica sand bed material, 1650°F average bed temperature, 6 ft/sec superficial bed velocity, and 20% excess air. Preliminary observations after the scheduled 96-hour run revealed no indications of agglomeration in the bed. Further operational results for the run will be presented when the necessary sample analyses have been completed.

Underbed pneumatic coal feeding was also used during the second run in the series, B54-0684. The run parameters were unchanged from the baseline test except that the average bed temperature was specified to be 1450°F instead of 1650°F. This run like the previous run was scheduled for 96 hours burning coal. Sampling of the bed material at run hour 50 produced some small agglomerates which were noted to consist of approximately ten ash-coated grains of silica sand cemented together. Subsequent bed material sampling showed an increasing degree of bed material agglomeration as evidenced by the

increasing size of the agglomerates. After 80 hours on coal, loss of fluidization caused total agglomeration of the bed forcing early shutdown of the run.

Previous testing had indicated that bed material agglomeration when burning Beulah lignite was a function of bed temperature. Higher bed temperatures were thought to promote agglomeration. Although high temperatures do promote bed agglomeration, it may also be true that bed agglomeration can occur at low bed temperatures. The preliminary visual observations from Run B54-0684 seem to support this but will not be verified until further results from the run are received.

11.2.1.2 Particulate and Gaseous Sampling Probe

Testing has been performed using the bed sampling probe shown schematically in Figure 11-3. The sampling probe is being used in conjunction with agglomeration testing to obtain representative bed material samples from within the bed at various locations and intervals during pilot-scale testing. A nitrogen quench is used for rapid cooling of particulate and the gas stream as they enter the probe to minimize chemical changes occurring on the surface of bed particles. The water cooled outer tube is used to minimize preheat of the nitrogen quench gas.

Four samples were obtained from three locations and at three time intervals during Run B51-0284. These samples along with three samples obtained from the bed drain are being compared using the scanning electron microprobe.

11.2.1.3 Laboratory Scale Testing

Although operating procedures tested have shown promise for controlling agglomeration, the actual causes and mechanisms of the agglomeration process are not fully understood. Several observations and postulates have been stated in recent reports regarding factors affecting agglomeration. As a more cost-effective program (compared to pilot-plant testing), various laboratory tests have been planned and initiated to identify factors such as mineral composition and operational conditions which are conducive to causing agglomeration. This will potentially result in the identification of additives that can control agglomeration and the conditions in the combustor where agglomeration is imminent. To accomplish this, laboratory tests have been performed using bed material generated in pilot-plant tests and tests with simple component systems simulating the materials that are present in the coal ash. Work is being performed in the following areas.

11.2.1.3.1 Heated Stage Microscopy

Particles of bed material have been heated in the Metallux II Heating Stage Microscope, with electron microprobe analyses conducted before and after heating. Preliminary results suggested that Na and S decreased in relative concentration on particle surfaces after heating to 750°C, while Ca and Si increased. In a more extensive test program, it was observed that this technique is subject to substantial experimental error, since significant changes occurred in analyses taken for a control sample not subjected to heat treatment, though otherwise handled in the same manner as the rest of the samples.

FIGURE 11-3. Sample probe.

Observations of sintering characteristics were made at a magnification of 200x. Samples consisted of silica sand particles (+30 - 60 mesh), Beulah high-sodium ASTM ash, and a low-temperature ash of a Beulah coal. The temperature regime in which sintering occurred was 880°-970°C. The mixture containing low-temperature ash sintered at lower temperatures. Individual particles of bed material were observed during heating. No physical changes were evident up to a temperature of 1000°C, at which point a liquid phase developed. This liquid phase did not occur in an ash from an ion-exchanged coal.

Because of problems related to accurate measurements of temperature and reproducibility, the heating stage microscope will be used only for qualitative comparisons of morphological changes upon heating. Specifically, the apparatus will be utilized to compare sintering temperatures as a function of particle size and of packing density to evaluate these effects in relation to use of the sintering test. The microscope heating

elements offer a rapid heating rate, thus providing a quick screening device to indicate whether a need exists for more quantitative measurements using the sintering test.

11.2.1.3.2 High-Temperature Dilatometry

A sintering test has been developed to evaluate the bonding strength of ash particles based on the relationship between a) temperature and electrical resistance as measured across a bed of ground sample, and b) temperature and shrinkage, the latter measured using a displacement transducer, concurrently with above.

This sintering test provides a method of evaluating fly ash or mineral mixture particle-particle interactions. To date, the test has been primarily used to determine the tendency of a particular coal to produce fouling deposits in the convective-tube banks of a utility boiler.

The goal of this work is to quantitatively compare the sintering properties of bulk bed materials to determine whether particle-particle behavior as observed in the sintering apparatus correlates with agglomeration, and to quantitatively relate sintering properties to bed particle residence time during an individual run.

Test plans include determining the relationships between sinter point, temperature, and run time using a) Beulah high-sodium ASTM ash mixed with varying proportions of added SiO_2 to evaluate the influence of the silica-to-sodium ($\text{SiO}_2/\text{Na}_2\text{O}$) ratio, and b) synthetic mineral mixtures of silicon dioxide, sodium oxide, calcium oxide, kaolin, calcium sulfate, sodium sulfate, and pyrite.

Figure 11-4 shows the sintering temperature (determined by plotting the log of resistance versus the reciprocal of absolute temperature) of ground bed materials as a function of the sodium oxide content in the bulk bed material for test BA1-2101. During this test run severe agglomeration occurred after 64 hours of operation. It can be seen that the sintering temperature decreased with increasing bed material sodium content. Further work will be required to determine if these results can be related to the agglomeration process.

11.2.2 TECHNOLOGY BASE REPORT

A comprehensive two-day review session was conducted by J.L. Cooper of Combustion Power Company and D.R. Hajicek of UNDERC to assess the status of the technology base report on the "Performance of Low-Rank Coal in Atmospheric Fluidized Bed Combustion." Details were worked out on the overall organization and the type of format to be used. Sections were identified where data and background information could more appropriately be located in an appendix to allow for continuity in the main body of the report and still retain pertinent information. In addition, sections were identified that require additional data or explanation for completeness in terms of technical information and clarity. The completed draft report will be ready for editing during the next quarter.

FIGURE 11-4. Sintering test results of BA1-2181 bed material.

11.2.3 SECOND GENERATION CONCEPTS

An "Evaluation of Second Generation FBC Concepts for Use with Low-Rank Coal" was completed. The following are the key points:

- o A major concern for fluidized bed combustion of low-rank coal is the ability to operate efficiently with an agglomerating (high sodium) coal.
- o Three of the seven concepts evaluated have good potential for avoiding agglomeration problems when operating with high-sodium, low-rank coals--the Battelle Ultra-High Velocity, the Westinghouse Draft-Tube, and the A.D. Little-Pulsed.
- o UNDERC would like to participate in developing low-rank coal tests plans for any of the advanced concepts that may be tested. It would be possible to evaluate the ability of the A.D. Little-Pulsed concept to prevent agglomeration by installing a pulse unit in the UNDERC AFBC.
- o Staged combustion for NO_x control is a common element among the advanced concepts. The UNDERC AFBC should be modified to allow testing of staged combustion of low-rank coals. Construction of a smaller test combustor should be considered for a more cost-effective operation.

12. LOW-RANK COAL/WATER SLURRY COMBUSTION

Project No.: 7211

B&R No.: AA3515050

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12.1 GOALS AND OBJECTIVES

The overall project goal is to develop basic data on 1) the combustion performance of slurries prepared from low-rank coals, primarily from the hot-water drying process, 2) the emissions from the combustion of these slurries and 3) slagging and fouling problems associated with their combustion.

Preliminary data from GFETC/UND studies indicate that hot-water drying shows potential as a viable technique to prepare low-rank coals for slurry combustion. In addition to removing moisture, removal of sodium and/or sulfur has been noted in lignites dried by this process. The dried coal appears to have a lower bulk density which may be contributing to the increased stability noted with suspensions prepared by hot-water drying. No prior work has been done, to our knowledge, on combustion of low-rank coal/water slurries that have been subjected to hot-water drying. A review of the literature on slurry combustion indicates that the more commonly used bituminous coals tend to reaggregate as the larger spray droplets containing them evaporate in a radiant environment, leaving particles substantially larger than the size to which the coal was ground. This results in relatively sluggish combustion and incomplete carbon burnout. Lignites, on the other hand, are completely non-agglomerating and have a high thermal friability such that with evaporation the particles will remain no larger than their initial size (300 microns, max.) and possibly significantly smaller.

The specific goals of the project for the second cooperative agreement year are:

1. Evaluate the initial results of bench-scale combustion testing by BYU of low-rank coal/water slurries provided by UNDERC.
2. Design, construct, and evaluate a pilot scale low-rank coal/water slurry combustion system by modification of the existing UNDERC ash fouling furnace.
3. Operate the pilot combustion system to characterize and compare performance of various commercial (bituminous) and UNDERC-produced (lignite) slurries with alternative hardware components.

12.2 ACCOMPLISHMENTS

12.2.1 COMBUSTION SYSTEM DESIGN

The existing 550,000 Btu/hr ash fouling furnace unit has been modified to allow combustion of slurry, as well as pulverized coal. A new bottom section consisting of a refractory-lined burner throat, air atomized slurry nozzle, gas ring imbedded in the burner throat, and an air register to impart swirl to the combustion air, was built to replace the existing bottom section during slurry combustion. All components of the new assembly are easily installed on the furnace to interface with flame safety controls. The skid-mounted slurry feed system, consisting of tanks, pumps, piping, and instrumentation, can be removed when not in use. The slurry feed system and modified ash fouling furnace are shown in Figures 12-1 and 12-2. The last quarterly report described the three alternate atomizers and details of the new burner assembly, which are now operational, and a high-velocity thermocouple probe.

An additional accessory item for use in the slurry combustor is a slag probe, shown in Figure 12-3. It will draw from the combustion zone a continuous sample of hot gas which will impinge on a brass plate, whose temperature is closely controlled by a stream of cooling water. Droplets of slag will condense on the plate for easy microscopic examination. Details of the probe design and operation are included in the Fundamental Combustion and Ash Fouling section of this quarterly report.

Scheduling of combustion tests with lignite slurries will depend upon completion and operation of the slurry preparation pilot plant, currently in final stages of construction. To establish a basis of comparison with other coal slurry combustion programs, 8 to 10 barrels of each of two commercially-available bituminous coal slurries have been received. These are ARC-COAL, purchased from Atlantic Research, and COL-AL, courtesy of Babcock and Wilcox, manufactured by Kennedy-Van Saun, both at 70% to 75% solids.

12.2.2 PRELIMINARY OPERATION

In the final days of this reporting period (June 27, 1984), the system was operated for 3 hours, firing ARC-COAL slurry, and shut down voluntarily. There were no apparent operating problems. From this brief, preliminary run, the following observations are encouraging:

1. After preheating the furnace with the gas ring burner, the coal slurry ignited with the gas ring turned off. Ignition was by electric spark and radiant heat from refractory walls, with secondary combustion air preheated to 600°F. Outlet temperature at the top of the furnace was steady at 2000°F. The slurry feed rate was 66 to 68 lb/hr or about 0.135 gpm.
2. Adjustment of the atomizing (primary) air flow and swirl adjustment on the burner gave conspicuous variety in the size, shape, and position of the flame.

FIGURE 12-1. Schematic of coal slurry feed system.

FIGURE 12-2. Slurry combustion furnace (modified ash fouling unit).

FIGURE 12-3. Slag probe.

3. After the 3-hour run, the bottom of the furnace was completely filled to above the dam around the burner with a very light, fluffy, free-flowing ash, as shown in Figure 12-4. It was very easily removed, showing none of the agglomeration typical of slags formed when burning dry, powdered coals in the same unit. Under a microscope, the particles were smoothly rounded, roughly in the range of 100 to 500 microns with a hollow, porous structure. During operation, the ash deposit appeared to fall back onto the burner but was easily blown out of the way by the air blast. In Figure 12-4, note the transition from the light-colored (redish-tan) surface of the ash heap to the near-black of the lower layer deposited earlier. Small amounts of the lighter material were also loosely deposited on the combustor walls. A quick analysis of the lower, black layer reveals it to be over half carbon, indicating incomplete burnout and an oxygen-deficient condition in the annular gutter.

FIGURE 12-4. Ash deposit in slurry combustion furnace.

4. Viewed through the sight ports, the flame contained many sparks and streaks, some quite large. Flaming particles, some possibly over a millimeter in diameter, were seen landing on the ash deposit's surface and burning there. This confirms the reagglomeration mechanism described above for bituminous coal slurries.

12.2.3 CONCLUSION

The coal-water slurry combustion system is essentially complete, has been tested briefly, and appeared to work as intended on the first attempt, with no obvious problems.

13. ASH AND SLAG CHARACTERIZATION

Project No.: 7302

B&R No.: AA1515050

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13.1 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 coal.

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 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 to continue work on several activities: collection of samples of low-rank coals; ashing and slagging of low-rank coal samples under controlled laboratory conditions, with attendant chemical and mineralogical analyses of the ashes; development of further understanding of mineral transformations during ashing by heating synthetic ash mixtures and development of an apparatus to measure surface tension of slags.

13.2 MINE SAMPLING

Two field trips have been conducted to obtain bulk samples for Coal Science research. A trip to the Freedom Mine near Beulah, North Dakota was conducted in May. The Freedom Mine is expected to supply 14 million tons of lignite per year to the Great Plains Coal Gasification plant and the adjacent Antelope Valley power plant. The Freedom Mine produces lignite from the Beulah-Zap bed

in the Sentinel Butte Formation. The bed is about 3 meters (12 feet) thick at this location with a minor clay parting in the middle. Samples were taken from subequal vertical intervals of the seam exposed along the high wall to fill five 5-gallon pails. Additional hand samples were also taken for lithotype analyses. The bulk sample of lignite was crushed and split into two pails of 1/2 inch coal, 2 pails of 8 mesh coal preserved in argon, and 65 250 ml bottles of 60 mesh coal preserved in argon.

A second trip was made in mid-June to the Rosebud mine near Colstrip, Montana and to the Wyodak Mine near Gillette, Wyoming. Both of these mines produce subbituminous coal from the Fort Union Formation in the Powder River Basin.

The Rosebud Mine produces 10-15 million tons of coal per year for an adjacent power plant and for shipping. The mine produces from the Rosebud seam which averages 7 meters (23 feet) thick with 6-60 meters of overburden. The seam was sampled in vertical intervals to yield seven 5-gallon pails of bulk coal.

The Wyodak Mine produces about 3 million tons of coal per year for an adjacent power plant and for shipping. The mine produces from the Wyodak (or Smith and Roland) seams which are cumulatively 25 meters (80 feet) thick with discontinuous clay partings. Approximately 15 meters of exposed coal was available for sampling. Again, seven 5-gallon pails were filled and lithotype samples were taken.

