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QUARTERLY TECHNICAL PROGRESS REPORT, APRIL—JUNE 1982

April 1984
Date Published

For
Morgantown Energy Technology Center
Morgantown, West Virginia

By
Grand Forks Energy Technology Center
Grand Forks, North Dakota

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QUARTERLY TECHNICAL PROGRESS REPORT

April-June 1982

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Date Published - April 1984

U.S. DEPARTMENT OF ENERGY

HIGHLIGHTS

Preparation of Low-Rank Coals

- Batch equilbrium tests showed removal of sodium from lignite with calcium chloride solution was significantly improved by high calcium chloride concentration.

- Sodium, calcium, and potassium in lignite were significantly reduced by ion exchange with magnesium chloride solutions, with sodium reduction as high as 92 pct.

- "Hot-water drying" tests on a North Dakota lignite of nominal 35 pct moisture showed significant moisture reduction, as high as 75 pct at 264°C, 15 minutes drying time, and 1.8:1 solid:liquid ratio. Over half the sodium was removed during the process at these conditions.

Low-Rank Coal Liquefaction

- Elemental sulfur and iron pyrite gave improved distillate yields, while mill scale and magnetite gave reduced distillate yields from lignite liquefaction with syngas in batch cold-charge autoclaves as compared to uncatalyzed experiments.

- Hot-charge liquefactions of a lignite and a subbituminous coal showed a consistent increase in product H/C ratio over uncatalyzed experiments, indicating possible improvement in slurry viscosity during recycle operation.

- Greater improvement in liquids yield over uncatalyzed reaction from H_2S and/or S addition was shown by a Texas lignite over a North Dakota lignite, possibly due to lower pyrite and sodium content of the Texas lignite.

- Hydrogen sulfide showed greater improvement in yields than solid additives FeS_2, Fe_2O_3, and elemental sulfur in once-through CPU tests with a North Dakota lignite and sygnas.

- Use of added catalysts permits lower temperature operation for a given yield.

- Solvent characterization studies reveal that hydrogen-donor compounds are maintained better after extended cycling in H_2S-catalyzed than in uncatalyzed runs in CPU recycle operation with North Dakota lignite and either hydrogen or syngas.

- Use of H_2S does not increase sulfur content in the vacuum distillate, although more sulfur-compounds are found in the lightest oil fraction.

- Mutagenic assays on extracted distillable CPU products showed no response to hydrocarbon or phenolic fractions of vacuum distillates whether or not H_2S was used.

- Quartz and calcium carbonate were major constituents in samples of reactor coke and reactor blowdown solids from CPU runs. Preliminary results indicate H_2S may inhibit oolite formation, since $CaCO_3$ was only a minor phase when H_2S was used.

- Studies by Advanced Coal Research on the kinetics of pyrolysis of Beulah lignite suggest that there may be two reactions responsible for coal decompositions, one dominating the low-temperature range and the other increasing in importance with increasing temperature. The lower-temperature reaction is postulated to be characterized by decarboxylation and dehydration, the higher by decomposition of phenolics, glysols, and benzylic hydroxyl compounds.

Slagging Fixed-Bed Gasification of Low-Rank Coals

- The current series of extended runs of the slagging fixed-bed gasifier was concluded with a 68-hour run (RA-120) and a 32-hour run (RA-121) with Indian Head lignite.

- Attempts to run Emery bituminous coal alone and mixed with Indian Head lignite were terminated in a few hours due to fuel bed problems and slag taphole plugging.

- A total of 30,000 gallons of wastewater was collected and stored in a freezer car for treatability studies during the total program.

- Time sampling of light oils indicates that waste stream composition lines out very early in a gasifier run, probably in less than 6 hours.

- In the operation of the Activated Carbon filter treatment of coal gasification wastewater at Georgia Instutute of Technology, an increase from 10 pct (1000 ppm TOC) to 15 pct (1500 ppm TOC) in wastewater concentration caused the system to fail.

- A wastewater treatment train, consisting of rough filtration, solvent extraction, and ammonia stripping, was leased from Resources Conservation Company and is being installed and operated by the University of North Dakota for test work to begin in the next quarter.

Atmospheric Fluidized Bed Combustion of Low-Rank Coal

- The last of a series of low-sodium Beulah lignite tests was performed on the 2.25-ft^2 AFBC with a low rate of nahcolite addition to evaluate sodium bicarbonate addition on sulfur capture and bed agglomeration. The added sodium was only 21 pct utilized, and agglomeration on the feed plate terminated the run after 42 hours.

- Four runs were made on the 2.25-ft^2 AFBC to investigate agglomeration with Beulah lignite samples with sodium lowered by ion exchange with sulfuric acid. The untreated coal gave severe agglomeration and termination after 62 hours, while three tests at various sodium levels with ion-exchanged coals gave little agglomeration, even at sodium levels (6.7 pct and 9.5 pct in ash) that would be expected to give trouble if present in untreated coals.

- Measurements of heat transfer coefficients on tubes in AFBC with Sarpy Creek subbituminous coal showed only a small (2 to 5 pct) effect on the coefficient for a heat transfer surface low in the bed and one near the top. Measurements varied from 40 to 60 Btu/hr-ft^2-°F for various conditions.

- A mechanism of quartz bed agglomeration is proposed in a report completed during the quarter by UND, postulating a four-stage process terminating in glass-cementing of large agglomerates.

Ash Fouling and Combustion

- A field test was commenced at the Leland Olds Station on effectiveness of additives in preventing ash fouling. Because the station is experiencing low demand, no fouling was obtained without additive use, and the test was discontinued.

- Morwell and Esperance lignite from Australia, containing high sodium as NaCl, were tested in the GFETC ash fouling unit and were found to be high fouling.

Combined Flue Gas Cleanup/Simultaneous SO_x-NO_x Control

- Morphological experiments were carried out by injecting limestone particles into the flue gas from a propane-fired combustor at temperatures from 1200° to 3000°F. Conversion from $CaCO_3$ to CaO commenced at 1800°F and was 90 to 95 pct complete at 2800°F. Surface area of the limestone after inspection was found to be relatively low (up to 3 m^2/g) and pore development was consequently poor.

- Investigation of a spray dryer flue gas desulfurization process by the University of Tennessee was commenced using 22 fly ash samples from various low-rank coal and bituminous coal-fired power stations. Sulfur dioxide removal efficiencies from 0 to 46 pct were obtained.

Particulate Control and Hydrocarbons and Trace-Element Emissions From Low-rank Coals

- Results of a detailed material balance performed under contract by GCA/Technology Division of Bedford, Massachusetts, on a Beulah lignite burned in the GFETC 2.25-ft^2 AFBC pilot plant are reported. Analyses for 24 elements were performed in all significant process streams. Particulate emission levels were lower than normal performance of conventional combustion systems and than the current New Source Performance Standard for steam-electric boilers by 1 and 2 orders of magnitude, respectively.

- Polycyclic organic matter concentrations in baghouse ash from AFBC with Beulah lignite were found to be substantially higher than those found in ash from pulverized coal firing.
- Ames tests (Salmonella mutagenesis assays) showed Beulah lignite AFBC ash to be only moderately mutagenic.

Waste Characterization and Disposal

- Concentrations of eight trace elements (As, Ba, Cd, Cr, Pb, Hg, Se and Ag) in four low-rank coal solid waste materials from the GFETC 2.25-ft^2 AFBC were reported. Differences among a North Dakota lignite with and without supplemental limestone, a Texas lignite, and an Illinois bituminous coal were roughly in the same range. The Illinois coal fly ash was low in arsenic and barium and high in chromium relative to the lignites.

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1. - PREPARATION OF LOW-RANK COALS

PTPA No.: 2-601 B&R No.: AA7505100

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Prepared by: L.E. Paulson, Project Manager, Coal Preparation Project

Assigned GFETC Personnel: W.A. Kinney

1.1 GOALS AND OBJECTIVES

The goal of the Coal Preparation Project at the Grand Forks Energy Technology Center (GFETC) is to develop environmentally acceptable and cost-effective preparation technologies for low-rank coals that address problems in storage, transportation, combustion, and conversion processes. The objectives of the project are to: 1) characterize and catalog the physical properties of low-rank coals; 2) develop, test, and demonstrate processes to upgrade low-rank coals by moisture removal and mineral matter alteration; 3) define, develop, and evaluate preparation processes for sulfur removal prior to combustion and for feedstock improvement for conversion processes; and 4) define and evaluate impacts of existing and potential preparation techniques and reduce such impacts to acceptable levels.

Specifically, objectives for FY 1982 project activities are to:

1. Continue ion exchange studies to remove sodium from low-rank coals.
    a. Develop basic kinetic data on removing sodium from lignite utilizing calcium or magnesium as the exchanging ion.
    b. Extend previously developed kinetic models for lignite to include subbituminous coal.
    c. Develop conceptual designs to remove sodium from lignite using calcium or magnesium as exchanging ions and determine costs.
2. Conduct laboratory tests to determine feasibility of hot-water/steam drying of low-rank coals for application in slurry transport, combustion of coal-water mixtures, and transport of solids into pressure vessels.

Objectives for third quarter of FY 1982 were to:

1. Continue laboratory studies to develop basic kinetic data for a mathematical model treating lignite with $CaCl_2$ solutions.