13.3 SLAG MINERALOGY

Slags produced from three North Dakota lignites, 1) Beulah low-sodium, 2) Beulah high-sodium, and 3) Beulah ion-exchanged, were studied in detail as to their mineralogy using x-ray diffraction and SEM microprobe. The SEM microprobe was used as an additional tool for analysis to identify minerals present below XRD detection limits, poorly formed crystalline phases and mineral phases present in solid solution series. Bulk compositions of the raw coal samples are presented in Table 13-1.

13.3.1 RESULTS OF BEULAH SLAG MINERALOGICAL ANALYSIS

Beulah Low-Sodium Slag - The following mineral phases were detected by XRD: Anhydrite (CaSO_4), pyroxene (Ca, Mg, Fe) (Mg, Fe, Al) ($\text{Si, Al}_2\text{O}_6$), and magnetite ($\text{Fe}^{+2}, \text{Fe}^{+3}_2\text{O}_4$). SEM microprobe analysis specifically distinguished the pyroxene as being fassaite ($\text{Ca(Mg,Fe,Al)(Si,Al}_2\text{O}_6$). Fassaite forms a solid solution with augite within the pyroxene family and is merely the calcium-rich end member of augite. Magnetite was identified by SEM microprobe to actually be spinel with a chemical formula of $(\text{Mg,Fe}^{+2})(\text{Al,Fe}^{+3})_2\text{O}_4$ thereby representing a solid solution phase between the spinel and magnetite series of the spinel mineral group. Trace quartz (SiO_2) and anorthite were also seen. No feldspathoids or silica-rich aluminosilicates, other than pyroxene, were observed.

TABLE 13-1
INORGANIC ANALYSES OF RAW COALS STUDIED BY XRF

Coal Name	Major and Minor Elements (Weight Percent of As-Received Coal)									
	Si	Al	Fe	Mg*	Ca	Na*	S	K	Ti	Ba*
Beulah Low Sodium	0.90	0.54	1.02	1.18	1.57	0.14	2.01	0.09	0.05	0.02
Beulah High Sodium	0.35	0.29	0.52	0.67	1.81	0.46	0.75	ND	0.06	0.04
+Beulah Ion Exchanged	0.78	0.62	0.52	0.26	1.01	0.39	0.72	ND	0.04	NA

+Beulah ion exchange analysis by XRF.

*Concentrations measured by neutron activation.

ND = Not Detected

NA = Not Available

Beulah High-Sodium Slag - The minerals identified by XRD and SEM are as follows: melilites $(Ca,Na,K)_2(Mg,Fe,Al)(Si,Al)_2O_7$, hauyne $(Na,Ca)_8(Si,Al)_{12}O_{24}(SO_4)_2$, nepheline $(NaAlSiO_4)$, magnetite $(Fe^{+2},Fe^{+3})_2O_4$, quartz (SiO_2) , and corundum (Al_2O_3) . According to SEM analysis, the melilite was characterized as being calcic, having a chemical formula of $Ca_2(Mg,Al,Fe)_{.94}(Si,Al)_2O_7$. SEM again distinguished magnetite as a spinel as in the Beulah low-sodium slag. In addition to minerals already mentioned, a sodium-calcium sulfate $(Na_{10}Ca_4(SO_4)_9)$ was detected by SEM. This particular sulfate was not originally identified by XRD.

Beulah Ion-Exchange Slag - Beulah ion-exchange coal was produced by a continuous process of exchange using .006 M H_2SO_4 for a period of 45 minutes on coal less than 1/4 inch in diameter. The process resulted in a 10% ion exchange of exchangeable cations. Mineralogical analysis of the slag sample contained a member of the sodalite group (Lazurite - $(Na,Ca)_8Al_6O_{24}(SO_4)_2$), a pyroxene (Fassaite - $Ca(Mg,Fe,Al)(Si,Al)_2O_6$), anhydrite $(CaSO_4)$, and a melilite $(Ca,Na)_{2.16}(Mg,Fe,Al)_{.27}1.91(Si,Al)_{.12}2O_7$.

13.3.2 CONCLUSIONS

A comparison of the slag mineralogies of these three slags supports the notion that a higher percentage of alkali cations contained within the original coal structure results in a larger percentage of complex calcium or sodium aluminosilicates typically found in slag deposits. Beulah low-sodium slag contained spinel and pyroxene but none of the feldspathoids common to fouling deposits. On the other hand, Beulah high-sodium slag contained a large variety of fouling feldspathoids, i.e., melilites, hauyne, and nepheline. The

presence of organically-bound sodium and calcium cations available for substitution within pre-existing aluminosilicates seems to be a prerequisite for producing minerals typical of fouling deposits.

Ion-exchanged Beulah slag contained slightly fewer types of aluminosilicates. Perhaps this may be explained by the fact that 10% of all exchangeable cations were removed prior to slagging. In fact, if the coal were exchanged to a greater degree there would probably be an even greater reduction in the formation of complex aluminosilicates in the slag.

13.4 MINERAL TRANSFORMATIONS DURING ASHING

Mineral transformations were determined for ashes from eleven low-rank coals from the Northern Plains and Gulf Coast (UNDERC Technical Progress Report January - March 1984). Ashes were produced at 125°, 750°, and 1000°C. The phases produced were often complex and dependent upon the form of the inorganics and minerals present in the coal.

To further understand the sources of the inorganics and processes responsible for mineral transformations in coal, work was initiated in examining mineral transformations that occurred when synthetic combinations of minerals and inorganic compounds typical of North Dakota lignites were heated to 750° and 1000°C. Two, three, and four component systems were examined at various molar ratios which were deficient or rich in calcium, sodium, or sulfur. Of particular interest was the simulation of high temperature compound mixtures responsible for forming feldspathic aluminosilicates characteristic of minerals formed when ashing some Fort Union coals.

Minerals were ground to -60 mesh to match the particle size of coal in the sample bank. Samples were rapidly heated to 750°C for 2 hours. Half of the sample was removed and air quenched. The remaining sample was returned to the furnace and heated up to 1000°C. After 2 hours the sample was removed from the furnace and air quenched. Calcium and sodium acetates were used to simulate organically-bound calcium and sodium. Minerals used in the systems include calcite, kaolinite, quartz, and pyrite. Ratios of reactants were determined on a molar basis.

The model systems of particular interest (presented in Table 13-2) will be discussed with concentration on mineralogical products. Of major concern are the interactions of calcium and sodium responsible for forming complex aluminosilicates typical of fouling deposits.

13.4.1 RESULTS AND DISCUSSION

Calcium - Calcite or calcium acetate were used as calcium sources in systems A, B, C, D, F, H, and I. CaO was present as a decomposition product in 750°C ash samples containing calcite (CaCO_3) (Systems A and C) but absent in samples where calcium acetate was the calcium source (Systems B, D, F, H, and I). Coals previously reported in the UNDERC Technical Progress Report January - March 1984 did not exhibit either CaO or CaCO_3 peaks in x-ray diffractograms of low-temperature or ASTM ashes. Calcite may have been present below detection limits of x-ray diffraction (<5%). Because of the absence of CaO and CaCO_3 in ashes produced at 750°C, we suggest that the source of calcium

TABLE 13-2

SYNTHETIC COMPOUND MIXTURES AND TRANSFORMATIONS THAT OCCUR DURING HEATING

Compound Mixtures	Molar Ratios	Temp., °C	Analyzed Minerals	Processes
A. Calcite (CaCO_3) + Kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$)	1:25	750	CaO + Calcite (CaCO_3) + Amorphous Phase	Oxidation; dehydration and collapse of kaolinite structure
		1000	Gehlenite ($\text{Ca}_2\text{Al}_2\text{SiO}_7$) + CaO + Mullite + Quartz (SiO_2)	Interstitial substitution in reordered kaolinite structure
B. $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$ + Kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$)	1:1	750	Amorphous	Dehydration, oxidation
		1000	Gehlenite ($\text{Ca}_2\text{Al}_2\text{SiO}_7$) + Quartz (SiO_2)	Interstitial substitution
C. Calcite (CaCO_3) + Pyrite (FeS_2)	1:2	750	Anhydrite (CaSO_4) + Calcite (CaCO_3) + Hematite (Fe_2O_3) + CaO	Oxidation; sulfur fixation
		1000	Anhydrite (CaSO_4) + Hematite (Fe_2O_3) + Magnetite (Fe_3O_4) + CaO	
D. $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$ + Pyrite (FeS_2)	2:1	750	Anhydrite (CaSO_4) + Magnetite (Fe_3O_4)	Oxidation; sulfur fixation
		1000	Anhydrite (CaSO_4) + Magnetite (Fe_3O_4) + Hematite (Fe_2O_3)	
E. $\text{NaC}_2\text{H}_3\text{O}_2$ + Kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$)	1:1	750	Unidentified peak + Amorphous	Dehydration
		1000	Nepheline (NaAlSiO_4)	Interstitial substitution in reordered kaolinite structure
F. $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$ + $\text{NaC}_2\text{H}_3\text{O}_2$ + Kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$)	1:1:1	750	Carnegieite (NaAlSiO_4)	Dehydration; interstitial substitution in reordered kaolinite structure
		1000	Nepheline (NaAlSiO_4) + Gehlenite ($\text{Ca}_2\text{Al}_2\text{SiO}_7$)	Interstitial substitution
G. Na_2SO_4 + Kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$)	1:1	750	NaSO_4 + Amorphous	Dehydration
		1000	Carnegieite (NaAlSiO_4) + Nepheline (NaAlSiO_4)	Interstitial substitution
H. Kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$) + Na_2SO_4 + $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$	1:1:1	750	Na_2SO_4 + Amorphous	Dehydration
		1000	Gehlenite ($\text{Ca}_2\text{Al}_2\text{SiO}_7$) + Nepheline (NaAlSiO_4) + Hauyne ($(\text{Na,Ca})_8(\text{Si,Al})_{12}\text{O}_{24}(\text{SO}_4)_2$)	Interstitial substitution
I. Kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$) + Quartz (SiO_2) + $\text{Na}(\text{C}_2\text{H}_3\text{O}_2)$ + $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$ + Pyrite (FeS_2)	1:2:1:1:1	750	Quartz (SiO_2) + Anhydrite (CaSO_4) + Hematite (Fe_2O_3)	Dehydration; oxidation, sulfur fixation
		1000	Quartz (SiO_2) + Anhydrite (CaSO_4) + Hauyne ($(\text{Na,Ca})_8(\text{Si,Al})_{12}\text{O}_{24}(\text{SO}_4)_2$) + Hematite (Fe_2O_3) + Magnetite (Fe_3O_4)	Interstitial substitution Oxidation

which formed aluminosilicates at high temperatures in coals studied was primarily organically-bound calcium with minor amounts of calcium contributed by calcite.

Calcium acetate was observed to react with pyrite at 750° and 1000°C to generate anhydrite peaks of greater intensity than calcite reacting with pyrite (Systems C and D). Sulfur fixation of calcium from calcium acetate by pyritic sulfur was greater due to the similar temperatures at which calcium acetate decomposed and pyrite oxidized (~400 to 500°C). Calcite, on the other hand, does not decompose until higher temperatures (~750) therefore the calcium necessary to form anhydrite was not as readily available. SO₂ formed by oxidation of pyrite is then lost to the atmosphere by the time calcite decomposes.

Calcium and Sodium - Mineral phases in Systems B and E contained calcium acetate and sodium acetate respectively mixed with kaolinite. In both systems minerals were largely amorphous at 750°C. In System F, where both sodium and calcium acetate were present in equal molar ratios, carnegieite was formed at 750°C as opposed to an amorphous phase.

Most aluminosilicates formed from interstitial substitution of calcium and sodium within dehydrated clay structures. These transformations often require reordering of the clay (kaolinite) structure which commonly occurs at 900°C; therefore reordered aluminosilicate minerals were not present in ashes produced at 750°C. However, in System F an aluminosilicate (carnegieite) was formed at 750°C. Possibly calcium acted as a catalyst in reordering of the clay structure.

In Systems B and E nepheline and gehlenite were formed respectively at 1000°C. In System F both nepheline and gehlenite were formed at 1000°C showing no mutual substitution of calcium and sodium within the same aluminosilicate framework.

Sodium - Sodium acetate as a sodium source mixed with kaolinite (System E) produced nepheline at high temperature (1000°C). Sodium sulfate in combination with kaolinite (System G) formed carnegieite and nepheline. Although the chemical formulas are identical, carnegieite and nepheline differ structurally and therefore differ in their physical properties. While XRD analysis of coals studied to date did not detect any carnegieite in high-temperature ash, previous work at the Center has reported this mineral present in deposits formed on the walls of the gasifier unit.

Feldspathoid Production - In Systems H and I sulfur was introduced in the form of sodium sulfate and pyritic sulfur. In both systems hauyne, a silica deficient mineral, was formed even when an excess of silicon was present. This supports the theory that in a solid state, quartz is relatively unreactive with previously existing aluminosilicate structures, i.e., dehydrated clays. In System I pyritic sulfur, calcium and sodium acetate were involved in forming anhydrite and hauyne. In System H sodium sulfate and calcium acetate were completely tied up in hauyne, gehlenite, and nepheline production. System H most closely resembles the more complex mineralogy typical of low-rank coal ash fouling samples studied so far.

13.4.2 CONCLUSION

Isolating the processes and components responsible for forming minerals typical of ash fouling deposits will aid in predicting the fouling behavior of specific coals. The role of organically-bound calcium and sodium in combination with clay structures was significant in forming minerals common to fouling deposits. By reducing the mineral interactions to two and three components one can build up to more complex mixtures and understand the processes involved as stated in Table 13-2. Ultimately the study will extend to adding known minerals and compounds to demineralized coal and tracing mineral transformations through various temperature phases.

14. ORGANIC STRUCTURE

Project No.: 7303

B&R No.: AA1515100

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14.1 GOALS AND OBJECTIVES

The objective of this research is to develop a description of the major organic structural features of low-rank coals, including the nature of the cyclic structures, aromaticity and degree of ring condensation; the structure and numbers of bridging groups; and the amount and distribution of hydroaromatic hydrogen. This work requires development and application of sophisticated analytical techniques, and the characterization of cellulose, lignin, humic acid, and wax residues in low-rank coals by novel chemical degradation processes.

14.1.1 INVESTIGATION OF LIGNITE MACROMOLECULES

One of the important parameters in the characterization of macromolecules derived from coal is the average molecular weight of the material. Information on the molecular weight distribution of a sample can aid in understanding the behavior of the macromolecule in various chemical and physical processes.

The goal of this research in lignite macromolecules is to find a way to apply polymer characterization methods such as low-angle laser light scattering (LALLS) photometry in a static mode and also in a coupled mode with size exclusion chromatography (SEC) or gel permeation chromatography to the analysis of macromolecules derived from coal by oxidation, pyrolysis, supercritical extraction, and chemical extraction. Although size exclusion chromatography is an excellent technique for separating polymers on the basis of size, it does not directly provide molecular weight data. The calibrations necessary to determine the molecular weights of eluted molecules and consequently obtain molecular weight distributions from the retention times are subject to large errors. These errors arise because the polymers used as calibration standards may not be similar enough to the polymer whose molecular weight is being determined. Other sources of error are changes in weight to size relationships in a sample and changes in analysis conditions, such as variation in flow rate or pressure. Since the low-angle laser light scattering photometer gives absolute molecular weight data, no calibration of the size exclusion chromatography column is necessary.