2. Continue development of data on chemical and physical properties of hot-water/steam drying coal as a function of process conditions. Initiate hot-water/steam drying of subbituminous coal and Texas lignites.

1.2 ACCOMPLISHMENTS

1.2.1 Ion Exchange

A study was made to determine the equilibrium sodium in lignite after ion exchange. Table 1-1 shows the percentage of sodium removed from lignite sized 14 X 20 mesh using a 0.01 and 1.0 N $CaCl_2$ solution. The duration of the batch run was 24 hours, and the liquid-to-solid ratio was 10:1, as expected. As expected, the higher $CaCl_2$ concentration of 1.N $CaCl_2$ gave far better results, removing over 89 pct of the sodium at equilibrium.

TABLE 1-1

EQUILIBRIUM SODIUM REMOVED FROM LIGNITE
(NORMALIZED DATA)

Initial $CaCl_2$ Conc. N	Percentage Sodium Removed at Equilibrium
0.01	39.3
1.0	89.4

Tests were made to determine the equilibrium between ions in lignite and magnesium from $MgSO_4$ (magnesium sulfate) solutions. The lignite tested contained 8½ sodium as oxide in the ash; $MgSO_4$ solutions concentrations varied from 0.005 to 0.14 molar; and contact between solution and solids was 24 and 48 hours. Lignite particle size was 14 X 20 mesh. Table 1-2 shows the metal analyses of as-received and treated coals. Results showed significant sodium, calcium, and potassium reduction. Data do not show an increase in magnesium content in coal as a function of increased treating solution strength.

A mathematical model to predict the removal of sodium from lignite using $CaCl_2$ solution is being developed. Variables which affect product sodium content included solution concentrations, solid and liquid residence times, particle size, and solid-to-liquid ratio. Typical data are shown in Figures 1-1 and 1-2. Figure 1-1 is a plot of percentage cations remaining in the lignite as a function of the residence time for particles sized 10 x 48 mesh, with a $CaCl_2$ solution concentration of 0.1 N, and a solid-to-liquid ratio of 1:2. Figure 1-2 is a plot of the percentage cations remaining in the lignite as a function of solid-to-liquid ratio in the range from 1:2 to 1:4, for 10 x 48-mesh particle size, $CaCl_2$ solution concentration of 0.1 N and solid residence time of 10 minutes.

TABLE 1-2

ANALYSIS OF METALS IN AS-RECEIVED LIGNITE AND LIGNITE HEATED WITH $MgSO_4$ SOLUTION

Initial $MgSO_4$ Conc. g mole/ℓ	Time, Hr.	Analysis of Lignite After ion Exchange												
		Moisture %	Ash (Dry Basis) %	Metal Ions In Lignite						Precent Ions Removed From Lignite				
				Na	K	Ca	Mg	Al	Fe	Na	K	Ca	Al	Fe
0	As Received	35.70	12.37	11232	402	20801	--	6102	8736	--	--	--	--	--
0.00480	24	55.99	13.83	3749	375	21424	6249	8569	13747	78.6	22.6	21.0	0	0
0.00480	48	42.57	10.23	2810	146	16295	4585	5956	9103	77.9	44.8	19.5	0	0
0.0480	24	41.13	10.07	974	172	12550	8114	3787	9196	91.3	42.9	34.0	0	0
0.0480	48	42.04	10.87	1776	237	13142	9472	6394	10480	86.2	40.8	41.5	0	0
0.140	24	42.91	11.34	884	184	11490	8207	4672	10480	92.5	41.1	46.7	0	0
0.140	48	44.83	10.71	706	179	9181	4120	6474	10005	90.3	43.2	51.0	0	0

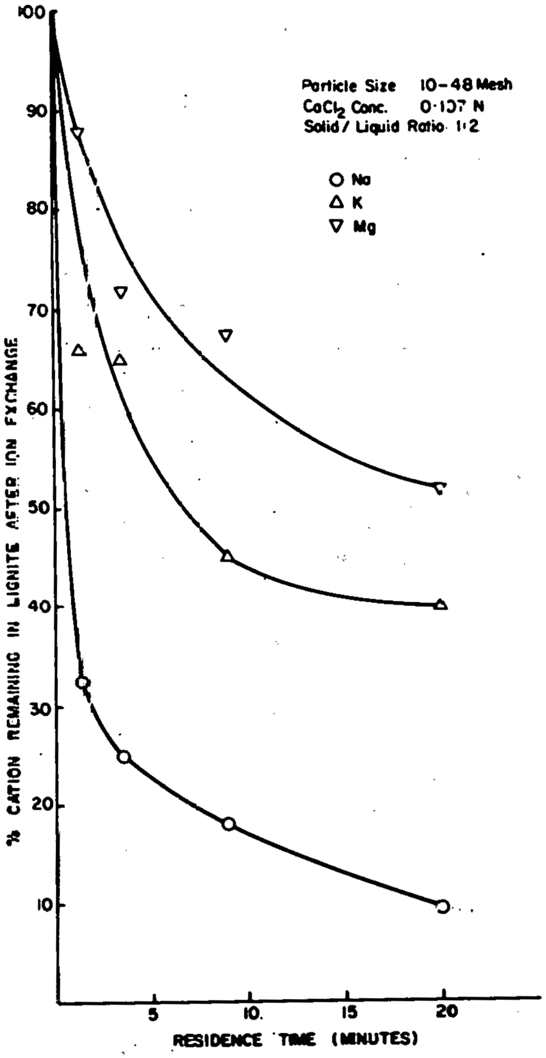

FIGURE 1-1. Lignite treated with $CaCl_2$ solutions. Cations remaining in coal as a function of residence time.

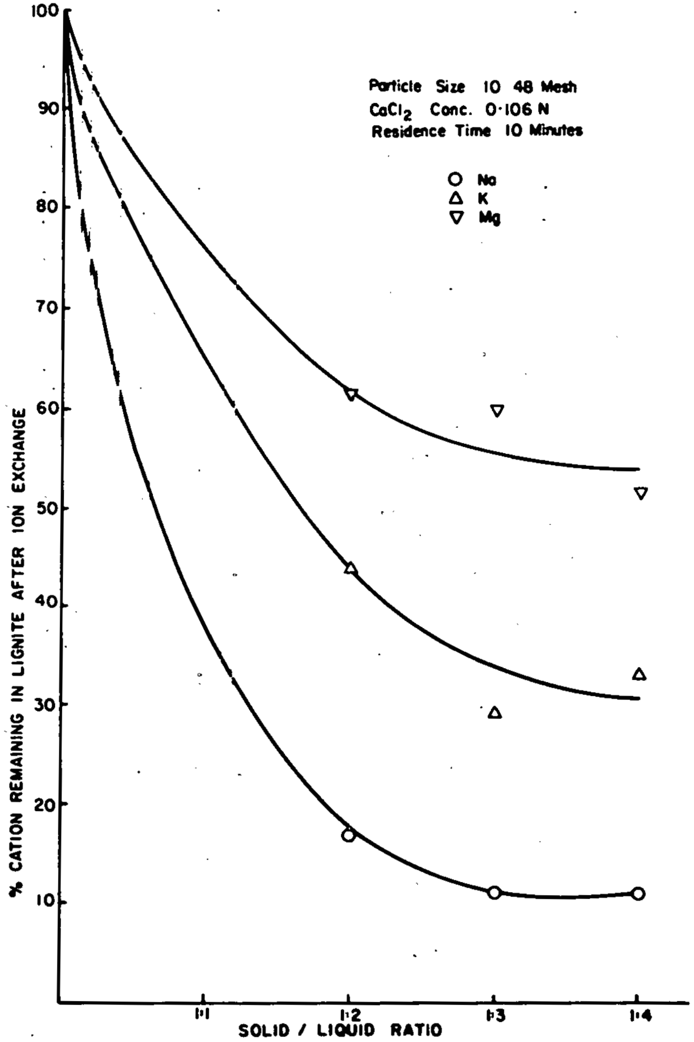

FIGURE 1-2. Lignite treated with $CaCl_2$ solution. Cations remaining in coal as a function of solid/liquid ratio.

1.2.2 Hot-Water/Steam Drying

A study was made of hot-water drying of low-rank coals. The lignite tested was from the Baukol-Noonan Mine at Larson, North Dakota. The coal contained 35 pct moisture, had an ash content of 6.9 pct (as received), and a particle size of 100 x 140 mesh. Table 1-3 shows moisture and ash content of the coal before and after drying. Tests were run at 214° and 276°C at a solid-to-liquid ratio of 3:1; at a solid-to-liquid ratio of 1:8 or 2:1 at temperatures of 261°, 264° and 225°C. Results show that increasing process temperature increases moisture removal. Hot-water drying does not remove ash.

TABLE 1-3

MOISTURE AND ASH CONTENT OF LOW-RANK COAL BEFORE AND AFTER HOT-WATER DRYING

				Moisture Content			Ash Content (Dry Basis)	
Run No.	Drying, Temp., °C	Drying Time, min.	Solid/ Liquid Ratio	Original Lignite, %	Dried Lignite, %	Moisture Reduction %	Original Lignite, %	Dried Lignite, %
81	261.4	15	1.8:1	33.25	14.03	67.07	6.46	6.15
82	264.2	15	1.8:1	33.21	11.02	75.07	6.59	6.26
83	225	15	2:1	33.02	18.83	48.23	8.08	7.55
84	214	15	3:1	33.65	23.28	40.02	7.64	7.24
85	276	15	3:1	31.96	13.14	67.67	7.40	7.39

Moisture reabsorption properties of hot-water-dried lignite were determined by placing the product in a humidity chamber at 71°C and 100 pct humidity and measuring changes in moisture content during a 23-day period. Figure 1-3 is a graph of moisture reabsorption as a function of drying temperature and time in a humidity chamber. Results show that equilibrium moisture in the sample was reached within several days and that product equilibrium moisture decreased with increasing process temperature.

The quantity of Na, K, and Ca removed from the lignite was measured for each of five test runs. The solid-to-liquid ratio was 1:1 and the drying temperature varied from 204° to 284°C. The ash analysis of the original lignite is shown Table 1-4; the percentage of inorganics removed as a function of process temperature is shown in Table 1-5. Of particular interest is that over 50 pct of the sodium was removed at 284°C.

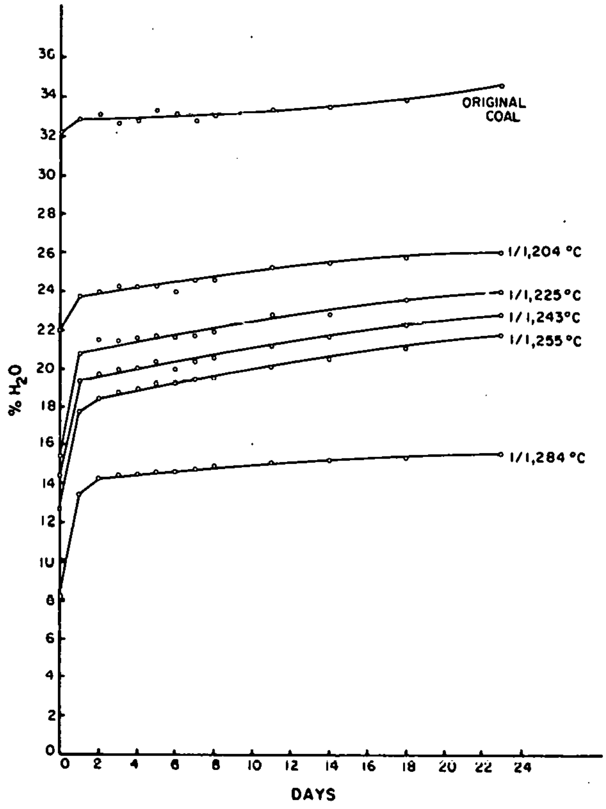

FIGURE 1-3. Twenty-three day moisture reabsorption test on slurry dried coal and original coal in 100 pct humidity chamber at 71°F.

TABLE 1-4

ASH ANALYSIS OF ORIGINAL LIGNITE

	maf Basis in Lignite, %	% Oxide in Ash
Sodium	0.3960	7.17
Potassium	0.0323	0.524
Calcium	0.9802	18.02

TABLE 1-5

IONS REMOVED BY HOT-WATER DRYING
SOLID/LIQUID RATIO = 1:1

Run No.	Drying Temp, °C	Percentage Removed From Lignite		
		Na	K	Ca
76	203.6	41.45	28.18	0.92
77	225	53.92	43.66	-5.67
78	242.8	49.60	-5.62	6.17
79	255	42.59	-8.55	-4.31
80	283.9	56.61	-21.05	0.64

Steam drying tests are being performed on Fairfield lignite and Sarpy Creek and Rosebud subbituminous coal. Moisture reduction and sulfur and ash changes in steam drying Rosebud subbituminous coal are shown in Table 1-6. In this series of tests, 1½-inch size coal was dried at temperatures varying from 271° to 314°C at a residence time of 20 minutes. The density ratio of dried coal to as-received coal and the average shrinkage after drying are listed in Table 1-7 for various drying temperatures.

The analysis of the residual gas in the reactor is shown in Table 1-8, and the analysis of the inorganics in the effluents is shown in Table 1-9. The gas analysis indicate that the concentration of CO_2, CO, and CH_4 increase with drying temperature. Sodium did not appear in the effluent from steam drying as it did in hot-water drying.

TABLE 1-6

ANALYSIS OF STEAM DRIED COAL

Run No.	Drying Temp., °C	Pressure psig	Moisture Content, %		Moisture Reduction %	Ash Content, % (Dry Basis)		Ash Reduction % (Dry Basis)	Sulfur Content, % (Dry Basis)		Sulfur Reduction % (Dry Basis)
			Initial	Dried		Initial	Dried		Initial	Dried	
					<u>Rosebud Subbituminous</u>						
16	271	750	25.70	8.09	75.30	10.44	7.73	28.13	0.48	0.50	-1.11
18	288	1000	25.70	5.72	82.86	10.44	8.34	21.95	0.48	0.43	12.47
19	300	1150	25.70	5.28	84.16	10.44	8.87	16.50	0.48	0.34	30.39
20	314	1210	25.70	4.45	86.74	10.44	9.05	14.64	0.48	0.43	11.79
21	300	1140	25.70	4.45	86.69	10.44	9.42	10.79	0.48	0.67	-38.01

TABLE 1-7

PHYSICAL PROPERTIES OF DRIED COAL

Run No.	Drying Temp., °C	Density, gm/ml		Density Ratio Of Dried To Original Coal	Shatter Strength		Shatter Strength Ratio of Dried To Original Coal	Average Shrinkage, %	
		Original	Dried		Original	Dried		Parallel To Bedding Plane	Perpendicular To Bedding Plane
					Rosebud Subbituminous				
16	271	1.30	1.40	1.08	0.356	0.253	0.711	10.1	10.1
18	288	1.30	1.10	0.85	0.356	0.125	0.351	5.9	5.2
19	300	1.30	1.17	0.90	0.356	0.191	0.537	--	--
20	314	1.30	0.96	0.74	0.356	0.191	0.537	8.3	6.4
21	300	1.30	1.36	1.05	0.356	0.112	0.315	7.3	2.5

TABLE 1-8

RESIDUAL GAS ANALYSIS

Run No.	Drying Temp., °C	Normalized Gas Analysis, %									
		CO_2	CO	CH_4	C_2H_6	C_3H_8	H_2	O_2	N_2	H_2S	NH_3
		Rosebud Subbituminous									
16	271	36.42	0.75	0.00	0.00	0.00	0.33	0.47	62.04	0.00	0.00
18	238	14.58	2.32	0.40	0.00	0.00	0.14	2.36	80.20	0.00	0.00
19	300	26.92	2.37	1.22	0.02	0.00	0.12	0.68	68.67	0.00	0.00
20	314	46.44	1.81	0.74	0.04	0.00	0.11	0.38	50.48	0.00	0.00
21	300	28.22	1.75	1.10	0.00	0.00	0.12	1.38	67.43	0.00	0.00

TABLE 1-9

EFFLUENT WATER ANALYSIS

Run No.	Drying Temp., °C	pH Of Distilled Water Charged	pH Of Bottom Water	Ion Concentration In Bottom Water, ppm				Sulfur Conc., ppm
				Na	K	Ca	Mg	
			Rosebud Subbituminous					
16	271	5.2	2.8	42	2.54	3.09	48.4	0
18	288	5.8	4.2	7	7.6	90.5	35.1	0
19	300	5.2	4.1	8	9.4	117	39.8	0
20	314	7.7	4.0	9	10.1	106.5	43.3	0
21	300	5.0	4.05	8	19.1	112	46.5	0
			Background					
	278	5.2	3.0	6	0.53	3	13	0

2. - APPLICATION OF LIQUEFACTION PROCESSES TO LOW-RANK COALS

PTPA No.: 618 B&R No.: AA2515050

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2.1 GOALS AND OBJECTIVES

The objectives of the liquefaction project at GFETC are to: 1) establish the engineering data base on the liquefaction behavior of low-rank coals; 2) study the use of process-derived product slurries and liquid fractions as recycle solvents; 3) evaluate reaction parameters to optimize liquid yield and quality; 4) study the effects of disposable catalysts such as iron pyrite, sulfur, ammonia, and hydrogen sulfide; and 5) characterize in detail all distillable products and correlate structure as determined by NMR, IR, UV, and MS to H-donor ability or solvent quality as determined from experimental yields.

The main activities outlined in the FY 1982 liquefaction work plan have the following goals:

1. Determine the effectiveness of H_2S and elemental sulfur as "disposable" catalysts on liquefaction by evaluating yields and product quality at reduced severity. Determine the threshold partial pressure of hydrogen with bottoms recycle and the equivalency of syngas at the hydrogen partial pressure threshold. Expand the data base on low-rank coals using two subbituminous coals and one lignite.

2. Characterize all product streams of recycle runs and correlate results with process conditions. Synthesize various hydrogenated model PNAs and determine their hydrogen donating ability with coal and coal-derived solvents. Study products of reaction of coal with labeled gases to gain insight into coal structure and mechanisms of reaction. Develop methods to determine the extent of sulfur incorporation, if any, in liquefaction products produced using H_2S as a catalyst.