Previous investigations with coal-derived macromolecules have been hindered by the intense absorptions of the light, making scattering difficult to observe. The high molar absorptivity is believed to result from extensive conjugation of arene systems, nitrogen heterocyclics, and semiquinone structures. Our objectives are to carry out mild hydrogenation and reduction

reactions which would hydrogenate the arene systems and reduce the semiquinones without changing the size of the macromolecule. Previously aromatic hydrogenations have been carried out at high temperatures and high pressure of hydrogen, conditions which could very likely lead to hydrogenolysis of the macromolecules into smaller segments. In this quarter we report the assembly of the necessary instrumentation, including interfacing to a computer, the mild hydrogenation reaction of coal-derived macromolecules using sodium borohydride with a rhodium (III) catalyst, and preliminary molecular weight data on two of these products.

14.2 ACCOMPLISHMENTS

14.2.1 REDUCTION OF ABSORPTIVITY

Since mild conditions for hydrogenation were desired, the rhodium (III) catalyzed reduction with sodium borohydride was attempted with several samples derived from lignites. This reagent was investigated earlier for the reduction of perylene and pyrene where it was successful in reducing several of the aromatic rings to yield a mixture of hydroaromatics with molar absorptivities very much lower than the original aromatic compound. The reaction was carried out at room temperature and atmospheric pressure.

A humic acid sample obtained by the extraction of Beulah lignite with sodium hydroxide was methylated using methyl iodide in a 2-phase system with a phase transfer catalyst. This procedure converted carboxylic acid groups to the methyl esters and phenols to the methyl ethers. The methyl humate was obtained in about 70% yield. This product was reduced in ethanol with rhodium (III) chloride and sodium borohydride to give a 65% yield of a yellow material.

The humic material obtained by methanol precipitation of the cadoxen extract of Beulah lignite (see UNDERC Quarterly Technical Progress Report for April through June 1983) was methylated with methyl iodide and reduced with rhodium chloride and sodium borohydride as above.

14.2.2 STATIC MEASUREMENTS WITH LALLS

A low-angle laser light scattering photometer (KMX-6) was purchased from LCD-Milton Roy. This was interfaced to an existing microcomputer, HP85, through a multichannel analog to digital converter obtained from Omega.

The determination of the weight average molecular weight, M_w , requires the measurement of the scattered light intensity (G_θ) at low forward scattering angles for a series of concentrations of the polymer solution. Thus, the photomultiplier output is sampled for 2 minutes to create a data file of G_θ intensities. Because of scattering from minute particles passing through the viewed volume of the cell, a series of spikes in the scattering intensity will be recorded (see Figure 14-1). This particulate "noise" will always be above the baseline intensity level (G_θ) due to the inherent scattering of solute and solvent. Using a 0.2 μ filter reduces the particulate noise but does not eliminate it. We have written a software program which simply chooses the minimum value from the intensity data file to represent G_θ .

FIGURE 14-1. Determination of G_θ .

A similar measurement is made for the intensity of the incident light (G_0). From G_θ , G_0 , and some measureable instrument constants, the Rayleigh scattering factor, R_θ , is calculated. The excess Rayleigh factor, R_θ , is obtained by subtracting R_θ of the solvent from R_θ of the solution. A third parameter must be determined for the molecular weight determination, the specific refractive index increment, dn/dc , which is the change in the solution refractive index as a function of the solute concentration.

The value of dn/dc for the reduced methylated cadoxen material in THF solution was determined with a laser differential refractometer (LDC - Milton Roy). This value obtained for dn/dc (.055) was used to calculate the optical constant, K , defined as

$$K = 4.079 \times 10^{-6} \left(\frac{dn}{dc} \right)^2 n^2$$

Our software then plots Kc/R_θ versus concentration (c) for several concentrations and calculates M_w from the reciprocal of the y intercept and the second virial coefficient A_2 from the slope (Figure 14-2).

$$Kc/R_\theta = \frac{1}{M_w} + 2 A_2 c$$

A number of polystyrene samples were run to confirm that the instrument was working properly.

FIGURE 14-2. K_c/R_θ versus c for static M_w determination.

For the reduced methylated cadoxen extracted material, a M_w of 1.47×10^4 was obtained. This value is in the range of molecular weights reported for soil humic acids obtained by other methods. More importantly we have demonstrated that the method of reduction to reduce light absorptivities will allow light scattering measurements to be made. The use of laser light allows low-angle measurements so that complex graphical extrapolations are not required. The use of a cell with a low "viewed" volume ($0.1 \mu\text{l}$) reduces the probability that particulates will scatter the light and give excessive noise, making G_θ values difficult to obtain.

14.2.3 SIZE EXCLUSION CHROMATOGRAPHY--LOW-ANGLE LASER LIGHT SCATTERING PHOTOMETRY

For the precise determination of molecular weight distribution, the KMX-6 LALLS photometer and a Waters differential refractive index (DRI) detector were coupled in series with a size exclusion chromatography system (see Figure 14-3). The DRI detector is calibrated to give concentration data which is stored as a file and used with the LALLS data file to calculate the molecular weight of uniform volume increments through the chromatography.

The reduced methylated humic acid from the base extraction of Beulah lignite was characterized in the SEC-LALLS-DRI system. Unfortunately the DRI response was too low for reliable concentration data; however, the LALLS response was adequate for producing a chromatogram (Figure 14-4). The chromatogram exhibited an interesting distribution consisting of two overlapping peaks,

FIGURE 14-3 Block diagram of the SEC-LALLS-DRI system.

FIGURE 14-4. SEC-LALLS chromatogram of reduced methyl humate.

suggesting the possibility of branched and unbranched macromolecular structures. Further work in preparative SEC is required so that dn/dc values for the two types of polymers can be determined. Further work in solvent selection is also required so that solvents can be used which result in maximum dn/dc values.

15. DISTRIBUTION OF INORGANICS

Project No.: 7304

B&R No.: AA1520150

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15.1 GOALS AND OBJECTIVES

The goals of this work are to develop a better understanding of the modes of occurrence of inorganic constituents in low-rank coals and to correlate the distribution of inorganic elements with maceral (organic part of the coal) and mineral portions of the coal. Method developments are to be conducted to ascertain the association of inorganics by selectively extracting the elements based on how they are associated in or with the coal and by use of instrumental techniques. The knowledge of the modes of occurrence of these inorganic elements can be used to predict their fate or impact during utilization.

The objectives of this reporting period were the following:

1. Examine the inorganic associations in low-rank coals to determine the specified chemical forms or bonding.
2. Continue chemical fractionation of samples collected in the Ash and Slag Characterization project and in separated lithotypes.
3. Examine carbon-oxygen bonding in a low-rank coal by an instrumental technique.
4. Begin correlating the distribution of inorganic constituents with macerals and microfossils.

15.2 ACCOMPLISHMENTS

15.2.1 CHEMICAL FRACTIONATION OF COALS AND SEPARATED LITHOTYPES

The coals investigated during this reporting period included lignites from the Indian Head mine, Mercer Co., ND and the Martin Lake mine, Panola Co., TX, subbituminous coals from the Navajo Mine, San Juan Co., NM; Spring Creek Mine, Big Horn Co., MT; and the Colorado Coal Company mine (Yampa), Routt Co., CO. Separated lithotypes (vitrain, durain, and fusain) from the Beulah Mine,

Mercer Co. of North Dakota were also investigated. Chemical fractionation was performed on these coals and lithotypes to determine the percent of elements associated as soluble salts or cations extractable with 1M ammonium acetate, the carbonates/oxides/coordinated species extractable with 1M hydrochloric acid, and the insoluble inorganic phases such as quartz, clay minerals, and pyrite. The extracts and residues are analyzed by a combination of x-ray fluorescence (XRF), neutron activation (NAA), and inductively coupled argon plasma spectroscopy (ICAP). The data presented here are not complete and are subject to change because not all of the XRF and NAA analyses have been completed.

15.2.1.1 Chemical Fractionation of Whole Coals

The results obtained for Indian Head, Spring Creek, and Martin Lake coals are summarized in Table 15-1, 15-2, and 15-3, respectively. The bulk coal elemental determinations were performed by XRF (Mg, Al, Si, K, Ca, Ti, Fe, and Ni) and NAA (Na, Mn, and Ba). The percent removal of the elements by NH_4OAc and HCl treatments were calculated from the ICAP analysis of extracts. It

TABLE 15-1
CHEMICAL FRACTIONATION OF INDIAN HEAD LIGNITE
(Moisture-Free Basis)

	Bulk Coal ($\mu\text{g/g}$)	Removed By NH_4OAc (%)	Removed By HCl (%)	Remaining (%)
Na	6221	76	0	24
Mg	9690	19	1	80
Al	4940	0	51	49
Si	7060	1	14	85
K	1150	2	1	97
Ca	15560	39	12	49
Ti	402	0	2	98
Mn	4.6	41	98	-39
Fe	6810	0	40	60
Ni	5	0	18	82
Ba	519	38	61	1

	Bulk Coal (%)	After NH_4OAc Treatment (%)	After HCl Treatment (%)
C	65.86	67.49	68.26
H	4.33	4.57	4.49
N	1.21	2.45	1.34
S	0.60	0.57	0.59
O (diff)	21.40	22.43	24.22
Ash	6.6	2.5	1.1

TABLE 15-2
CHEMICAL FRACTIONATION OF SPRING CREEK SUBBITUMINOUS
(Moisture-Free Basis)

	Bulk Coal ($\mu\text{g/g}$)	Removed By NH_4OAc (%)	Removed By HCl (%)	Remaining (%)
Na	2710	102	1	-3
Mg	4250	17	1	82
Al	2180	0	65	35
Si	2050	1	3	96
K	ND	18 ($\mu\text{g/g}$)	0 $\mu\text{g/g}$	
Ca	9030	41	11	48
Ti	203	0	2	98
Mn	6.3	41	105	-46
Fe	1450	0	65	35
Ni	ND	0 ppm	0 ppm	
Ba	361	40	40	20
	Bulk Coal (%)	After NH_4OAc Treatment (%)	After HCl Treatment (%)	
C	72.88	72.55	72.61	
H	4.64	4.75	4.58	
N	0.87	1.90	1.21	
S	0.13	0.13	0.13	
O (diff)	18.28	19.68	20.77	
Ash	3.2	1.0	0.7	

should be noted that the HCl treatments were performed on the residues left after the NH_4OAc treatments. The percentage of the elements remaining in the coal was found by difference. Table 15-4 shows the amounts of the elements removed from the Navajo and Yampa coals by the two types of treatments as determined by the ICAP analyses of the extracts. The percentage of the elements removed could not be calculated because the bulk coal elemental analyses are not yet available. The ultimate analyses of the bulk coals are also presented. All data is on a moisture free basis.

The ash contents from the ultimate analysis listed in Tables 15-1 through 15-4 for the coals and residues provide a means of determining the approximate amounts of ash-forming constituents removed with NH_4OAc and HCl . The coals from the Powder River and Fort Union regions contain the highest percentages of inorganic constituents extractable with NH_4OAc , which are associated as cations or soluble species. For example, the NH_4OAc extractable constituents of Indian Head (Fort Union) and Spring Creek (Powder River) coals constitute 62% and 69% of the total ash-forming components, respectively. On the other hand, the NH_4OAc extractable constituents of Martin Lake coal from the Gulf

TABLE 15-3
CHEMICAL FRACTIONATION OF MARTIN LAKE LIGNITE
(Moisture-Free Basis)

	Bulk Coal ($\mu\text{g/g}$)	Removed By NH_4OAc (%)	Removed By HCl (%)	Remaining (%)
Na	964	98	2	0
Mg	11510	17	1	82
Al	4630	0	54	46
Si	7920	0	12	88
K	993	2	2	96
Ca	15530	52	21	27
Ti	203	0	2	98
Mn	94	28	83	-11
Fe	11090	0	21	79
Ni	<5	0 ppm	1.2 ppm	--
Ba	280	64	52	-16

	Bulk Coal (%)	After NH_4OAc Treatment (%)	After HCl Treatment (%)
C	64.01	66.12	67.15
H	4.70	4.86	4.73
N	1.18	2.53	1.59
S	1.03	0.98	1.03
O (diff)	19.67	19.20	20.50
Ash	9.4	6.3	5.0

Coast region comprise 33% of the ash-forming constituents. The amounts of ash-forming constituents extractable with HCl were 21% for Beulah, 9% for Spring Creek, and 13.8% for Martin Lake. These percentages are only approximations due to the volatilization of ash forming constituents during ashing.

15.2.1.2 Chemical Fractionation of Lithotypes

The relationship of low-rank coal lithotypes and macerals with inorganic constituents is important in understanding their eventual fate during utilization. Lithotypes and macerals have specific chemical and physical properties. For example, huminite and liptinite maceral groups have higher concentrations of volatiles than the inertinite group. The inorganic constituents associated with the more volatile groups are more likely to be liberated at lower temperatures than those associated with inertinites during utilization. Chemical fractionation was performed on separated lithotypes to identify the modes of occurrence of inorganic elements within the lithotype.

TABLE 15-4
CHEMICAL FRACTIONATION OF NAVAJO AND YAMPA COALS
(Moisture-Free Basis)

	Navajo		Yampa	
	Removed By NH ₄ OAc (μg/g)	Removed By HCl (μg/g)	Removed By NH ₄ OAc (μg/g)	Removed By HCl (μg/g)
Na	1701	44	70	16
Mg	152	175	375	286
Al	0	2999	0	4139
Si	125	3312	116	3106
K	0	0	44	139
Ca	2017	433	1458	745
Ti	0	24	0	2
Mn	9.0	22.1	3.7	9.0
Ni	0	2.7	0	1.9
Ba	131	66	175	62
	Bulk Coal (%)		Bulk Coal (%)	
C	63.37		68.65	
H	4.92		3.82	
N	1.31		2.15	
S	1.23		0.67	
O (diff)	12.28		9.61	
Ash	16.9		15.1	

Approximately 25 kilograms of each of the lithotypes (vitrain, durain, and fusain) were separated and collected directly from the yellow pit at the Beulah Mine. These samples were collected as part of the Ash and Slag Characterization project. Descriptions of lithotypes have been reported by Kleesattel (1). Petrographic analysis was performed to determine how good a separation was made at the mine. The results of the petrographic analysis are summarized in Table 15-5. Certain petrographic constituents should be concentrated in specific lithotypes. For example, vitrain has 84% huminite content, fusain has 49% inertinite content, and the durain (or attrital coal) has a mixture of huminite and inertinite. The liptinite macerals do not appear to be closely related to any one lithotype. The separation of fusain was not as successful as had been anticipated because it occurs in fine layers in seam and is dispersed with the other lithotypes. Proximate and ultimate were also performed on the lithotypes and are summarized in Table 15-6.

TABLE 15-5
PETROGRAPHIC ANALYSIS OF BEULAH LITHOTYPES
(% by Volume)

	Vitrain	Durain	Fusain
<u>Huminite:</u>			
Textinite	4	0	tr
Ulminite	64	34	27
Attrinite	10	16	9
Desinite	4	5	3
Gelinite	1	2	1
Corpohominite	4	2	2
Total Huminite	84	59	42
<u>Liptinite:</u>			
Sporinite	3	2	1
Cutinite	2	1	1
Resinite	1	1	1
Suberinite	1	1	0
Liptodetrinite	1	2	2
Total Liptinite	9	7	5
<u>Inertinite:</u>			
Fusinite	tr	tr	15
Semifusinite	2	10	25
Sclerotinite	tr	1	1
Inertodetrinite	2	20	9
Micrinite	1	tr	tr
Total Inertinite	5	31	49

tr = trace

TABLE 15-6
PROXIMATE AND ULTIMATE ANALYSIS OF LITHOTYPES
FROM THE BEULAH MINE
(Moisture-Free Basis, %)

	Vitrain	Durain	Fusain
<u>Proximate:</u>			
Volatile Matter	45.9	43.9	40.3
Fixed Carbon	47.5	46.5	48.4
Ash	6.6	9.6	11.3
<u>Ultimate:</u>			
Hydrogen	4.70	4.01	3.85
Carbon	66.93	65.14	65.30
Nitrogen	.81	1.03	.92
Sulfur	1.05	0.76	1.61
Ash	6.6	9.6	11.3
Heating Value (Btu/lb)	11215	10669	10800

The differences in the chemical fractionation analyses of the lithotypes shown in Table 15-7 were that more Na was extracted from vitrain with ammonium acetate, more Ca was removed from fusain with ammonium acetate, and more Ca was extracted from the durain with HCl. Empirical correlations have shown strong positive relationship between inertinites and Ca (2) which supports the relationship of Ca with fusain in this work. This work is still in preliminary stages because NAA and XRF analyses are not complete. Interpretation of these results may lead to further understanding of the relationships of inorganic and petrographic constituents.

15.2.2 MAJOR, MINOR, AND TRACE ELEMENT ANALYSIS

Major, minor, and trace element concentrations have been determined for coals collected as part of the Ash and Slag Characterization project. The values are reported in Table 15-8. These data were determined by neutron activation analysis. Ultimate analyses are also included.

15.2.3 THE PALYNOLOGY OF THE HAGEL BED (LIGNITE) AND ASSOCIATED SEDIMENTS, SENTINEL BUTTE FORMATION, NORTH DAKOTA

The inorganic material associated with plant matter at the time of deposition is probably one of the least known aspects of inorganic constituents of coals. Low-rank coals have abundant quantities of microfossils, specifically pollen and spores (polymorphs) which allow the identification of plant material that were responsible for the coal formation.

TABLE 15-7

CHEMICAL FRACTIONATION OF WHOLE COAL AND SEPARATED LITHOTYPES ($\mu\text{g/g}$ OF DRY COAL)

	Beulah High-Sodium		Durain		Fusain		Vitrain	
	Removed By NH_4OAc ($\mu\text{g/g}$)	Removed By HCl ($\mu\text{g/g}$)	Removed By NH_4OAc ($\mu\text{g/g}$)	Removed By HCl ($\mu\text{g/g}$)	Removed By NH_4OAc ($\mu\text{g/g}$)	Removed By HCl ($\mu\text{g/g}$)	Removed By NH_4OAc ($\mu\text{g/g}$)	Removed By HCl ($\mu\text{g/g}$)
Na	5412	26	2685	18	3854	28	5569	80
Mg	1913	179	1644	410	2355	312	2095	104
Al	0	2323	0	3064	0	2292	0	3044
Si	13	423	66	1418	53	963	42	318
K	31	166	0	0	31	0	31	0
Ca	3135	7136	5434	6536	8041	4876	7132	2747
Ti	0	11	0	23	0	7	0	3
Mn	13	32	14	70	17	60	13	37
Fe	5	2144	5	1659	3	1613	0	1411
Ni	0	0.6	0	1.4	0	1.9	0	1.7
Ba	346	428	156	668	299	451	338	350

TABLE 15-8

MAJOR, MINOR, AND TRACE ELEMENT ANALYSIS OF COALS COLLECTED (PARTS PER MILLION, MOISTURE-FREE)

Element	Velva ND Lig.	Center. ND Lig.	High-Na Beulah ND Lig.	Low-Na Beulah ND Lig.	Gascoyne Red ND Lig.	Gascoyne Blue ND Lig.	Falkirk ND Lig.	Indian Head ND Lig.	Martin Lake TX Lig.	San Miguel TX Lig.	Pike County AL Lig.	Mt. Spring Creek Subbit.	Yampa CO Subbit.	Navajo NM Subbit.
Aluminum	3346.67	3284.59	2275.50	4449.34	1644.53	4411.67	3504.88	3024.14	7339.29	14435.26	9793.65	1643.31	21178.12	20591.83
Antimony	0.49	0.63	0.11	3.30	0.62	0.42	0.62	0.22	0.29	0.81	0.10	0.04	0.31	0.33
Arsenic	4.90	5.24	1.73	19.01	1.88	1.38	3.07	5.02	2.27	8.47	1.50	0.10	2.81	6.21
Barium	306.89	366.18	718.28	469.48	399.17	909.26	529.26	518.77	280.31	246.48	1177.42	361.03	359.17	240.99
Bromine	1.59	0.45	0.68	0.72	1.36	0.97	0.88	1.13	2.68	3.80	6.55	0.39	0.39	0.99
Cadium	0.16	0.05	0.05	0.17	0.05	0.05	0.08	1.00	0.50	3.35	1.55	0.08	1.22	1.61
Calcium	9839.41	7663.81	7765.42	7498.66	8788.20	9723.59	6977.32	3759.80	9681.63	8206.63	14789.80	2557.73	4076.02	4585.20
Cerium	4.64	4.38	4.21	5.11	9.85	5.41	3.63	7.80	8.83	24.84	11.75	1.68	21.20	7.00
Cesium	0.27	0.15	0.04	1.91	0.20	0.11	0.06	0.12	0.20	0.49	0.13	0.03	1.17	0.30
Chlorine	18.57	51.19	9.35	27.59	6.01	10.01	10.00	15.98	28.28	529.40	141.78	10.74	20.00	45.53
Chromium	2.36	4.31	1.62	7.07	5.56	3.07	5.10	2.04	6.19	4.43	14.39	1.46	6.93	4.57
Cobalt	0.81	1.07	0.60	1.82	0.37	0.59	1.35	1.60	0.83	1.71	0.93	0.28	0.87	1.55
Copper	0.81	1.07	0.60	1.82	0.37	0.59	1.35	1.60	0.83	1.71	0.93	0.28	0.87	1.55
Europium	0.07	0.08	0.06	0.11	0.18	0.08	0.07	0.09	0.18	0.52	0.24	0.04	0.28	0.33
Gold	--	--	--	--	--	--	--	--	0.00	0.00	0.00	--	0.00	0.00
Iodine	0.62	0.34	0.35	0.50	0.50	0.50	0.50	3.00	0.50	0.50	0.50	0.50	0.50	0.50
Iron	2620.37	5718.32	4803.87	10560.40	4852.72	2322.09	3235.00	3566.79	1884.78	4430.07	3158.82	785.77	1977.06	4488.53
Lanthanum	2.22	1.60	1.40	2.39	5.01	2.91	2.19	4.69	5.01	13.88	8.11	1.23	8.10	8.32
Magnesium	1148.22	939.70	978.61	1476.14	537.33	1468.81	495.98	411.91	713.11	605.10	2360.45	75.00	963.92	823.15
Manganese	26.32	10.87	23.58	52.14	13.07	72.61	94.56	4.58	93.72	129.01	61.69	6.25	14.31	33.49
Nickel	2.52	6.99	6.68	8.96	6.75	7.15	19.87	25.00	25.00	25.00	25.00	8.53	25.00	25.00
Potassium	500.00	500.00	500.00	275.71	661.31	500.00	336.84	500.00	500.00	971.70	500.00	200.00	1570.75	500.00
Rubidium	1.08	0.62	0.65	1.02	1.82	0.37	5.74	5.00	1.02	24.90	3.42	2.03	20.67	2.02
Samarium	0.40	0.32	0.24	0.42	0.57	0.34	0.41	0.36	0.59	2.61	0.84	0.15	0.97	1.07
Scandium	0.52	0.90	0.38	1.60	1.13	0.59	0.83	1.26	3.69	7.22	3.74	0.29	3.47	3.61
Selenium	0.61	0.29	0.50	0.96	1.10	0.38	0.99	0.50	8.20	1.53	9.30	0.56	1.03	1.41
Silver	0.71	0.76	0.91	0.86	0.88	0.75	0.39	0.08	0.02	0.02	0.02	0.39	0.02	0.02
Sodium	916.31	4017.50	4624.64	1378.81	1316.58	2694.33	69.58	6220.63	964.28	7320.12	7181.64	2709.66	185.27	1520.43
Thorium	0.93	0.70	0.75	1.16	2.71	1.01	0.69	1.02	2.19	5.92	1.91	0.30	3.96	3.95
Titanium	177.75	120.93	103.94	281.32	196.42	134.83	117.64	108.43	776.12	534.67	485.86	93.09	813.42	825.28
Uranium	1.24	0.27	0.44	0.80	0.95	2.36	1.30	0.29	1.03	5.18	1.18	0.18	1.55	1.62
Vanadium	3.33	5.55	1.82	12.64	1.68	3.26	5.52	3.00	19.93	22.12	4.77	1.48	18.77	18.02
Ytterbium	0.22	0.23	0.25	0.34	0.55	0.29	0.33	0.35	0.44	2.20	0.40	0.07	0.67	1.08
Zinc	3.01	3.75	2.75	5.35	5.98	2.16	8.78	6.39	10.00	38.32	10.00	4.83	13.42	14.80
Carbon (%)	63.84	64.06	66.36	61.43	58.32	54.48	63.51	66.79	51.22	50.70	ND	72.40	68.65	57.72
Hydrogen (%)	4.39	4.13	3.60	4.10	3.99	5.19	3.63	3.87	4.53	4.19	ND	4.32	3.82	4.47
Nitrogen (%)	0.92	1.13	0.87	0.42	0.88	0.84	1.41	0.97	0.65	0.74	ND	1.27	2.15	1.19
Oxygen														
(diff) (%)	22.51	21.08	19.52	18.24	19.55	29.28	21.98	19.61	17.46	28.87	ND	18.75	9.66	11.19
Sulfur (%)	0.59	1.16	1.22	3.16	1.71	1.36	0.50	0.58	3.20	2.87	ND	0.28	0.67	1.12
Ash (%)	7.76	8.04	8.43	12.65	15.54	8.85	8.97	8.18	12.93	12.64	ND	2.98	15.05	16.94

ND = No Data.

This initial work is intended to characterize the palynomorphs of the Hagel lignite bed, North Dakota and to investigate their utility as tools for North Dakota lignite research (4). The primary emphasis of this work are:

1. To describe and characterize the palynomorphs of the Hagel lignite bed.
2. To differentiate and characterize any palynomorphic associations or zonations present within the Hagel bed.
3. To use the palynomorphs found within the Hagel bed to help characterize the contributing flora.
4. To identify and characterize chemical and mineralogic zonations or variations present within the Hagel bed.
5. To compare the palynological, mineralogic, and chemical variations present within the Hagel bed.

15.2.3.1 Location

The Hagel bed is present throughout the Knife River drainage basin as well as in adjacent areas in McLean and Oliver Counties (2). The Hagel bed is mined commercially at three locations in McLean and Oliver counties, the Center Mine near Center, ND, the Glenharold Mine near Stanton, ND, and the Falkirk Mine near Falkirk, ND. West of the mined area, the Hagel bed is known from cores and outcrop.

Samples for this study were taken from mine high-walls at each of the three mines presently mining the Hagel bed. The mine high-walls afforded samples which were fresh (not oxidized), and which possessed good stratigraphic control.

15.2.3.2 Procedures

An efficient method to separate palynomorphs (acid-insoluble microfossils) from their confining matrices is a prerequisite to a successful palynological study. This process is called maceration. A successful maceration leaves a residue containing a large number of palynomorphs and a minimum of extrinsic organic and inorganic particles. The palynomorphs should be relatively unaffected by the maceration process. Corrosion or differential destruction of specimens should be avoided.

Palynomorphs are often well preserved and abundant in coals and existing maceration methods used for coal are numerous. Most coal maceration methods utilize strong oxidizing agents such as Schultze's solution ($2\text{KClO}_3:\text{HNO}_3$), or various nitric acid reagents (4). While strong oxidation is an effective means of breaking down the coal's organic matrix, it can also have the effect of corroding and differentially destroying the organic-walled palynomorphs. For this reason current maceration procedures only partially oxidize the coal. This partial oxidation is an attempt to reach a compromise of adequately dispersing palynomorphs from the matrix while leaving them relatively unaffected by the oxidation. Attaining the above compromise is difficult and often inconsistencies arise.

Standard oxidation methods were attempted in order to macerate Hagel bed lignite samples. The results of these macerations were disappointing since the lignite appeared to be especially resistant to oxidation. Several oxidizing agents were tried. It was found that an abbreviated oxidation procedure using trifluoroperoxyacetic acid (TFA) resulted in a maceration residue rich in apparently unharmed palynomorphs. This procedure proved to be a relatively quick, easy, and consistent means of macerating Hagel bed lignite and was used on all the lignite samples.

Although the exact chemical structure of coal is poorly understood, coals are generally thought to be composed of aromatic rings connected to one another with aliphatic structures (5). Oxidation of coals by standard methods (Schultze's solution or nitric acid compounds) breaks the coal matrix down by attacking benzylic hydrogen resulting in the destruction of aliphatic structures (6). In oxidation of coals with TFA the aromatic ring is attacked often preserving the aliphatic structure (7). TFA oxidation is, in effect, an "inverse" oxidation of coal when compared to standard oxidation methods.

The chemical structure of sporopollenin (the substance of which spore and pollen exines are made) is also poorly understood. Generally, however, sporopollenin is thought to be composed of complex long-chain aliphatic structures. Sporopollenin is remarkably inert; Brooks and Shaw (7) believe that both Cretaceous and Carboniferous coals contain sporopollenin preserved intact. The aliphatic nature of pollen and spores exines within lignite might explain the efficiency of TFA as a macerating agent of lignite.

The initial phase of the palynological analysis consisted of scanning slides. When a palynomorph was observed for the first time it was described and its location on the slide noted. These descriptions were refined into palynomorph type-sheets which include: 1) a diagnosis, 2) a photograph, 3) assignment to a published genus or species when possible, and 4) inferred botanic affinities. The type-sheets were organized according to aperature condition and served as a guide to the taxonomic assignments made throughout the study.