The work reported this quarter has been divided into twelve segments and covers the activities of the GFETC liquefaction process group; the GFETC organic and inorganic analytical research groups; and the University of North Dakota (UND) hot-charge autoclave program.

2.2 ACCOMPLISHMENTS

2.2.1 Status of CPU Liquefaction Tests and Equipment Modifications

Continuous Process Unit (CPU) test studies during this reporting period included five bottoms recycle runs (85, 86, 87, 88, and 89) and eight once-through tests. The recycle runs were made as part of a temperature study with added H_2S, while the once-through tests accomplished three tasks: 1) test Highvale subbituminous coal with and without H_2S; 2) test Big Brown lignite (BB2) with different additives including sulfur and iron pyrite; and 3) test Beulah lignite (B3) with raw and hydrotreated anthracene oil. The results for these tests are incomplete and will be reported in subsequent quarterly reports.

CPU equipment modifications included installing eight new reactor temperature controllers and refurbishing the associated solid state electrical switching devices. Drawings for a second tubular reactor for the CPU were completed and mailed to 36 prospective bidders.

2.2.2 Effects of Several Disposable Catalysts on Lignite Liquefaction

Following is a generalized summary of results obtained to date in both the batch autoclaves and the CPU with respect to disposable catalysts. Some of these results have been reported in previous quarterly reports but are repeated here for added clarity and comment.

Several "disposal" catalysts were investigated in the cold- and hot-charge autoclaves, and an exploratory set of experiments were performed in the CPU. The catalysts were mainly sulfur or iron compounds.

In cold-charge autoclave experiments, lignite from the Beulah mine was charged to the autoclave along with a solvent (A0D2) and a 50:50 mixture of H_2 and CO. The reaction mixture was heated to 420°C and then immediately cooled. Results from tests with added S, FeS_2, millscale, and Fe_3O_4 are shown in Table 2-1. Adding elemental sulfur produced the greatest overall conversion along with the best yield of distillate oil. Pyrite also increased conversion and distillate oil yield, while both Fe_3O_4 and Fe_2O_3 had little effect on total liquid yield (SRL + oil). The two iron oxides, however, did increase the H/C ratio of the product slurry when compared to the baseline test.

TABLE 2-1

EFFECT OF ADDITIVES WITH BEULAH LIGNITE[a]

Additive:	None	Sulfur	Pyrite	Millscale	Magnetite
wt % maf coal:	0	10	15	15	15
H_2 partial pressure, psig	1200	1250	1190	1190	1150
Yields, wt % maf Coal:					
Gas & water	31.1	30.4	28.7	27.1	29.5
Distillate	18.2	23.5	22.4	15.8	2.9
SRL	40.1	43.5	42.0	42.5	57.7
Conversion	86.9	92.9	88.8	82.0	86.9
H_2 equiv. consumed	2.5	4.5	4.3	3.4	3.2
H/C atomic ratio of product:	1.27	1.24	1.13	1.32	1.35

[a] All tests were made in the cold-charge autoclave at 420°C using distilled anthracene oil (AOD2) as the vehicle solvent.

The observed increases in product H/C ratio when using the two iron oxides show a potential for reduced recycle slurry viscosity with increased product hydrogenation. Since product slurry H/C ratios have been linked to operability as a function of hydrogen partial pressure, as discussed in the previous quarterly report, raising the H/C ratio by using a disposable catalyst could result in a lowering of the overall total pressure requirements for the process.

Cold-charge autoclave tests were also made to determine the effects of FeS_2 with a subbituminous coal. With the exception of the coal, the reaction parameters for these tests were identical to those used in the cold-charge experiments just discussed. Iron pyrite addition with a Montana subbituminous coal did not improve overall conversion or the combined yield of SRL and oil; it did, however, significantly affect the product distribution. The yield of distillate increased, while the yield of SRL decreased proportionately (Table 2-2).

Cold-charge autoclave results with both Beulah lignite and Absaloka subbituminous coal indicate that all of the solid additives tested increased reducing gas consumption. This was due partly to formation of H_2S and reduction of iron pyrite and partly by increased product hydrogenation.

In hot-charge autoclave experiments, the spectrum of additives was increased to include mixtures of Fe_3O_4 and K_2CO_3, mixtures of Fe_3O_4 and S, and H_2S gas. The effects of these additives, with the exception of H_2S, were determined using the 1-liter, hot-charge autoclave system. Hydrogen sulfide gas was tested using the 1-gallon, hot-charge autoclave.

TABLE 2-2

EFFECTS OF ADDED PYRITE[a]

Coal:	ABS1[b]	ABS1
Solvent:	AOD2[c]	AOD2
Additive:	None	Pyrite
wt % maf coal	0	15
Yields, wt % maf coal:		
Gas & water	22.7	20.0
Distillate	11.1	21.0
SRL	56.7	44.8
IOM	11.8	17.9
H_2 equiv. consumed	2.3	3.7

[a] All tests were made in the cold-charge autoclave at 420°C.

[b] Montana subbituminous coal (Absaloka mine)

[c] Distilled anthracene oil.

Effects on product distribution, overall conversion, and the H/C ratio of the product slurry were determined for two coals: Indian Head and Absaloka. Most tests were made with the additive level at between 12 and 15 wt pct of the maf coal. The experiments were performed at 460°C using both pure hydrogen and a 50:50 mixture of H_2 and CO. The solvent employed was AOD2. Analysis of the effects of the different additives in the one liter hot-charge autoclave was confined to changes in product H/C ratio and its implications regarding product viscosity and unit operability because the solvent used in these tests proved unstable at 460°C with large losses due to hydrocracking and polymerization. This, coupled with low mass recoveries, confounded the yield determinations. Comparison criteria assumed that H/C ratios which were greater than the no-additive case would lower product viscosity and improve operability on continuous bottoms recycle. With both Absaloka subbituminous coal and Indian Head lignite, the addition of sulfur, Fe_3O_4, and FeS_2 contributed to enhanced H/C ratios in the product slurry (Table 2-3).

When using syngas, the effect of a particular additive was not the same for both coals. For instance, adding Fe_3O_4 plus K_2CO_3 or S to Absaloka coal provided the greatest increase in the H/C ratio of the product, while its addition with Indian Head lignite showed only an intermediate increase as compared with the base case. For the Indian Head lignite the greatest increase in product quality (H/C) was seen with added FeS_2.

The addition of a combination of Fe_3O_4 plus S resulted in H/C ratios greater than for either Fe_3O_4 or S additions alone. Adding K_2CO_3 to Fe_3O_4 also contributed to enhanced hydrogenation of the product slurry for both coals, with the level of hydrogenation above that for Fe_3O_4 alone.

TABLE 2-3

SUMMARY OF RESULTS FOR ADDITIONS OF IRON COMPOUNDS AND SULFUR TO LIGNITE AND SUBBITUMINOUS COAL[a]

Coal:	ABS1[b]	ABS1	ABS1	ABS1	ABS1	ABS1	ABS1	ABS1
Solvent:	AOD2[c]	AOD2	AOD2	AOD2	AOD2	AOD2	AOD2	AOD2
Additive:	None	Sulfur	Millscale	Pyrite	Magnetite	Mag+K_2CO_3	Mag+S	Pyrite
wt % maf coal	--	12.5	15	15	15	22.5	27.5	15
Reducing Gas:	H_2+CO	H_2+CO	H_2+CO	H_2+CO	H_2+CO	H_2+CO	H_2+CO	H_2
H/C ratio of product	0.87	1.08	1.05	1.18	1.02	1.18	1.18	1.15
Coal:	ZAP1[d]	ZAP1	ZAP1	ZAP1	ZAP1	ZAP1	ZAP1	ZAP1
Solvent:	AOD2	AOD2	AOD2	AOD2	AOD2	AOD2	AOD2	AOD2
Additive:	None	Sulfur	Millscale	Pyrite	Magnetite	Mag+K_2CO_3	Mag+S	Pyrite
wt % maf coal	--	12.5	15	15	15	22.5	27.5	15
Reducing gas:	H_2+CO	H_2+CO	H_2+CO	H_2+CO	H_2+CO	H_2+CO	H_2+CO	H_2
H/C ratio of product	1.03	1.08	1.15	1.20	0.99	1.05	1.12	1.25

[a] All tests were made using a 1-liter hot-charge autoclave. Reaction Temperature was nominally 460°C. Reaction pressure was about 4000 psig.

[b] Montana subbituminous coal from the Absaloka mine.

[c] Distilled anthracene oil.

[d] North Dakota lignite from the Indian Head mine.

Using pure H_2 rather than synthesis gas (H_2 + CO) when adding FeS_2 affected the H/C ratio of the product only slightly but in opposite directions for the two coals. For the Absaloka subbituminuous coal using pure hydrogen with FeS_2 lowered the H/C ratio slightly, while the same combination used with Indian Head lignite improved the H/C ratio when compared to similar tests with syngas and pyrite. Compared to the no additive case, pyrite significantly increased the H/C ratio regardless of whether pure hydrogen or syngas was used.