Table 15-9 represents the palynomorphs for which type-sheets are currently complete and botanic affinities are known.

Lignite is composed almost entirely of plant-derived material. However, the plant material has undergone extensive biodegradation. Knowledge of the contributing flora aids directly in understanding the original botanic chemistry and paleochemistry of the coal.

15.2.4 EXAMINATION OF CARBON-OXYGEN FUNCTIONALITIES OF BEULAH VITRAIN BY ESCA

The use of electron spectroscopy for chemical analysis (ESCA) provides a means of determining surface composition and may be used to suggest reactivity of the surfaces of low-rank coals. Determining the reaction of oxygen with the surface of low-rank coals is important in relation to processes where surface properties are important. For example, processes such as coal flotation, coal-liquid mixtures, and coal dewatering depend on the nature of the surface of the coals. In this study, the reactivity of the surface of a small piece

TABLE 15-9
SPECIES IDENTIFIED IN THE HAGEL BED

Species Name	Botany Affinity	Common Name (Botanic Affinity)
<u>Monosulcites crescentus</u>	Gymnospermae	Conifers and relatives
<u>Taxus sp.</u>	<u>Taxus</u>	Yews (conifers)
<u>Spheripollenites subgranulatus</u>	<u>Taxus</u>	Yews (conifers)
<u>Pinus semicircularis</u>	<u>Pinus</u>	Pine trees
<u>Abietinaepollenites foveoreticulatus</u>	<u>Pinaceae</u>	Pine trees
<u>Abietinaepollenites latisulcus</u>	<u>Pinaceae</u>	Pine trees
<u>Abietinaepollenites varius</u>	<u>Pinaceae</u>	Pine trees
<u>Podocarpus sellowiformis</u>	<u>Pinaceae</u>	Pine trees
<u>Sequoipollenites paleocenicus</u>	<u>Sequoia</u>	Redwoods and relatives
<u>Taxodiaceapollenites hiatus</u>	<u>Taxodiaceae</u>	Redwoods, cyprus
<u>Fraxinus variabilis</u>	<u>Fraxinus</u>	Ash tree
<u>Tricolpopollenites clavireticulatus</u>	<u>Salicaceae</u>	Willow family
<u>Corylus sp.</u>	<u>Corylus</u>	Hazel tree
<u>Corylus granilabrata</u>	<u>Carpinus</u>	Beech tree
<u>Engelhardtia microfoveolata</u>	<u>Juglandaceae</u>	Nut trees (walnut, etc.)
<u>Caryapollenites simplex</u>	<u>Carya</u>	Pecan-hickory trees
<u>Alnipollenites trina</u>	<u>Alnus</u>	Alders
<u>Cingulatisporites dakotaensis</u>	<u>Selaginella</u>	Evergreen herbs resembling mosses
<u>Foreasporis triangulus</u>	<u>Selaginella</u>	Evergreen herbs resembling mosses
<u>Perotrilites sp.</u>	<u>Filicineae</u>	Ferns
<u>Osmunda conaemensis</u>	<u>Osmunda</u>	Ferns
<u>Laevigatesporites haardtii</u>	<u>Polypodiaceae</u>	Ferns
<u>Laevigatesporites sp.</u>	<u>Polypodiaceae</u>	Ferns
<u>Steriosporites antiquasporites</u>	<u>Sphagnum</u>	Peat moss

of Beulah vitrain was studied to determine the carbon-oxygen groups that form when exposed to air at room temperatures and at elevated temperatures.

A sample of vitrain was collected from a freshly-exposed seam at the Beulah mine, Mercer Co., North Dakota and immediately purged with argon. Upon receipt at UNDERC, a small piece of vitrain was placed under vacuum to expel most of the moisture prior to placing it in the ESCA instrument. An ESCA spectrum was collected on the fresh coal, and after exposure to air at room temperature for five days; air at 95°C for one day; air at 150°C for one day; and air at 200°C. All of these treatments were done on the same piece of vitrain. The resulting ESCA carbon (1s) spectra are shown in Figure 15-1. The most obvious change that occurs during oxidation is increase in intensity of the carboxylate peak at 289 eV. This is most apparent when the samples were heated to 150° and 200°C. To separate the peak in the carbon 1s spectra a computerized spectral decomposition routine was used. The peaks that can be deconvoluted include the following: hydrocarbon (aliphatic and aromatic) at 285 eV, ether or hydroxyl at 286.6 eV. Difficulties have been encountered using the spectral decomposition methods because of the extreme peak overlap and charging effects that shift the peaks. Once the peaks are separated, peak areas can be determined and ratios calculated. The ratios were determined by taking peak intensities to total intensity of the carbon 1s spectra. The atomic oxygen-to-carbon ratios were determined from the carbon and oxygen 1s peaks. Table 15-10 summarizes the results obtained for the series of treatments. In the first experiment, where the sample was exposed to air for five days, little oxidation was detected by the ESCA, only a slight increase in ether or hydroxyl and carboxyl. In contrast, when the sample was heated to 95°, 150°, and 200°C an increase was noted in the carboxyl and ether or hydroxyl ratios. The carbonyl decreased with increasing temperature indicating an increase in the conversion of carbonyl to carboxyl. The organic oxygen-to-carbon ratio (O/C) increased slightly after being exposed to air for five days shown in Table 15-9. The O/C ratio increased after 5 days but decreased after heating to 95°C, possibly due to moisture losses. The O/C increased from in going from 95° to 200°C.

TABLE 15-10
OXIDATION OF BEULAH VITRAIN DETERMINED BY ESCA

Time/Temperature	Organic O/C	Aliphatic or Aromatic	Ether or Hydroxyl	Carbonyl	Carboxyl
0/25°C	0.23	0.95	0.04	0.0	0.2
5 days/25°C	0.25	0.89	0.08	0.03	0.0
24 hrs/95°C	0.19	0.93	0.03	0.03	0.01
24 hrs/150°C	0.24	0.91	0.04	0.04	0.02
24 hrs/200°C	0.31	0.63	0.27	0.01	0.09

FIGURE 15-1. Carbon (1s) spectra from unreacted and oxidized Beulah vitrain.

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16. PHYSICAL PROPERTIES AND MOISTURE

Project No.: 7305

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16.1 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 are as follows:

1. Establish credible testing procedures to define the properties of coarsely-crushed coals which define their behavior in a settling bed gasifier. These properties are the mechanical and thermal friabilities as functions of dryness, coal petrography, and other readily measurable properties.
2. Determine the pore size distribution in coals by small angle x-ray scattering, and any change that results during heating, drying, and pyrolysis which is relevant to the release and reabsorption of moisture during processing. (This is being studied by 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 the Mohs scale, which has, until now, only been applied to large surfaces by means of scratch testing. 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.

16.2 OPERATION OF A DIFFERENTIAL HEATS OF WETTING CALORIMETER

16.2.1 THE POROUS STRUCTURE OF CARBONS

Different methods of assessing the specific surface area of, for example, activated carbons, usually give results between 400 and 900 m² gm⁻¹. From data on volume and surface area of pores, it is possible to conclude that pores are extremely small, i.e., about 3×10^{-7} cm in diameter.

There are three conceivable systems for the distribution of the pores:
(Dubinin 1947-1955)

1. polydisperse system,
2. monodisperse system, and
3. an intermediate system, the polymode system.

A polymode system has several relative narrow maxima in the distribution curve of pore radius; i.e., it possesses groups or varieties of pores with definite intervals between the dimensions of each variety. Pores may also be graded in terms of their size and may be classified into three groups:

1. macropores
2. transitional pores
3. micropores

The diameters, pore volumes, and surface areas of these three types of pores are shown in Table 16-1.

TABLE 16-1
PHYSICAL PROPERTIES OF VARIOUS TYPES OF PORE (1)

Pores	Diameter °A	Pore Volume cc	Surface Area m ² gm ⁻¹	Observation By
Macropores	500 → 2000	0.2 → 0.5	0.5	Optical Microscopy
Transitional Pores	40 → 200	0.02 → 0.1	20 → 150	Electron Microscopy and Hysteresis
Microprobes	20			Hysteresis

Macropores can be seen by optical microscopes; transitional pores require the electron microscope. Both of the above can be studied by forcing mercury into the pores. Transitional pores and micropores can be investigated by measuring the adsorption isotherms for the condensation of vapors in the carbon. Micropores cannot be observed directly even by means of an electron microscope. They can however be investigated by the hysteresis methods developed by Dubinin in 1946 (2,3). These methods lead to the conclusion that micropores approach molecular dimensions in order of magnitude.

16.2.2 EXPERIMENTAL - LINEARITY OF THE CALORIMETER INSTRUMENT

One of the first tasks after the optimization of the completed system (see UNDERC Quarterly Technical Progress Report - January to March 1984) was to determine the linearity of the calorimeter. This was done by repeatedly applying power to the working dewar's heater and noting the deflection produced. This procedure not only calibrated the temperature rise for a simple value of heat input ($Q = IVt$) but also showed that the temperature rise was proportional to the heat input. The heater was switched on for a different length of time in the 2 calibrations. The temperature rises due to these different times were thus also different. However, the corrected temperature rises should be in the same ratio as the length of time it was switched on; e.g., the corrected temperature rise when the heater was switched on for 120 seconds was twice that for a heating time of 60 seconds. Proof of this indicates that the method used to obtain the correct temperature rise was an accurate one.

16.2.3 COOLING CURVE CORRECTED TEMPERATURE RISES

The correct temperature rises were obtained by extrapolating the cooling curve until it crossed the vertical line drawn from the point when the heater was initially switched on, or the point when the coal was added. In this way the effect of the cooling of the dewar, which would occur during the time the heater was on, would be nullified. Therefore, each time the heater was turned on or the coal was added, enough time had to elapse afterwards for a representative amount of the cooling curve to be recorded for an accurate extrapolation to be made. This vertical distance would be measured and treated as the corrected temperature rise.

In most cases, the slope of the temperature against time curve before and after heat input was the same, making the actual time at which the corrected temperature rise was determined, not critical.

16.2.4 EFFECT OF MESH SIZE OF SAMPLE

Immersion calorimetry tests were carried out on various mesh sizes of Colorado subbituminous coal, determining if the external or apparent surface area was a significant factor in the total (including internal pores) surface area value.

Mesh sizes of -16, -30, -60, and powder less than -60 were used without significant variation in the heat output. The total surface area of a coal is therefore very tolerant of sample powder size, the internal pore surface area term being dominant when compared to the external or apparent surface area term. This is the expected result if the pores are very small.

16.2.5 A COMPARISON OF THE HEAT OF IMMERSION OF SUBBITUMINOUS AND LIGNITE COALS

A two-gram sample of Gascoyne Red lignite was tested in the calorimeter and its heat output (determined in Figure 16-1) was found to be 65.74 Joules per gram or 15.49 calories per gram. Using a 10.7 conversion factor (4) of Bond and Spencer this gives a surface area of $165.72 \text{ m}^2 \text{ gm}^{-1}$.

FIGURE 16-1. Characteristic of lignites.

A similar sample of Colorado subbituminous was tested and gave rise to the trend depicted in Figure 16-2. It is interesting to note the stark contrast between the near instantaneous heat output of the Gascoyne Red lignite (the exothermic heat of wetting was liberated in a few seconds), and that of the Colorado subbituminous. Here the heat output occurred over several hours, presumably as the methanol wetting liquid explored the system of micropores which were approaching molecular dimensions.

Three other lignite-type coals have been tested in the calorimeter and the results are shown in Table 16-2. The specific heat outputs and corresponding surface areas for the Colorado subbituminous coal have been omitted because of the difficulty in obtaining the required information from Figure 16-2.

16.2.6 RECOMMENDATIONS

More coal samples will be tested in the calorimeter to build up a data bank of results and experience. A series of experiments are envisaged in which wetting liquids of various molecular sizes will be used to investigate the pore size distributions of porous coals.

FIGURE 16-2. Characteristic of subbituminous coals.

16.3 DIELECTRIC RELAXATION STUDIES OF WATER PRESENT IN LOW-RANK COALS

Using the specially-prepared teflon annulus discussed in the last quarterly report (UNDERC Quarterly Technical Progress Report - January to March 1984), a series of experiments were conducted to test the effect of using different mesh sizes of coal granules of just one type of coal on spectral peaks and spectral quality. This experiment was to determine if the size of the particle had any effect on the type or amount of water content of the coal. The coal chosen for these experiments was Colorado subbituminous, which was sieved into mesh sizes -16 (largest particle size), -30, -60, and fines less than -60. The phase shift against temperature graphs for the -16, -30, and -60 mesh size are shown in Figures 16-3, 16-4, and 16-5 for each of the three test frequencies, namely 100 HZ, 1000 HZ, and 10,000 HZ.

The spectral quality for the first set of peaks (presumably corresponding to the tightly-bound water of hydration) improves as the size of the specimen particle decreases. The spectral peaks are much more clearly defined for the -60 mesh size than for those at -16 mesh.

To see what effect compaction of a powdered coal in a press has upon the quality of the spectral peaks is now envisaged. A technique has been perfected for producing the compacted discs and the results will soon be forthcoming.

TABLE 16-2

SURFACE AREA CALCULATED USING A 10.7 CONVERSION FACTOR (4)

	Sample Number				
	1	2	3	4	5
<u>Heating Period I:</u>					
Time Duration (seconds)	60	60	60	60	60
Current I (amps)	0.340	0.340	0.345	0.388	0.340
Voltage V (volts)	5.84	5.95	6.06	5.89	5.96
Watts I.V.	1.986	2.023	2.091	2.285	2.026
Corrected Deflection (mm)	76	75	79	76	74
<u>Sample:</u>					
Corrected Deflection (mm)	--	80	62	83	68
Mass of Sample (gms)	2.00	2.00	2.00	2.00	2.00
H_c (cal gm ⁻¹)	--	15.49	11.78	17.91	13.36
H_j (J gm ⁻¹)	--	64.74	49.23	74.86	55.85
<u>Heating Period 2:</u>					
Time Duration (seconds)	60	60	60	60	60
Current I (amps)	0.364	0.342	0.345	0.340	0.340
Voltage V (volts)	6.06	6.03	6.09	5.96	5.96
Watts I.V.	2.21	2.06	2.10	2.026	2.026
Corrected Deflection (mm)	75	73	77	77	75
Surface Area S ($H_c \times 10.7$)	--	165.72	126.05	191.64	142.97

Key (all of -60 mesh powder):

1. Colorado subbituminous
2. Gascoyne Red lignite
3. San Miguel lignite
4. Indian Head lignite
5. Beulah lignite

FIGURE 16-3. Colorado subbituminous (-16 mesh).

FIGURE 16-4. Colorado subbituminous (-30) mesh.

FIGURE 16-5. Colorado subbituminous (-60 mesh).

16.4 MECHANICAL AND THERMAL FRIABILITIES OF COALS AND THEIR LITHOTYPES

The objective of this study is to characterize coals by their fracture characteristics, expressed in terms of shifts in particle size distribution functions during standardized tumbling and heating procedures. The scope of this study to date has been limited to establishing a methodology by which to provide fundamental data on the structure of coals and their individual lithotypes.

Qualitatively, Figure 16-6 indicates the three mechanisms of ideal, brittle fracture behavior: crushing, impact and attrition. An ideal brittle solid is one such that all particles of it, when subjected to an equal probability or severity of mechanical or thermal abuse, will have an equal probability of breaking into the same proportional size and number of smaller particles. In spite of their heterogeneous, non-isotropic structure, most coals come surprisingly close to ideal brittle solid behavior. The methods developed in this study express coals' fracture behavior numerically, as ideal brittle solids and indicate graphically where they depart from ideal behavior.

Crushing and impact severe enough to transmit destructive forces throughout a particle result in such approaches to ideal behavior. During heating, differential thermal expansion and structural weakening due to moisture removal have a similarly uniform effect on the breakage patterns of non-caking coals. Abrasion is the result of mild mechanical damage, in which destructive forces do not penetrate initial particles deeply enough to cause massive fracturing. Mechanical deviation from ideal fracture behavior results from variation in fragility of a coal's different lithotypes or concentrations of mineral components, as indicated in Figure 16-7. Thermal deviation from ideal behavior occurs in caking coals, which display a reverse thermal friability.

SHEAR AND COMPRESSION

WORK INPUT = $F(\Delta x)$

JAW AND ROLL CRUSHERS

FIGURE 16-6. Fracture mechanisms.

IMPACT

WORK INPUT = MV^2

HAMMER AND BALL MILLS

ABRASION

WORK INPUT: INSIGNIFICANT

MISC. HANDLING AND TUMBLING

FIGURE 16-7. Non-ideal fracture behavior of composite material.

Experimental procedure here consisted of first, uniformly crushing large lumps of mine-fresh coals in a jaw crush set to a 1 inch nip. Part of the resulting coarsely crushed sample was then tumbled in a jar with lifter bars, as specified for the ASTM tumbling test (5). Numerical description of the shift in particle size distribution, described below, is defined here as the coal's mechanical friability. A second portion of the same sample is then heated to 1000°F in an inert atmosphere. The particle size shift during this heating is defined as the thermal friability. Finally, the remaining char is again tumbled and screened, the final size shift being designated as Combined Friability. A complete set of such data, in two replications, is shown in Figure 16-8 for Indian Head (North Dakota) lignite.

FIGURE 16-8. Indian Head (North Dakota) lignite - thermal and mechanical friability.

In Figure 16-8, the lines represent least-square fits (of correlation factor, $R^2 = 0.95$ to 1.00) with the data points in the range for which the lines are drawn for the following mathematical form.

$$\log \left(\log \frac{100}{X} \right) = a + b \log d = Y \quad [1]$$

where d = particle size.

X = cumulative weight percent greater than each particle size.

a, b = empirical constants.

Before interpretation of Figure 16-8, consider the theoretical basis of this correlation. The inclination of crushed, reasonably homogeneous, brittle solids to form parallel, straight lines and the amount of information conveyed by them was discussed in an earlier UNDERC report (6). The fundamental law of brittle fracture behavior, developed by Rosin and Rammler for ground coal (7,8), states that if any size particles of an ideal, brittle solid, as defined above, are crushed, impacted, or otherwise reduced to a size range of which the largest is significantly less than the smallest of the original particles, the resulting distribution will be of the following form.

$$X = 100 e^{-(d/\bar{d})^n} \quad [2]$$

where X , d are as defined in equation [1].

$\bar{d}$ is an empirical average or characteristic size constant, that locates a straight line when plotted as in Figure 16-8.

n is another empirical constant, defining the size distribution, or slope of the line.

For ease of data reduction and statistical curve fitting, equation [2] was rearranged to give equation [1], which is used throughout this project. For comparison with equivalent data in the literature, a and b are readily convertible to Rosin-Rammler constants, $\bar{d}$ and n .

Either equation defines a straight line spanning the range $d = 0$ to infinity. Since any sample of coal must have a maximum dimension, which could not exceed the thickness of the seam, the uppermost data points must deviate from the ideal distribution to approach a vertical line at the maximum particle size present. Therefore, it is essential to crush samples beyond the maximum particle size of interest, so that sieve analyses include one or two points to be discarded from numerical curve fitting. Thus the downward curvature at the upper (right hand, coarse) end of the line on Figure 16-8 is an experimental artifact. The rest of the data, used in plotting the lines as sketched, convey information about the coal.

For any mechanical comminution or simple handling sequence, there will be some attrition, generating more fines than accounted for by the above straight line relationships. Such deviation varies from one coal to another. Figure 16-9 shows a "dusty" lignite from Texas, in which the after-tumbling line, defining mechanical friability, shows a striking curvature toward the horizontal at particle sizes below about 6 mm. When heated and when tumbled after heating, note that overall downward shifting of the lines is significantly greater than for the North Dakota lignite, suggesting that in a fixed bed gasifier it would lead to greater problems with plugging than experienced with North Dakota lignites (9). The shift due to thermal comminution alone (after heating to 1000°F) shows no such kink or curvature, indicating ideal behavior, with no attrition. That the line for the tumbled char after heating, defining the combined friability, also shows no curvature suggests that thermal fracturing and subsequent tumbling broke up the sample to sizes generally below the maximum dimension of components mainly responsible for the kink in the mechanical friability line. Such a dimension would be the typical maximum thickness of the laminae of the fine or soft component sketched in Figure 16-7.

FIGURE 16-9. Phillips (Texas) lignite - thermal and mechanical friability.

The initial size distribution line in Figure 16-8 is a composite curve fit to four separate screen analyses, discarding the one or two points approaching the coarse vertical asymptote and ignoring the slight curvature attributed to some unavoidable attrition in the jaw crusher. To determine numerical friabilities, however, separate distribution functions were determined for each set of sieve data. In Figure 16-9, the two portions of the total sample showed enough difference to justify plotting separate starting lines for this illustration. With small samples (700 to 1000 grams) including large particles, a difference of one or two such large particles (up to 1" x 2") can significantly shift the line vertically. This appears to present no problem since the significant parameter is the vertical shift in either line during heating or tumbling, normalized by expressing it as a percentage of the initial value at a point of interest.

Introducing another dimension of complexity, Figure 16-10 shows an equivalent set of data for a mildly caking bituminous coal, having a free swelling index (10) of 1.5 to 2.0. Its mechanical friability is not greatly different from the dusty Texas lignite. Upon heating, however, note the reverse thermal friability, indicating the tendency of coal particles to reaggregate. While it is not surprising that particle size distribution during thermal comminution should follow the same Rosin-Rammler brittle fracture law describing mechanical comminution, it was a surprise to find that the fundamental, statistical process actually works in reverse, as tacky particles are reagglomerated. While the lines in Figure 16-10, before and after heating, are straight line approximations, note that even the curvature of the initial line is preserved through reagglomeration. Note also that the kink

FIGURE 16-10. Energy (Utah) bituminous coal - thermal and mechanical friability.

between 6 mm and 9 mm appears after tumbling for both the raw and heated samples, again suggesting the presence of laminae of exceptionally friable material, as in Figure 16-7, having about this thickness, which appear unaffected by heat. This behavior is consistent with this coal's performance as a gasifier feed (6,9), where the entire upper two-thirds of the fuel bed (22" diameter by about 10') formed an interlocking, semi-fused mass of char.

Finally, the same tests were performed on a highly caking bituminous coal from Waynesburgh, West Virginia, with a free swelling Index of 6+. When heated, the entire sample swelled up substantially and fused into a single, rigid, glassy loaf, which had to be manually broken into several pieces before it could be tumbled to give the combined friability line of Figure 16-11. If we define thermal friability as the vertical shift in the "ideal" portion of the data plots, defined numerically, in equations [1] and [2] as Δa or Δd respectively, the Waynesburgh coal shows a value of minus infinity. Note however, that following final tumbling, the size distribution pattern for the completely agglomerated but fragile char is identical in form to the line obtained by tumbling the raw coal.

FIGURE 16-11. Waynesburgh bituminous coal - thermal and mechanical friability.

The same tests were performed on individual lithotypes, hand picked from the coal seams. Figures 16-12, 16-13, and 16-14 are some new examples of the thermal and mechanical friabilities of the major lithotypes (vitrain, durain, and fusain) from another North Dakota bituminous coal (Beulah) whose combined characteristics are similar to the data of Figure 16-8. They are presented here to invite free speculation, pending detailed analysis. It is immediately apparent that the difference between the lithotypes is substantial, so that such data must be based on fairly large, well-mixed samples to be considered representative of each coal.

FIGURE 16-12. Beulah vitrain - thermal and mechanical friability.

The numerical data corresponding to the lines in Figures 16-8 through 16-11 are summarized in Table 16-3, along with comparable data from six other coals selected simply by immediate availability of big-lump samples as required for this procedure. The most obvious numerical definition of friabilities is the shift in the weight percent over 10 mm, or $X(10)$, since $d = 10$ mm is roughly

FIGURE 16-13. Beulah durain - thermal and mechanical friability.

FIGURE 16-14. Beulah fusain - thermal and mechanical friability.

TABLE 16-3
FRIABILITY SUMMARY

Coal	Relative Friabilities, % ¹			Wt Loss % ²
	Mechanical	Thermal	Combined	
Indian Head Lignite	10.8, 10.6	22.3, 36.2	86.0, 63.8	42.0, 46.2
Phillips (TX) Lignite	15.9	66.5	99.8	46.2
Gascoyne White Lignite	18.0, 15.8	96.2, 98.8	99.9, 100.	50.0, 54.7
Baukol-Noonan Lignite	15.0, 15.2	63.2	97.2, 97.5	46.9, 48.0
Glenharold Lignite	33.9	74.7	99.9	51.6
Beulah Lignite, Whole	11.0	89.0	99.9	51.0, 51.9
Vitrain	18.4	65.2	100.	53.3
Durain	36.1	76.0	99.9	49.3
Fusain	32.3	49.0	96.6	45.2
Emery (Utah) Bituminous	16.0	-21.8	30.8	25.4
Waynesburgh (WV) Bit.	16.2	∞	58.6	13.0
Anthracite	21.9, 21.2	0.79, 0.36	23.8, 24.4	1.8, 1.7

¹% Change in % oversize at 10 mm from curve (least squares fit) of screen data, $\Delta X(d)/X(d)$ at $d=10$.

²During drying and pyrolysis to 1000°F.

in the middle of the data range. The variable $a = \log (\log 100/X)$ at $d = 1$, which is outside the data range. Statistical deviation of the points furthest to the ends of the range have a disproportionate effect on the slope, b , and hence on the error in $X(1)$. Still more meticulous sieve data, at least for thermal friabilities without the "attrition kink" could add another data point in the range of say 0.10 mm to 0.50 mm to give statistically far more accurate values for the slope, b . An earlier work (12) on thermal comminution of six non-caking, Wyoming bituminous and subbituminous coals indicated neatly parallel shifting of $X(d)$ lines, without significant changes in slope, clear down to 0.10 mm and below, which suggests that there was no significant deviation from ideal behavior down to at least this size range. Major changes in coal structure due to laminae of inorganic components tend to exist on an even smaller scale. In North Dakota lignites, for instance, there are occasional aggregates of soft clays up to 0.4 mm in thickness, though all other identified mineral species occur in the 0.005 mm to 0.040 mm range (13).

While the data of Table 16-3 is still a bit sparse and preliminary to support quantitative conclusions with any statistical validity, a few qualitative observations are in order. The range of thermal and combined friabilities of lignites shows no overlap with those of the higher-rank coals. The Beulah lithotypes fall within ranges of both mechanical and thermal friability that do not overlap these values for the unsegregated Beulah lignite, which was obtained and crushed separately from a different position in the seam. Thus, it is not possible from this data to relate the properties of the whole coal to any composite of its lithotypes' properties. A major source of error is the degree of predrying of the samples, which an earlier study (6) indicated to have a major effect on the mechanical friability. Although all samples were "mine-fresh", there was no control over the degree of atmospheric exposure they may have undergone on the mine face before removal.

The friabilities of the Beulah lithotypes vary in ways consistent with current theories on their geological origins. Vitrain is presumably formed in place with more of its more degradable plant tissues undisturbed, accounting for its lower mechanical and thermal friabilities than durain, which appears to be of detrital origin, having passed through an unconsolidated phase early in its formation. Fusain appears to be the carbonized remains of ancient bog or forest fires, leaving mainly of char, stripped of its more volatile components. Thus, it is less subject to thermal degradation than the other two lithotypes.

Of the whole coals, anthracite represents the extreme case of this chemical evolution, being completely stripped of volatiles and immune to thermal degradation.

Of all the lignites examined, it is significant that the Indian Head showed the lowest friabilities, which is consistent with its satisfactory performance in UNDERC's exceptionally sensitive pilot scale fixed-bed gasifier. Further efforts will be made to expand this data with a wider variety of coals and hand-sorted lithotypes and to seek out statistical correlations with their intrinsic (bound) moisture, volatiles, and fixed-carbon content.

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17. SUPERCRITICAL SOLVENT EXTRACTION

Project No.: 7306

B&R No.: AA1515100

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17.1 GOALS AND OBJECTIVES

The goals of this project are to investigate the fundamental principles of solute-solvent interactions at or above the critical point of the solvent, as applied to low-rank coal research, and to use supercritical solvent extraction for determining the composition of various molecular fractions present in low-rank coals.

The objectives of the current reporting period were to:

1. Investigate the ability of supercritical carbon dioxide to regenerate spent Calgon F-400 granulated activated carbon (GAC) used in the treatment of gasification wastewater. These experiments are primarily concerned with removing the nonbiodegradable 5,5-dimethylhydantoin and 5-methyl-5-ethyl hydantoin that were absorbed on the GAC.

Previous work performed by other investigators (1,2,3) has demonstrated the ability of supercritical CO₂ to remove organic impurities from spent activated carbon. Several advantages of supercritical fluid regeneration include: 1) supercritical CO₂ is a good solvent for several organics, 2) dissolved organics can be easily separated from the CO₂, 3) the activated carbon is spared the thermal degradation which occurs with thermally regenerating the activated carbon, and 4) CO₂ is a relatively cheap non-hazardous and non-toxic solvent. A particular problem encountered at the University of North Dakota Energy Research Center (UNDERC) has been the removal of 5,5-dimethylhydantoin and 5-methyl-5-ethylhydantoin from the wastewaters generated from UNDERC's slagging fixed-bed gasifier. Adsorption onto granulated activated carbon has been the only method found to date that will effectively remove these hydantoins from the wastewater. A major expense involved in using activated carbon as a wastewater treatment method is the cost incurred in replacing the activated carbon burned off when the activated carbon is thermally regenerated. While regeneration of the activated carbon using methanol to extract the hydantoin has been shown to be effective (4), it was suggested that employing supercritical CO₂ to regenerate the spent GAC might be

another way to reduce some of these regeneration costs; therefore, a small series of experiments was performed to investigate the effectiveness of using supercritical CO₂ to remove hydantoins from the spent Calgon F-400.