The effects of elemental sulfur and H_2S were investigated using the one-gallon hot-charge autoclave at 420°C with Big Brown lignite. The results (Table 2-4) indicate that conversions with raw anthracene oil, AO4, were relatively low without hydrogen sulfide. Adding H_2S not only significantly increased conversion, it also generated much higher yields of distillate and lower yields of gas. Similar effects were noted when the hydrotreated solvent, HAO61, was used but the enhancement was not as great. However, even with the hydrotreated solvent, H_2S did increase distillate yields and lower the net gas make.

In scouting tests to evaluate the effects of H_2S at three CO concentrations (0,50, and 100%), it was found that as the CO concentration increased, the conversion and net gas production also increased while the distillate yield decreased (Table 2-4), Runs 65, 93 and 94). The yield of the THF soluble vacuum bottoms (SRL) remained essentially unchanged.

Adding elemental sulfur to the coal slurry did not increase conversion above that obtained with H_2S but did result in an appreciable increase in distillate yield and a decrease in net gas. The yield of SRL was mid-range between that obtained with no additives and that obtained with added H_2S.

Hydrogen sulfide was also tested with a second lignite, Indian Head, and a comparison of results with those obtained with the Big Brown lignite is shown in Table 2-5.

The addition of H_2S in these tests appears to affect the two coals somewhat differently; the distillate and SRL yields, as previously mentioned, increase for Big Brown lignite while, on the other hand, no change or a slight decrease in the distillate yield occurred for the Indian Head lignite. The overall conversion increased for both lignites; however, the conversion was high even in the absence of H_2S, which was typical for liquefaction with the hydrogenated solvent. Adding H_2S benefits both lignites in that the H/C atomic ratio in the product slurry was increased. The increased product H/C ratios implies that continuous processes using bottoms recycle would be enhanced with the addition of H_2S to the process.

Autoclave studies have shown different coals respond differently to sulfur and H_2S, with Big Brown lignite more favorably affected than some of the other coals. A partial explanation for this may lie in the inorganic makeup of the coal. The Big Brown lignite was much lower in sodium than the other three coals tested and had a lower percentage of its natural iron present as pyrite (Table 2-6); both sodium and pyrite have been demonstrated to be catalytic.

TABLE 2-4

EFFECTS OF H_2S AND S AT 420°C WITH AO4 and HA061 SOLVENTS[a]

Run No.	N89	N92	N79	N94	N65	N93	N55
Solvent:	AO4[b]	AO4	HAO61[c]	HAO61	HAO61	HAO61	HAO61
Additive:	None	H_2S	None	H_2S	H_2S	H_2S	S
Gas	H_2+CO	H_2+CO	H_2+CO	H_2+CO	H_2	CO	H_2+CO
Net Yields wt % maf coal:							
C4 + distillate	4	34	11	24	29	22	37
SRL	40	42	44	50	49	48	47
Gas & H_2O	25	10	35	20	11	26	10
Conversion	69	86	90	94	89	96	94
H/C ratio of product	0.93	1.16	1.06	1.29	1.07	1.05	1.29

[a] All tests were made using the one-gallon hot-charge autoclave using Big Brown lignite with its normal moisture content. Solvent-to-maf-coal ratio was 2:1.

[b] Raw anthracene oil

[c] Catalytically hydrotreated anthracene oil

TABLE 2-5

COMPARISON OF RESULTS OF ADDING H_2S TO TWO LIGNITES[a]

Coal:	BB1[b]	BB1	ZAP1[c]	ZAP1
Additive:	None	H_2S	None	H_2S
Yields, wt % maf coal:				
Distillate	11.0	23.7	23.8	18.2
SRL	44.2	50.5	41.0	39.8
Gas & H_2O	34.6	19.8	27.2	35.9
Conversion	89.7	94.0	92.0	93.8
H/C ratio of product	1.06	1.14	0.92	1.06

[a] All tests were made using the 1-gal hot-charge autoclave at 420°C. Hydrogenated distilled anthracene oil (HAO61) and a 50-50 mixture of H_2 and CO were used throughout.

[b] Texas lignite from the Big Brown mine.

[c] North Dakota lignite from the Indian Head mine.

Following the UND autoclave studies, four relatively cheap and disposable additives were tested in a series of once-through CPU tests with a North Dakota lignite (Beulah-3). These were: 1) an ore rich in FeS_2; 2) an ore rich in Fe_3O_4; 3) elemental sulfur; and 4) H_2S. The generalized results of these once-through tests with regard to coal conversion and product slurry H/C ratio are shown in Figure 2-1. The results shown were averaged to simplify the comparison.

The results of these tests indicated that liquid yields, reducing gas consumption, and product quality are all influenced to varying degrees depending on the coal moisture and the reducing gas used. In general, for systems using syngas, adding FeS_2 improved the yields of SRL and distillate while similarly increasing the H/C ratio of the dry product slurry. Reducing gas consumption was higher with FeS_2 than for the "no additive" case; this resulted in improved product quality, increased H_2S yields, and greater coal conversion. Adding elemental sulfur improved overall conversion compared to the "no additive" case but not to the level achieved with FeS_2 (Figure 2-1). Magnetite also improved liquid yields and overall conversion but to a level much less than when pyrite or H_2S was used. Magnetite enhanced the H/C ratio of the product slurry, raising it to near the same level achieved with FeS_2.

Hydrogen sulfide was found in once-through tests to result in greater improvements to conversion than any of the solid additives tested (Figure 2-1). Once-through CPU studies evaluating the effects of added H_2S with

TABLE 2-6

COAL ANALYSIS

Mine:	South Beulah	Indian Head	Big Brown	Absaloka
Rank:	Lignite	Lignite	Lignite	Subbituminous
State:	ND	ND	Texas	Montana
Abbreviated ID:	B3	ZAP1	BB1	ABS1
Proximate Analysis:				
As Received:				
Moisture	28.84	36.62	27.55	21.07
Volatile matter	28.99	26.07	32.10	26.48
Fixed carbon	30.76	30.50	30.72	35.16
Ash	11.70	6.81	9.63	17.29
Heating Value, Btu/lb	6731	6807	8016	7772
Ultimate Analysis:				
Moisture-free:				
Ash	16.44	10.75	13.29	21.91
Moisture- & ash-free:				
Carbon	69.49	70.41	73.15	72.40
Hydrogen	4.43	5.45	5.22	5.08
Nitrogen	0.99	1.40	1.40	1.15
Oxygen	22.26	21.70	18.93	18.29
Sulfur	2.81	1.04	1.30	3.08
Heating value, Btu/lb	12021	12033	12760	12609
H/C ratio	0.76	0.93	0.86	0.84
Ash Analysis:[a]				
(wt % of ash):				
SiO_2	27.62	26.25	40.60	45.88
Al_2O_3	13.96	10.73	14.40	21.96
Fe_2O_3	14.17	14.03	7.80	11.28
TiO_2	0.61	0.53	1.20	0.78
P_2O_5	0.21	0.42	0.60	0.10
CaO	14.48	15.95	13.20	7.55
MgO	3.90	4.88	3.70	1.67
Na_2O	5.54	7.97	0.50	2.94
K_2O	0.41	0.85	0.70	0.88
SO_3	19.09	18.39	16.80	6.96
Coal Inorganic Content				
(wt % of mf coal):				
Fe	1.69	1.06	0.73	1.73
Ca + Mg	2.08	1.54	1.55	1.40
Na + K	0.73	0.71	0.13	0.64
FeS_2[b]	1.18	1.05	0.30	3.02
Pct of total Fe as FeS_2	33	46	19	81

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[a] Determined by x-ray fluorescence analysis of the ash.

[b] All analyzed pyrite sulfur assumed to be FeS_2.