2. Continue efforts to determine the effect of supercritical water extraction on the inorganic matter in the coal.
3. Perform a supercritical water run on the UNDERC liquefaction continuous process unit (CPU) to determine if operating a continuous unit under supercritical conditions is feasible and to compare this extract with that using the semicontinuous supercritical unit.
4. Continue with a few selected supercritical water runs to determine the residence time effects on the percent conversions in the larger extraction vessels.

17.2 ACCOMPLISHMENTS

17.2.1 REGENERATION OF ACTIVATED CARBON USING SUPERCRITICAL CARBON DIOXIDE

Five experiments were run using supercritical CO₂ ($T_c = 31.4^\circ\text{C}$, $P_c = 1071$ psig) at 50°C and 2000 psig. In order to determine if any substances present in the GAC itself were soluble in the supercritical CO₂, a baseline run using fresh GAC was extracted with CO₂ at 50°C and 2000 psig. There was no yield of any material in the extract collection vessel. Table 17-1 shows the operating conditions and the resulting percent yields of hydantoins collected in the extract collection vessels. Three runs (SCSE 54-56) were performed on GAC which had been saturated with known amounts of 5,5-dimethylhydantoin and 5-methyl-5-ethylhydantoin. Two of the samples were oven-dried at 60°C while the third was freeze-dried in an effort to determine what effects different methods of drying would have on the amount of hydantoins extracted from the GAC. The yields obtained for these three runs was extremely low (<0.1 wt %) as shown in Table 17-1. Because of these results an experiment using supercritical CO₂ under similar operating conditions was run on pure 5,5-dimethylhydantoin to determine its solubility under these conditions. The yield from this run was similar to the 5,5-dimethylhydantoin results obtained from the previous runs. A supercritical CO₂ run was also performed on a sample of spent GAC obtained from carbon columns used in treating the gasifier wastewater. The weight of hydantoins obtained from the spent GAC was comparable to those obtained from the saturated samples, but since the actual hydantoin loading on the GAC was not known, a yield could not be calculated. Based on these results, it would have to be concluded that both hydantoins are not very soluble in supercritical CO₂ under these operating conditions, although it would appear that the 5-methyl-5-ethylhydantoin is more soluble than the 5,5-dimethylhydantoin.

Attempts were made to use the SCSE system at higher pressures in an attempt to determine if other operating conditions might significantly improve the yields of the hydantoins, but the pressurized liquid CO₂ in the accumulator diffused through the sealing O-ring causing it to rupture. A supercritical CO₂ experiment was performed on the semicontinuous supercritical solvent

TABLE 17-1

OPERATING CONDITIONS AND % YIELDS RESULTING FROM SUPERCRITICAL CO₂
REGENERATION OF GRANULATED ACTIVATED CARBON

Run Number	Operating Temp., °C	Operating Pressure (psig)	Solvent Flow Rate (cc/hr) at RT	GAC Residence Time (min)	GAC Sample Description	% Yield 5,5-Dimethyl Hydantoin	% Yield 5-Methyl-5-Ethylhydantoin	Total % Yield (MF)
53	50	2000	120	60	Spent GAC	*	*	*
54	50	2000	120	40	Sat. GAC Oven-Dried	0.012	0.045	0.057
55	50	2000	120	40	Sat. GAC Oven-Dried	0.022	0.042	0.064
56	50	2000	120	60	Sat. GAC Freeze-Dried	0.018	0.034	0.052
57	50	2000	120	50	5,5-Dimethylhydantoin	0.011	--	0.011
Demonstration Run	75	6000	480	120	Sat. GAC Freeze-Dried	0.237	0.052	0.289

*It is not possible to calculate a percent yield since the adsorbed weight of hydantoins on the Calgon F-400 is not actually shown.

extraction demonstration unit located at the Autoclave Engineers manufacturing plant in Erie, PA. This run used CO₂ at 75°C and 6000 psig to extract absorbed hydantoins from a freeze-dried sample of the saturated GAC. The yield of this run was still less than 1.0% of the total hydantoins absorbed on the GAC, but there was a significant increase in the yields with the increase in operating temperature and pressure.

17.2.2 SUPERCRITICAL WATER EXTRACTION EFFECTS ON INORGANIC MATERIAL

One observation made since starting to use the larger extraction vessels was that the percentages of ash in the supercritical water extracts have taken a ten-fold decrease from those observed in smaller vessels. This suggests that a large percentage of the ash in the extracts obtained using the smaller extraction vessels was due to startup effects.

The effect of supercritical water extraction at 380°C and 3265 psig on the inorganic material present in Indian Head lignite was investigated using x-ray diffraction (XRD) and scanning electron microscope (SEM) techniques. Both XRD and SEM analyses of the supercritical water residues indicated the definite presence of CaCO₃. Due to the organic nature of the extracts, poor closures on SEM and a highly amorphous signal on XRD were obtained. Both the extract and residues were then ashed to remove the organics and reanalyzed by XRD and SEM. Table 17-2 shows the results of the XRD analyses of an ash sample from

TABLE 17-2

RESULTS FROM XRD ANALYSES OF ASH SAMPLES FROM ORIGINAL INDIAN HEAD LIGNITE AND THE RESIDUE AND EXTRACT OBTAINED FROM A SUPERCRITICAL WATER RUN

Indian Head Lignite Ash Sample	Supercritical Water Residue Ash Sample	Supercritical Water Extract Ash Sample
Major Components	Major:	Major:
Anhydrite (CaSO ₄) Quartz (SiO ₂)	Gehlenite Anhydrite Hematite	Amorphous silica* (possibly chalcedony)
Minor Components:	Minor:	
Hematite (Fe ₂ O ₃) Nepheline (NaAlSiO ₄)	Magnetite Nepheline	
Trace Components:	Trace	
Gehlenite (Ca ₂ AlSiO ₇) Magnetite (Fe ₃ O ₄) Akermanite (Na ₃ KAl ₄ Si ₄ O ₁₆)	Akermanite	

*A highly-amorphous spectrum was obtained from this sample.

the original Indian Head lignite and the ash samples obtained from a supercritical water residue and extract, respectively. The small ash sample from the extract was also analyzed by SEM analysis with silica comprising the bulk of the inorganic material. The disappearance of quartz in the residue when it was a major component in the original lignite, and the high concentration of silica in the extract suggests that part of the ash sample in the extract could be due to solubility of quartz in supercritical water (5).

17.2.3 CONTINUOUS SUPERCRITICAL WATER EXTRACTION TESTS

In conjunction with UNDERC coal-water slurry preparation and low-rank coal liquefaction personnel, the liquefaction continuous process unit (CPU) was modified to allow continuous supercritical water extraction of Indian Head lignite. Two run periods (RP-4, RP-5) each 3 hours long were completed on the CPU using operating temperatures between 370° and 380°C and operating pressures of 3375 and 4000 psig, respectively. For these tests, the slurry flow rate was approximately 10 lb/hr of a 50-50 wt % mixture of "as-received" Indian Head lignite (mass mean diameter 48 μ m) and deionized water. The feed slurry was pumped through the modified process piping which provided for downflow through the vertical tubular reactor with the reactor outflow connected in parallel with the high-pressure liquid level controller and the slurry letdown valves. The depressurized slurry then was passed through a low-pressure flash tower where any vaporized water, volatiles, and dissolved gas could be collected. The remaining slurry was collected in steel pails located in the receiving pots. In an effort to obtain a separation of the supercritical water extract from the residual coal, the CPU was also modified to take a slipstream off the reactor outflow and meter a small portion of the slurry through an in-line high-pressure filter to remove the residual coal and collect the depressurized water and extract in high-pressure sample cylinders. Problems with plugging the in-line filter caused low yields of coal-free extract, but resulted in ideas for a better design should a similar sampling method be tried again. Samples from the resulting slurry were filtered in Buchner funnels before being submitted for analyses.

In order to obtain organic analyses of the extract and proximate and ultimate analyses of both the extract and the residue, the extract was separated from the residual coal by 24-hour Soxhlet extractions of the filter cakes with methanol and then methylene chloride. Table 17-3 shows the amounts of extract obtained using these two solvents. The yield of extract from these runs is lower than those obtained using the semicontinuous supercritical unit. This decrease in the amount extracted could be due, in part, to residence time effects, limited mass transfer between solvent and solute as the water becomes saturated with organics and to the fact that the actual slurry temperature was approximately 370°C, which is slightly subcritical.

Samples of the filtrate and the flash tower condensate were analyzed by GC for soluble organics. The results of these analyses are summarized in Table 17-4. The calculated total weight of soluble organics was based on the slurry sample being representative of the total slurry collected (i.e., the same weight % of filtrate would be obtained from any sample). The calculated yield of organics in the water is lower than those usually obtained using the semicontinuous supercritical unit. This lower yield is probably due to the

TABLE 17-3

RESULTS FROM 24-HOUR SOXHLET EXTRACTION OF SCE-1 FILTER CAKES
USING METHANOL AND METHYLENE CHLORIDE SEQUENTIALLY

	RP-4		RP-5	
	Wt %	mf Basis Wt %	Wt %	mf Basis Wt %
MeOH Extract	7.13	13.97	8.15	15.38
MeCl ₂ Extract	1.62	3.17	1.66	3.13
Residue	42.29	82.85	43.13	81.48
Water (by difference)	48.96	--	47.01	--
	100.00	100.00	100.00	100.00
Air Dry Moisture	22.94%		28.00%	

TABLE 17-4

RESULTS OF ORGANIC WASTEWATER ANALYSIS OF THE CPU SCE-1 RUN
PERIODS 4 AND 5 FILTRATE AND FLASH TOWER CONDENSATE

Compound	RP-4		RP-5	
	Filtrate Conc. (mg/l)	FT Condensate Conc. (mg/l)	Filtrate Conc. (mg/l)	FT Condensate Conc. (mg/l)
Methanol	1220	11700	1580	15070
Ethanol	10	20	ND	20
Acetone	210	8200	320	10220
Acetonitrile	ND	ND	ND	110
2-Butanone	10	1420	20	1840
Propionitrile	ND	10	ND	10
Phenol	180	814	245	949
o-Cresol	7	121	11	142
p-Cresol	19	139	18	153
m-Cresol	6	84	10	92
Calc. Total Wt. (gms)	8.4	5.7	10.4	7.4
% Yield (Based on 10 lb/hr flow rate)	0.20	0.14	0.27	0.19
Total % Yield for RP		0.34		0.46

ND = Not Detected

incomplete separation of all the water from the slurry and to some readsorption of organics back onto the surface of the coal.

Two samples of the product gas were collected in each run period; one sample being the product gas off the flash tower and the other sample being dissolved gas off the receiver pot. Table 17-5 shows the product gas compositions and yields obtained from the two run periods. The air-free product gas composition is typical of product gas composition obtained from the supercritical unit but the yield appears to be significantly lower than a typical gas yield from the semicontinuous unit. This low gas yield was due in part to the remaining dissolved gas which continued to bubble out of the slurry after the product receiver pots had been removed from the end of the CPU.

TABLE 17-5

NORMALIZED AIR-FREE PRODUCT GAS COMPOSITION AND YIELDS OBTAINED FROM CPU SUPERCRITICAL WATER RUNS

Component	RP-4		RP-5	
	PG	DG	PG	DG
H ₂	0.46	0.53	0.50	0.49
CO ₂	96.16	96.99	95.81	95.64
C ₃ H ₆	0.28	0.27	0.27	0.26
H ₂ S	0.27	--	0.09	0.06
C ₂ H ₄	0.09	0.09	0.07	0.09
C ₂ H ₆	0.38	0.45	0.47	0.45
CH ₄	2.21	1.40	2.59	2.76
CO	0.09	0.08	0.06	0.06
C ₄ 's	0.08	0.09	0.12	0.15
TOTAL	100.00	100.00	100.00	100.00
Calc. % Yield		5.1%		5.6%

PG = Product gas from flash tower.

DG = Dissolved gas from product receiver pot.

17.2.4 CONTINUING SUPERCRITICAL WATER WORK ON THE SEMICONTINUOUS SUPERCRITICAL UNIT

In the previous quarter an experiment (SCSE 50) was run using a solvent mixture of water and CO (~10 mole % CO) to extract Indian Head lignite. The purpose of this run was to investigate the effect of adding a reducing gas such as CO on the molecular composition of the resulting extract. The operating conditions and the experimental results are shown in Table 17-6. The conversion obtained compares favorably with that obtained for a run using pure H₂O under similar conditions (see Run SCSE 46 in Table 17-6). The resulting extract was separated and then analyzed by NMR, IR, and molecular weight GPC. Proximate and ultimate analysis of the extract and residue were done as well. Table 17-7 compares the proximate and ultimate analyses of the residues and extracts for runs using supercritical water (SCSE 46) and the supercritical water-CO mixture (SCSE 50). The C/H ratio is substantially lower for the run using the H₂O-CO mixture which suggests the possible addition of H₂, which was generated by the water-gas shift reaction, to some of the extracted molecules. Also shown in this table are the results of the column chromatography analysis used to separate the extract into aliphatic, aromatic, and polar fractions. As indicated by these results, the extract obtained using the H₂O-CO mixture appears to be more polar than an extract obtained from a straight supercritical water run. Figure 17-1 shows the 200 MHz ¹H NMR spectra of the three separate fractions. The aliphatic fraction was found to contain only alkanes as shown in ¹H NMR spectrum. In the aromatic fraction, no individual hydrocarbons were recognized, but the large CH₂ and CH₃ resonances may indicate the presence of waxes. Both ¹H NMR and IR analyses of the polar fraction indicated the presence of phenols and long-chain aliphatic esters (waxes). Figure 17-2 shows a comparison of the molecular weight profiles determined by gel permeation chromatography (GPC) of two extracts. One extract was obtained using supercritical water (SCSE 44) while the other run (Run SCSE 50) used the supercritical water-CO mixture. It appears that the addition of CO to the supercritical water has slightly shifted the molecular weight profile of the resulting extract to lower values.

Two runs were performed using nitrogen as the carrier in the semicontinuous unit at supercritical water conditions (i.e., 380°C and 3265 psig) to compare the percent conversions obtained using supercritical water to those obtained under pyrolytic conditions. The operating conditions and percent conversions for these two runs SCSE 48 and SCSE 58 are summarized in Table 7-6. It can be seen that the percent conversions obtained were only 27.5% and ~20% for "as-received" and air-dried Indian Head lignite (30.5% and 16.6% moisture, respectively). This compares to a 42.7% conversion using supercritical water under similar operating conditions and to a 25% conversion using "as-received" Indian Head lignite in the small pyrolysis reactor (SPR) using a helium stream at atmospheric pressure with a similar temperature profile. Table 17-8 shows the proximate and ultimate analyses of the residue and the extract obtained from a run (SCSE 48) using N₂. The lower C/H ratio and the lower yield of an extract obtained using N₂ when compared to those obtained using supercritical water indicates that supercritical water extraction is able to separate more components from the coal than direct pyrolysis.