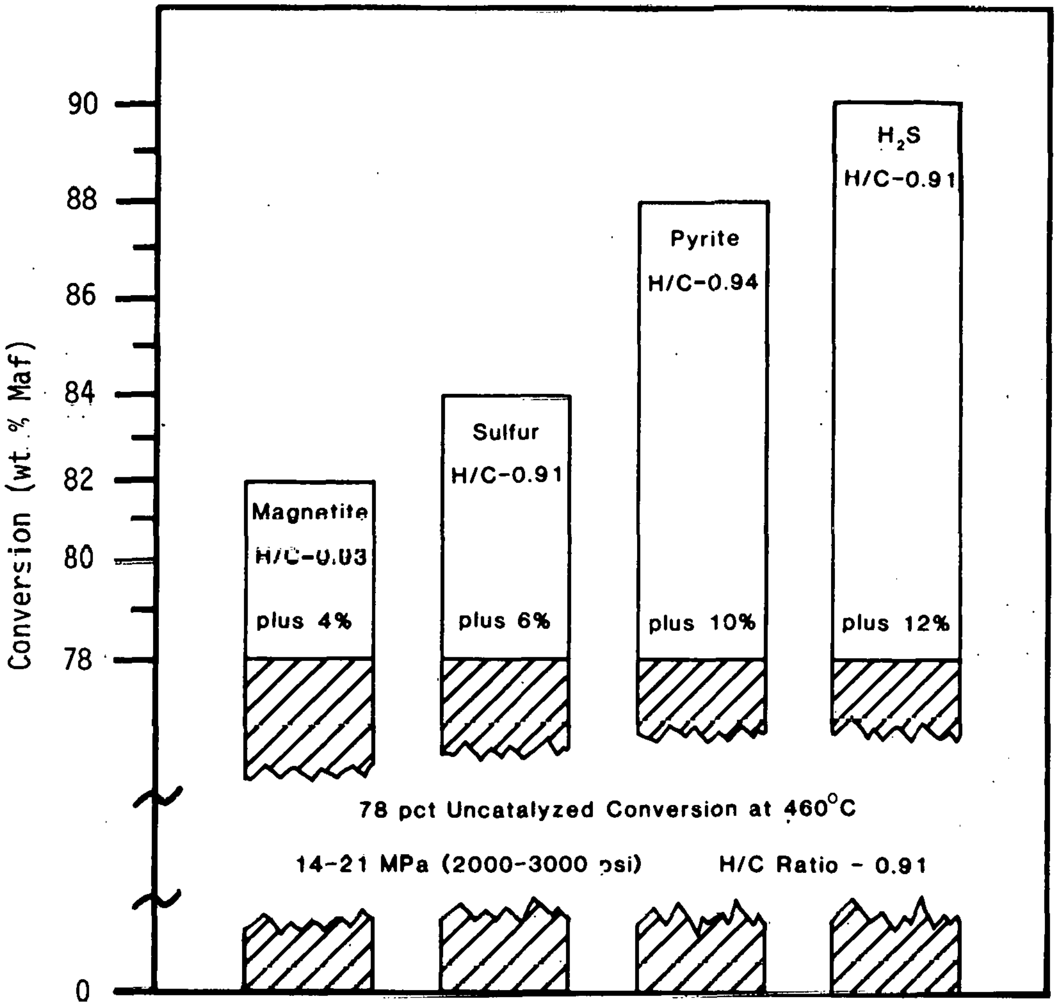


FIGURE 2-1. Averaged effects of added promoter on conversion of Beulah, North Dakota lignite. Reactions were carried out in the 5 lb coal/hr GFETC CPU (tubular reactor) on as-received and slurry-dried lignite using either H_2 gas or syngas. Benefits were more pronounced with syngas and water than with hydrogen.

temperature indicated liquefaction temperatures may be reduced by at least 20°C with no penalty in distillate or SRL yields. Reduced liquefaction temperature has the benefits of lowering hydrogen demand and greatly decreasing hydrocarbon gas formation.

In making the once-through CPU liquefaction tests, it was noted that the benefits of the different additives were more pronounced with syngas and water than with hydrogen or with syngas and dried coal.

In summary, the results discussed in this section suggest the following:

1. The effects of added FeS_2, Fe_3O_4, S, and H_2S as disposable catalysts on liquefaction of low-rank coal were found to depend on the coal, solvent, coal moisture, and reducing gas employed. These additives were found to work best with full moisture lignite processed using a mixture of H_2 + CO.

2. Adding iron-containing materials containing iron improved the quality of the products as evidenced by increased H/C ratios.

3. Added H_2S catalyzes liquefaction reactions to the extent that good yields can be obtained at temperatures significantly lower than the non-catalyzed optimum. This results in reduced hydrogen consumption due to reduced production of hydrocarbon gases.

4. The importance of some additives may not be in increased distillate yields but rather in improved product quality and lowered product viscosity with a resultant enhancement in process operability.

2.2.3 UND Hot-Charge Autoclave Tests

Four runs, L003 through L006, using isotope-labeled reactants, Big Brown lignite, equilibrium recycle solvent, and syngas were completed in the hot-charge autoclave facility during the quarter. The objective of the series was to provide liquefaction reaction products for use in developing analytical methods specific for tracking deuterium and ^{13}Carbon. Run L003 was made as the control using no additives; 1,2,3,4-tetrahydrophenanthrene was added in Run L004; 1,2,3,4-tetrahydrophenanthrene -1, 4-$^{13}C_2$, 1,1-$^2H_2$ was added in Run L005; and 1,2,3,4-tetrahydrophenanthrene together with deuterium gas was added in Run L006. The solvent used in each of the runs was the vacuum distillate from CPU Run 66, which was a continuous bottoms recycle run at 460°C and 2600 psig using syngas and Big Brown, Texas, lignite (BB1). A summary of autoclave run conditions together with net product yields is given in Table 2-7.

Results from the autoclave tests showed good reproducibility between runs, although the indicated material balance closures were lower than normally seen, averaging 91 to 94 pct. The low closures were due mainly to unmeasured product gas sampling which was done immediately after quenching the reaction mixture to provide sufficiently large samples for development of GC techniques for idenfication of components containing either deuterium or ^{13}Carbon. Material balance calculations were normalized accordingly.

Although evaluating the effects of the solvent was not an objective of these tests, it is apparent that the equilibrium vacuum distillate from CPU Run 66 was not a "good" solvent. In autoclave tests with this solvent, lignite conversion was low at approximately 70 wt pct of the maf coal fed, and recovery of process solvent (defined as the fraction boiling between 100 and 230°C at 5 torr) was only 90 pct. Gas production was also relatively high, averaging about 15 pct of the maf coal.

Using the reaction products from Runs L003 through L006, methods will be developed at GFETC that will allow investigation of the roles of the solvent

TABLE 2-7

SUMMARY OF HOT-CHARGE AUTOCLAVE TESTS USING ISOTOPE-LABELLED ADDITIVES OR REACTANTS

Run No.:	L003	L004	L005	L006
Coal:	Big Brown	Big Brown	Big Brown	Big Brown
Solvent:	66PBD	66PBD	66PBD	66PBD
*Additive:	None	THP	THP-D2 W CO	THP W D2
Run Time (min.)	20	20	20	20
Avg. Temp. (°C)	447	447	450	450
Max. Press. (psig)	3700	3650	3700	3700
% H_2 Feed Gas	44.4	50.0	44.6	51.2
Moisture (gms)	28	30	30	30
Net Yields (wt % maf coal charged):				
CO	-21.4	-20.0	-17.1	-16.8
H_2	0.4	- 0.6	- 0.1	- 1.5
CO_2	29.5	20.9	25.3	24.9
C_1-C_3	5.8	5.3	4.7	6.9
H_2S, NH_3	0.8	0.5	0.3	0.4
H_2O	1.8	4.1	4.3	2.3
Gas + H_2O	16.9	10.3	17.5	16.2
Lt. Oil	24.7	28.6	20.0	28.9
Mid. Oil	-20.7	-16.6	-17.8	-23.0
Hvy. Oil	0.0	0.0	0.0	0.0
C_4 + Dist.	4.0	12.1	2.2	5.9
Soluble Residuum (SRL)	51.5	47.6	47.7	48.4
IOM	27.6	30.0	32.7	29.4
Solvent Rec.	89.7	91.7	91.1	88.5
H_2 Equiv. Consump.	1.1	2.0	1.3	2.7
IOM/gram Ash	7.3	7.3	7.3	7.3
Conversion	72.4	70.0	67.3	70.6
Mat. Bal. Closure	92.8	92.8	90.8	94.5

* THP = tetrahydrophenanthrene
THP-D2 = isotope-labeled tetrahydrophenanthrene
W = with
D2 = deuterium

and of the gas in the liquefaction reaction. Liquid products will be analyzed using deuterium and ^{13}C NMR and GC-MS techniques will be developed for product gas analysis.

2.2.4 The Effect of Added H_2S on the Composition of CPU Recycle Slurry Vacuum Distillates

A study was designed to compare the composition of CPU recycle slurry vacuum distillates from the processing of Beulah lignite (B3) with and without added hydrogen sulfide. The concentrations of hydrocarbons and ethers were determined by capillary gas chromatography and 200 MHz proton NMR spectroscopy after the distillates were fractionated by silica gel chromatography. A description of the separation technique can be found in an article by S.A. Farnum and B.W. Farnum published in Analytical Chemistry, 1982, 52, 979. The gas chromatography was carried out using a DB5 narrow bore 60 meter fused silica capillary column with a flame ionization detector (FID). The gas chromatograph was also fitted with a post column splitter which divided the column effluent between the FID and a flame photometric detector (FPD) selective for sulfur. Samples were screened for organic sulfur compounds using the FPD. Identification of compounds was carried out by comparison with known standards and by capillary gas chromatography/mass spectrometry. A table comparing analyses from CPU Runs 65 and 79, both made with hydrogen and without H_2S addition, with analyses from CPU Run 72 made using syngas with added H_2S is shown in Table 2-8. These analyses show that H_2S when added to syngas will maintain concentrations of hydrogen donors such as the tetralins, hydrophenanthrenes, and hydropyrenes as high or higher than similar tests at higher partial pressure of hydrogen. As reported last quarter, the solvent characterization work showed that there was an increase in the H-donor concentration corresponding with an increase in hydrogen partial pressure and that this result was found true whether the reducing gas used in the liquefaction tests was hydrogen or syngas. The results with added H_2S indicate that an advantage is gained by the addition of H_2S in that lower hydrogen partial pressures may be utilized while the concentration of H-donors and the quality of the recycle solvent is maintained.