TABLE 17-6
OPERATING CONDITIONS AND EXPERIMENTAL RESULTS FOR INDIAN HEAD LIGNITE
(Run SCSE 50)

Run	Operating Temp., °C	Operating Press., psig	Solvent Flow Rate (cc/hr at RT)	Coal Residence Time (hr)	Coal Size (mesh)	Solvent	Conversion maf, %	Volatile Matter (maf basis)	% H ₂ O As Run Coal
46	380	3265	120	1	-60 to 230	H ₂ O	42.7	52.4	31.5
48	380	3265	1.2*	1	-60 to 230	N ₂	27.5	52.4	30.5
50	383	3300	120+	1	-60 to 230	H ₂ O-CO	41.2	52.4	29.4
58	380	3265	3.8*	1	-60 to 230	N ₂	~20.0	52.4	16.6
59	380	3265	120	.25	-60 to 230	H ₂ O	~17.3	52.4	27.5
60	380	3265	120	.5	-60 to 230	H ₂ O	~29.7	52.4	31.5

*Solvent flow rate at atm pressure and temperature (ft³/hr)

TABLE 17-7

COMPARISON OF EFFECTS AND RESIDUES FOR SUPERCRITICAL
WATER AND SUPERCRITICAL WATER + CO

Conversion, % (maf)	Indian Head Lignite			
	Water		Water + CO	
	42.7%		41.2%	
	Extract	Residue	Extract	Residue
Proximate (mf)				
Volatile Matter	79.8	30.4	99.6	27.6
Fixed Carbon	19.8	61.0	0.4	60.7
Ash	0.4	8.6	0.0	11.7
Ultimate (mf)				
Hydrogen	7.63	3.53	8.58	3.41
Carbon	78.73	75.10	79.67	72.55
Nitrogen	0.84	1.38	0.86	1.40
Sulfur	0.42	0.38	0.36	0.39
Oxygen (diff.)	11.97	11.01	10.52	10.54
Ash	0.4	8.6	0.0	11.7
Column Chromatography				
Alkanes	5.2		Trace	
Aromatics	26.0		14.2	
Polars	68.8		85.8	

Two more supercritical water runs (SCSE 59 and 60) were completed using varying coal residence times to investigate the effects of using larger extraction vessels on the time needed to achieve a relatively complete extraction. The operating conditions and the approximate percent conversions are shown in Table 17-6. Increasing the size of the reactor vessel by a factor of 5 has increased the residence time necessary to obtain a relatively complete extraction (i.e., from a 38.4% conversion at 15 minutes using the smaller vessel to only 17.3% at 15 minutes and 29.7% at 30 minutes) using the larger extraction vessels with the same solvent flow rate. The use of the larger extraction vessels will enable a better understanding of the effects residence time and solvent flowrate have on supercritical solvent extraction.

FIGURE 17-1. 200 ^1H NMR spectrum of column fractions from a supercritical $\text{H}_2\text{O}-\text{CO}_2$ solvent mixture at 383°C and 3300 psig.

FIGURE 17-2. Comparison of the molecular weight profiles of the extracts obtained from runs using supercritical water and a supercritical water-CO mixture.

TABLE 17-8

PROXIMATE AND ULTIMATE ANALYSIS OF RESIDUE AND EXTRACT
FROM RUN SCSE 48 USING N_2 AT $380^\circ C$ AND 3265 PSIG

	Residue	Extract
Proximate (mf)		
Volatile Matter	31.8	98.4
Fixed Carbon	57.3	1.2
Ash	10.9	0.4
Ultimate (mf)		
Hydrogen	3.68	9.26
Carbon	72.47	80.49
Nitrogen	1.49	0.71
Sulfur	0.51	0.71
Oxygen (diff)	10.95	8.75
Ash	10.9	0.4

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18. PYROLYSIS AND DEVOLATILIZATION

Project No.: 7307

B&R No.: AA8545050

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18.1. GOALS AND OBJECTIVES

The primary goal of the Pyrolysis and Devolatilization project is to determine the product composition of the pyrolysis or devolatilization of low-rank coals under heating rates, particle sizes, and atmosphere typical of low-rank coal processing, as the basis of an understanding of effluent production from fixed-bed gasification. A second goal of the project is to use the pyrolysis experiments to determine mechanisms, kinetics, and thermodynamics of devolatilization as a guide to understanding reactivity of low-rank coals.

During this reporting period, work centered on pyrolyzing Indian Head lignite in the redesigned and tested SPR trap system. The lower molecular weight products were of greatest concern and interest, because they would be of particular importance in design of water treatment systems for gasification plants.

18.2 ACCOMPLISHMENTS

18.2.1 THE SMALL PYROLYSIS REACTOR (SPR)

A test matrix using Indian Head lignite was implemented to produce and analyze the water-soluble organics. Four set point temperatures of 180°, 380°, 690°, and 850°C were used in the test matrix. The Indian Head lignite was pyrolyzed on an as-received basis in the SPR and was maintained at each set point temperature listed above for 30 minutes under an inert atmosphere of helium. These temperature regimes were selected to determine the onset of water-soluble compound evolution. Two runs were made at each set point temperature using a slow heating rate of 5°C/min and a fast heating rate of 45°C/min. The water-soluble portion was recovered in the vacuum trap immersed in liquid nitrogen and was analyzed by gas chromatography. The water analyses for pyrolysis products from Indian Head lignite at 380°, 690°, and 850°C at 5° and 45°C heating rates are summarized in Tables 18-1 and 18-2 and in Figures 18-1 and 18-2. These results indicate that a change in heating rate affects the phenolic concentrations in the product liquor. It is apparent that at the

TABLE 15-1

ANALYSIS OF WATER-SOLUBLE ORGANICS AT 5°C/MIN OF INDIAN HEAD LIGNITE PYROLYSIS

	<u>Lignite at 380°C</u> <u>Helium Flow of 30 cc/ min</u>	<u>Lignite at 690°C</u> <u>Helium Flow of 30 cc/min</u>	<u>Lignite at 850°C</u> <u>Helium Flow of 30 cc/min</u>
Water Analysis	5°C/min heating rate μg/g maf coal	5°C/min heating rate μg/g maf coal	5°C/min heating rate μg/g maf coal
Methanol	2085	1435	1250
Ethanol	16	35	26
Acetone	1003	1370	1224
Acetonitrile	79	290	231
2-Butanone	253	400	358
Phenol	1996	3600	2995
o-Cresol	475	1020	1097
p-Cresol	778	1400	1280
m-Cresol	633	1430	1355
Catechol	1462	1550	1836

TABLE 18-2

ANALYSIS OF WATER-SOLUBLE ORGANICS AT 45°C/MIN OF INDIAN HEAD LIGNITE PYROLYSIS

	<u>Lignite at 380°C</u> <u>Helium Flow of 30 cc/ min</u>	<u>Lignite at 690°C</u> <u>Helium Flow of 30 cc/min</u>	<u>Lignite at 850°C</u> <u>Helium Flow of 30 cc/min</u>
Water Analysis	45°C/min heating rate μg/g maf coal	45°C/min heating rate μg/g maf coal	45°C/min heating rate μg/g maf coal
Methanol	906	1400	1609
Ethanol	13	36	23
Acetone	479	1420	1368
Acetonitrile	29	214	229
2-Butanone	135	411	357
Phenol	1369	2528	2366
o-Cresol	350	607	569
p-Cresol	550	1042	826
m-Cresol	447	1054	839
Catechol	1482	2379	2300

FIGURE 18-1. Analysis of water-soluble organics of Indian Head lignite pyrolyzed at 5°C/min heating rate.

FIGURE 18-2. Analysis of water-soluble organics of Indian Head lignite pyrolyzed at 45°C/min heating rate.

slower heating rate that the phenolic concentrations are greater compared to the faster heating rate. Analysis of alcohols, ketones, and nitriles produced at 690° and 850°C by 5° and 45°C/min heating rates reveal the same effective concentrations in the liquor product, concentrations being considerably higher than those produced at 380°C.

To ensure that the data from the SPR was reproducible, a duplicate run was made at 850°C and the corresponding runs were compared, as shown in Figure 18-3. The reproducibility of the SPR Runs 13-61 and 8-57 results are within 10%.

FIGURE 18-3. Pyrolysis results of two corresponding SPR runs at 850°C at 45°C/min showing the reproducibility of the SPR apparatus.

The length of time and the temperature at which the lignite sample is pyrolyzed significantly affect the yield of the water-soluble organics produced. Four SPR runs will be discussed where two set point temperatures of 380° and 850°C have been completed on the SPR varying only in the length of time the sample is held at a set point temperature. Two of the four runs utilizing Indian Head lignite were heated at 45°C/min and held isothermally for 30 minutes at 380° or 850°C. The remaining runs were not held isothermally once set point temperature was reached but were immediately shut down and cooled. There is a dramatic difference in the concentrations of water-soluble organics between the run held at 380°C for 30 minutes and the run where the sample was cooled quickly after reaching maximum temperature. The sample with no isothermal produced only trace water-soluble organics, with 63.7% of as-received material remaining, while a 380°C, 30 minute isothermal run produced appreciable concentrations of water-soluble organics with 51.3% of the as-received lignite remaining. Residence time does not appear to

affect the amount of char material remaining for runs at 850°C or concentrations of water-soluble organics produced at 850°C (Figure 18-4). The values for the as-received coal material remaining for runs at 850°C with a 30-minute isotherm and no isotherm are 39.2% and 39.4%, respectively.

FIGURE 18-4. Residence time effects on water-soluble organic yields of pyrolysis Indian Head lignite at 850°C.

Considerable information may be acquired by analysis of data obtained from ultimate and proximate analyses of the pyrolyzed coals. Figure 18-5 shows the mass fraction of coal and hydrogen, carbon and oxygen remaining on an maf basis upon pyrolysis at a 5°C/min heating rate and a subsequent 30 minute isothermal pyrolysis at the final temperature. By 850°C, more than 90% of the maf hydrogen and oxygen has been evolved but only slightly less than 25% of the maf original carbon has been released. The maf coal mass apparently stabilizes after 700°C, indicating that further hydrogen and oxygen elemental release have little effect on the total mass since hydrogen and oxygen have been reduced to small fractions of the char. Figure 18-6 shows the effect of maintaining the pyrolysis temperature at 850°C for 30 minutes compared to slowly cooling the sample. The isothermal period had no appreciable effect on the oxygen and carbon quantities remaining but greatly affected the hydrogen content in the char as it was reduced by 66% during the isothermal program. Evidently, at these high temperatures, hydrogen elemental release is strongly a function of time while oxygen and carbon elemental release are mainly a function of temperature.

FIGURE 18-5. Mass function of coal and hydrogen carbon and oxygen remaining on a maf basis upon pyrolysis at a 5°C/min heating rate and 30 minute isothermal.

FIGURE 18-6. Effect of maintaining the pyrolysis temperature at 850°C for 30 minutes compared to slowly cooling the sample.

Figure 18-7 shows the mass fraction remaining of maf coal and elemental constituents upon pyrolysis at a 45°C/min heating rate. Figure 18-7 differs little with Figure 18-5 except when comparing the oxygen fraction. However, since the oxygen ultimate content was determined by difference, the accuracy of the oxygen content is most affected by experimental error.

FIGURE 18-7. Mass fraction remaining of maf coal and elemental constituents upon pyrolysis at a 45°C/min heating rate.

Figure 18-8 and 18-9 again plot maf elemental percent remaining versus temperature for both heating rates, with the inclusion of sulfur and nitrogen contents. No conclusions on nitrogen reactivity could be reached because of the erratic nature of the data, probably due to the relatively small concentration but corresponding precision in comparison to carbon and hydrogen determinations. However, sulfur analysis reveals a consistent fraction remains upon pyrolysis above 400°C. It is suggested that sulfur forms be included in the analysis of future SPR char samples to determine the extent of organic and pyritic sulfur volatilization.

The average composition of the volatilized compounds may also be determined by subtraction of the char data from the original maf coal. From this data, hydrogen-to-carbon ratios, an important parameter in synthetic fuel production processes, may be calculated for the char and volatile fractions. Figures 18-10 and 18-11 show the hydrogen-to-carbon (H/C) molar ratios for 5°C/min and 45°C/min heating rates. Both figures show increases in the cumulative volatile H/C ratio as temperature increases and a corresponding decline in the char H/C ratio. In Figure 18-11 the H/C ratio falls as low as 0.064 for the sample heated to 850°C. However, a corresponding sample heated to 850°C but allowed to cool slowly thereafter, instead of prolonged exposure (30 minutes) at 850°C, contained a H/C ratio of 0.19, again evidence that hydrogen evolution is highly time dependent.

FIGURE 18-8. maf Elemental percent remaining versus temperature upon Indian Head lignite pyrolysis at a 45°C/min heating rate.

FIGURE 18-9. maf Elemental percent remaining versus temperature upon Indian Head lignite pyrolysis at a 5°C/min heating rate.

FIGURE 18-10. Hydrogen-to-carbon (H/C) molar ratios of Indian Head lignite pyrolysis products for a 5°C/min heating rate.

FIGURE 18-11. Hydrogen-to-carbon (H/C) molar ratio of Indian Head lignite pyrolysis products for a 45°C/min heating rate.

The H/C ratio for the volatile fraction increases most sharply for the 5°C/min heating rate in 300° to 400°C range, temperatures at which the onset of pyrolysis of North Dakota lignites is normally associated and which has the highest definition because of a relative wealth of data points. This change in slope is not nearly as evident for the 45°C/min heating rate, probably because only one sample was pyrolyzed within the 200° to 400°C interval. After 400°C, the cumulative volatile H/C ratio increases steadily, reaching 2.76 for the faster heating rate. On further evaluation of the volatile elemental content, the H/C ratio between consecutive set temperatures may be determined. Figure 18-12, showing the results of this calculation series, indicates the H/C molar ratio of the temperature-dependent volatiles increases exponentially with temperature, ranging from 1.24 at 200°C to 16.7 at 850°C. With an H/C ratio of 16, it is mathematically inevitable that most of the gaseous volatile volume evolved at these high temperatures must be attributed to hydrogen gas or hydrogenated inorganic compounds (H_2S , H_2O). Assuming the carbon evolved at these high temperatures is fully hydrogenated, as in methane, the volatiles evolved above 650°C would contain a maximum of 14.3% hydrocarbons. However, since most of the pyrolysis weight loss occurs between 350° and 500°C, the cumulative H/C ratio will be most affected by the H/C molar ratio of the volatiles evolved at these lower temperatures.

FIGURE 18-12. Set point temperature interval hydrogen-to-carbon (H/C) molar ratio of pyrolysis-produced volatile compounds from Indian Head lignite.

18.2.2 ONE-POUND MACROREACTOR

A macroreactor with a sample capacity up to 500 g has been used to process five coke samples for subsequent catalytic gasification and lignite for a devolatilization-pyrolysis project. Indian Head lignite was pyrolyzed at 850°C in nitrogen gas at one atmosphere.