The solvent characterization studies for sulfur and sulfur compounds indicated that the dibenzothiophenes were the only sulfur-containing organic compounds present in measurable amount in the recycle slurry vacuum distillates. There were also a few very small unidentified peaks in the FPD trace that gave no measurable FID response. This result was true whether H_2S was used or not. The concentration of the main sulfur-containing organic compound, dibenzothiophene, was essentially at the same level for the vacuum distillates for the two runs, with and without added H_2S and was about 0.3 pct. The presence of dibenzothiophene and two C_1-dibenzothiophene isomers was confirmed by capillary GC-MS analysis in both distillates. Thus it was determined that addition of H_2S to the liquefaction of Beulah lignite did not incorporate sulfur into the vacuum distillate which amounts to 85 or 90 pct of the total distillate product.

A rapid survey of the light oils obtained from CPU Runs 72 and 79 showed that the light distillate from Run 72 to which H_2S was added contained a much larger variety of organic sulfur compounds and also contained greater quantities of elemental sulfur. Thus, while there is no evidence of sulfur

TABLE 2-8

ANALYSIS OF CPU RECYCLE SLURRY VACUUM DISTILLATES BY SILICA GEL CHROMATOGRAPHY, CAPILLARY GAS CHROMATOGRAPHY, 200 MHz ^{1}H NMR SPECTROMETRY AND GAS CHROMATOGRAPHY/MASS SPECTROMETRY

(Wt % of Recycle Distillate Calculated From FID Area Percent)

Run Conditions:			
CPU Run No.	65	79	72
Coal	B3	B3	B3
Processing Gas	H_2	H_2	H_2/CO
Temperature, °C	461	457	454
Pressure, psig	2733	2652	2737
P_{H_2}, psig	2582	1986	1199
H_2S Addition	No	No	Yes

Components	Wt %		
indan	0.006	0.005	0.11
5-methylindan	0.02	0.05	0.23
tetralin	0.85	0.17	0.10
1-methyltetralin	0.02	0.03	0.02
2-methyltetralin	0.03	0.09	0.22
6-methyltetralin	0.65	0.10	0.64
2,6- and 2,7-dimethyltetralin	0.03	0.03	0.08
2-ethyltetralin	Not Determined	0.02	0.02
5-ethyltetralin	0.003	0.002	0.02
6-ethyltetralin	0.03	0.07	0.16
naphthalene	1.6	1.5	3.6
1-methylnaphthalene	0.14	0.38	0.47
2-methylnaphthalene	3.4	2.1	3.0
1,3-dimethylnaphthalene	0.004	0.23	0.38
2,6-dimethylnaphthalene	0.53	0.60	0.61
1- and 2-ethylnaphthalene	0.60	1.3	1.5
acenaphthene	1.1	0.87	1.1
phenanthrene	5.2	7.5	5.3
1-methylphenanthrene	0.06	0.24	0.01
2-methylphenanthrene	0.34	0.58	0.65
3-methylphenanthrene	0.31	0.49	0.46
4-methylphenanthrene	0.20	0.36	0.12
9,10-dihydrophenanthrene	0.41	0.25	0.40
1,2,3,4-tetrahydrophenanthrene	0.98	0.09	0.28
octahydrophenanthrene	Not Determined	0	0.06
pyrene	1.2	1.2	0.39
2-methylpyrene	0.40	0.06	0.16
4,5-dehydropyrene	0.12	0.02	0.09
4,5,9,10-tetrahydropyrene	Not Determined	0.20	0.34
C_1-dihydropyrene	Not Determined	0.15	0.43
fluorene	2.3	2.4	2.0
1-methylfluorene	0.51	0.53	0.69

TABLE 2-8--Continued

Run Conditions:			
CPU Run No.	65	79	72
Coal	B3	B3	B3
Processing Gas	H_2	H_2	H_2/CO
Temperature, °C	461	457	454
Pressure, psi	2733	2652	2737
P_{H_2}, psi	2582	1986	1199
H_2S Addition	No	No	Yes
Components:	Wt %		
2-methylfluorene	0.39	0.22	0.21
4-methylfluorene	0.16	0.09	0.07
biphenyl	0.48	0.62	0.73
2-methylbiphenyl	0.40	0.38	0.19
3-methylbiphenyl	Not Determined	0.33	0.49
4-methylbiphenyl	1.0	0.13	0.13
dibenzofuran	1.3	1.7	1.5
fluoranthene	0.28	0.30	1.3
phenyl ether	0.49	1.3	2.1
dibenzothiophene	1.2	0.31	0.28
C_1-dibenzothiophene	Not Determined	0.008	0.01
C_1-dibenzothiophene	Not Determined	0.01	0.02

incorporation into the vacuum distillate, additional sulfur-containing organics as well as elemental sulfur are introduced into the lightest oil fraction. Since this fraction comprises only about 10-15 pct of the total distillate product, incorporation of minor amounts of sulfur detracts little from the positive effects of H_2S addition, which include notably enhanced levels of H-donors in the vacuum distillates.

2.2.5 The Effects of H_2S Addition on the Toxicity of Liquefaction Products

Many heterocyclic sulfur compounds have been reported to be carcinogens. Since the reported activities are high, very small amounts of sulfur compounds may be harmful. To determine if added H_2S significantly enhanced the toxicity of the liquefaction products, the light oils and recycle slurry vacuum distillates from runs made with and without added H_2S were fractionated by solvent extraction into phenolic, basic and hydrocarbon fractions. Bacterial mutagenesis assays (Ames Salmonella strain TA98 with metabolic activation) were carried out on each fraction under the direction of Dr. C.A. Reilly, Jr. at the Argonne National Laboratory. The results, Table 2-9, showed no detectable response to the hydrocarbon and phenolic fractions from either Run 72 (with H_2S) or Run 79 (without H_2S). The activity of the basic fraction from each run was within the expected response region usually associated with coal-derived liquids. These results further support the belief that either sulfur incorporation is negligible when H_2S is added during liquefaction or that if it occurs it must be present in only the lightest species with little mutagenic potential.

TABLE 2-9

MUTAGENIC ASSAY (AMES SALMONELLA STRAIN TA98 WITH METABOLIC ACTIVIATION) OF EXTRACTED DISTILLABLE CPU PRODUCTS

*CPU Run No./Sample	Rev/µg	Fraction % of whole
72PB20P	<1	21.6
72PB20B	93	7.1
72PB20HC	<1	65.1
72LO25P	<1	27.9
72LO25B	15	3.5
72LO25HC	<1	60.3
79PB13P	<1	25.3
79PB13B	47	5.6
79PB13HC	<1	62.5
79L013P	<1	17.1
79L013B	48	2.0
79LO13HC	<1	57.2

* P = Phenolic fraction
B = Basic fraction
HC = Hydrocarbon fraction
PB = Recycle slurry
LO = Light oil
Run 72 made with added H_2S
Run 79 made without added H_2S

2.2.6 Results of Lineout Studies using Hydrogenated Startup Solvent

CPU Run 85 was made in the bottoms recycle mode using hydrogenated anthracene oil (HA04) as the startup solvent. The objective of the run was to generate pass-by-pass samples so that the effects of startup solvent could be investigated. The changes in the hydrocarbon and ether composition of the recycle slurry vacuum distillate for CPU Run 85 were followed using quantitative ^{13}C NMR spectroscopy after first fractionating by solvent extraction. Changes in the phenolic composition were followed using capillary gas chromatographic analysis of the extracted phenols. The results of the study are shown in Table 2-10.

TABLE 2-10

VARIATION IN CONCENTRATIONS OF SELECTED COMPONENTS OF THE RECYCLE SLURRY VACUUM DISTILLATE FROM CPU RUN 85 STARTED UP WITH HYDROGENATED ANTHRACENE OIL HA04, RUN CONDITIONS INCLUDED 440°C, 2800 PSIG, CO + H_2 AND BB2 LIGNITE

Reactor Pass No.	0 (Solvent HA04)	1	4	6	9	11	13
Components:				Wt. %			
dibenzofuran	3.6	3.4	3.3	3.2	2.1	2.4	2.2
phenyl ether	ND*	ND	ND	ND	ND	ND	ND
acenaphthene	4.0	4.2	4.1	3.4	2.1	2.2	1.8
fluorene	5.2	4.6	4.1	4.1	3.0	2.7	2.5
fluoranthene	5.0	5.6	4.8	4.6	3.8	2.8	2.2
tetralin	ND	2.16	ND	0.98	0.51	0.41	0.84
phenanthrene	12.8	12.9	13.8	13.2	10.7	10.5	9.4
C_1alkanes (as C_{20})	1.04	1.9	1.6	2.8	3.2	3.5	3.2
tetrahydroacenaphthene	1.9	1.2	ND	ND	--	0.36	0.37
dihydrophenanthrene	2.4	1.6	1.0	1.3	--	0.84	0.86
tetrahydrofluoranthene	1.2	ND	ND	ND	ND	ND	ND
tetrahydrophenanthrene	1.7	0.4	0.5	2.9	ND	ND	ND
octahydrophenanthrene	0.4	ND	ND	ND	ND	ND	ND
dihydropyrene	0.6	ND	ND	ND	ND	ND	ND
phenol	0**	0.10	0.44	0.57	1.03	--	1.80
o-cresol	0	0.06	0.24	0.31	0.49	--	0.84
m-,p-cresol	0	0.01	0.02	0.04	1.39	--	2.62
2,6-dimethylphenol	0	0.03	0.08	0.10	0.06	--	0.09
2-ethylphenol	0	0.03	0.08	0.10	0.14	--	0.21
2,4-dimethylphenol	0	0.04	0.13	0.16	0.25	--	0.45
2,5-dimethylphenol	0	0.02	0.08	0.11	0.19	--	0.33
4-ethylphenol	0	0.04	0.16	0.19	0.31	--	0.51
3-ethylphenol, 3.5-dimethylphenol	0	0.03	0.08	0.14	0.31	--	0.42
2,3-dimethylphenol	0	0.01	0.06	0.08	0.12	--	0.11
3,4-dimethylphenol	0	0.01	0.06	0.07	0.11	--	0.26
2,4,6-trimethylphenol	0	0.002	0.01	--	0.02	--	0.02
2,3,6-trimethylphenol	0	0.002	0.01	0.01	0.02	--	0.03
2-n-propylphenol	0	0.01	0.02	0.04	0.05	--	0.07
3-isopropylphenol	0	0.01	0.04	0.05	0.08	--	0.11
4-ethyl-2-methylphenol	0	0.01	0.05	0.07	0.11	--	0.16
5-ethyl-2-methylphenol	0	0.01	0.05	0.05	0.08	--	0.12
4-n-propylphenol	0	0.01	0.06	0.09	0.13	--	0.19
3-ethyl-5-methylphenol	0	0.04	0.11	0.17	0.23	--	0.61
2,4,6-trimethylphenol	0	0.003	0.01	0.02	0.02	--	0.04
4-indanol	0	0.03	0.09	0.13	0.20	--	0.34
5-indanol	0	0.05	0.14	0.20	0.30	--	0.61

---

*ND = Not Detected

**No phenols are present in the solvent, HAO4

The H-donors that are so abundant in the starting solvent, HA04, were rapidly depleted during the first several passes. Low level H-donors, such as octahydrophenanthrene and dihydropyrene, are essentially absent after the first pass.

The buildup of selected phenols is illustrated in Figure 2-2. No leveling in concentration is apparent by pass 13, indicating that lineout conditions have not yet been achieved. Also, since there were no phenols initially present in the startup solvent, all of the phenols produced are probably derived directly from reactions of the lignite.

The trends shown by this study suggest that start-up with a hydrogenated solvent followed by bottoms recycle will not appreciably change the yield structure or the lineout solvent composition as compared to startup with a raw anthracene oil because the H-donors were lost early during recycle and not regenerated at the conditions employed (440°C - 2800 psig syngas).

2.2.7 Analyses of Liquefaction Reactor Solids

Fifteen samples of reactor coke and reactor blowdown solids were analyzed using X-ray diffraction (XRD) and X-ray fluorescent (XRF) methods. The samples were selected so that the results might be correlated with the partial pressure of hydrogen, feed coal, and reducing gas (H_2, H_2+CO, H_2+CO + H_2S). The results of the study are inconclusive, but the following observations were made.

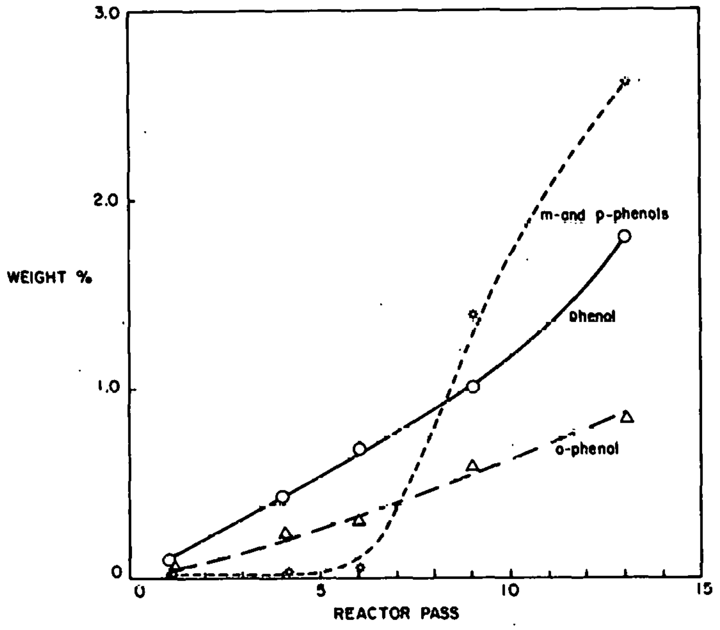


FIGURE 2-2. Weight percentage phenols in recycle slurry vacuum distillate (Run 85) versus reactor pass number.

1. Quartz (SiO_2) was a major constituent in all of the reactor solids samples analyzed.

2. Pyrrhotite ($Fe_{1-x}S$) was present in either minor or trace quantities in every sample.

3. Calcium carbonate ($CaCO_3$) was found in the reactor solids from runs where low-rank coals were used. These coals included North Dakota (Beulah) and Texas (Big Brown) lignites and Wyoming (Wyodak) subbituminous coal. Calcium carbonate was not present in the reactor solids from the runs where Ohio (Powhatan) bituminous coal was used.

4. Carbonized material was found predominately in reactor coke samples; it was generally not found in the free-flowing reactor blowdown solids.

5. Trace quantities of clay material were found usually in reactor blowdown samples.

6. XRD analysis of the reactor solids suggest H_2S may inhibit oolite formation. Although the results are qualitative, the analyses show SiO_2 and $CaCO_3$ to be major phases and $Fe_{1-x}S$ to be minor phases present when no H_2S was added during liquefaction. When H_2S was used, SiO_2 was the major phase while $CaCO_3$ and $Fe_{1-x}S$ were the minor phases. This trend was true for both the free-flowing reactor solids and the wall scale.

2.2.8 The Use of $1,1^1$-Binaphthyl to Study Hydrogen-Donor Solvent Reactions

The reactions of $1,1^1$-binaphthyl with several H-donors at 470°C were examined to determine if $1,1^1$-binaphthyl could be used as a model compound to study hydrogen transfer reactions. The H-donors included tetralin; dihydronaphthalene; 9,10-dihydrophenanthrene; 1,2,3,4-tetrahydrophenanthrene; octahydrophenanthrene; 9,10-dihydroanthracene; octahydroanthracene; di and tetrahydropyrene mixture; and 1,2,3,6,7,8-hexahydropyrene.

Binaphthyl was found to accept hydrogen from an active donor leading to the coupled product perylene. Differing amounts of perylene were observed when binaphthyl reacted with different donors, suggesting this model compound can differentiate donor abilities. Hydrogen shuttling by some donors was also indicated, suggesting $1,1^1$-binaphthyl could be used to study this phenomenon.

The investigative study just outlined is being conducted for GFETC by Professor Eugene Kline and graduate student Mark E. Harrison at the Tennessee Technological University. Additional reports will be included as they become available.

2.2.9 Synthesis of Model Compounds for Standards

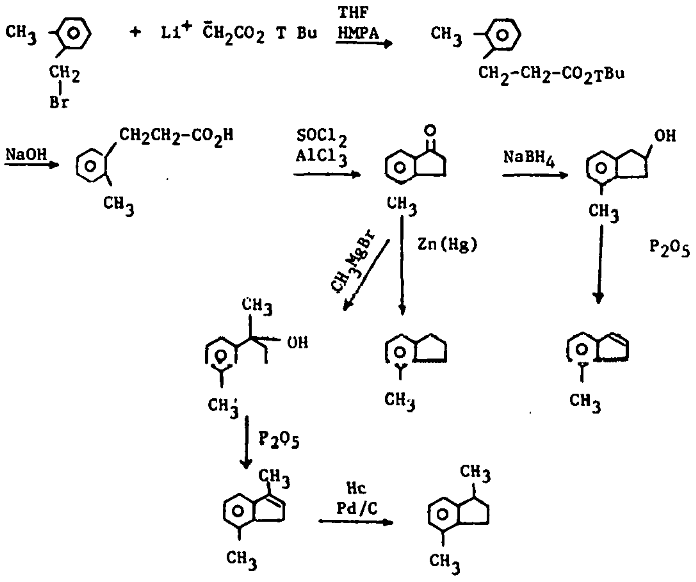
In the spectroscopic analyses of liquefaction products, numerous standards are required for identification of an unknown. Because many of these compounds are not available commercially, synthesis in the laboratory is required.

New model compounds synthesized during the subject reporting period were 6-methyl-2-naphthol, 2-methyl-6-hydroxytetralin, 5-methyl-2-naphthol, 1-methyl-5-hydroxytetralin, 3-methyl-2a,3,4,5-tetrahydroacenaphthene, and 4-methylindan.

The naphthols and hydroxytetralins were prepared from tetralones via Grignard reactions. For example, 5-methyl-2-naphthol was prepared by converting 6-methoxy-1-tetralone to 4-methyl-7-methoxy-1,2-dihydronaphthalene via the Grignard reaction, dehydrating the product with P_2O_5 and then dehydrogenating the dihydronaphthalene by heating with 5-pct Pd on carbon. The methoxyl group was removed with 30-pct HBR in acetic acid to yield 5-methyl-2-napthol.

3-Methyl-2a,3,4,5-tetrahydroacenaphthene was prepared from 2-methyltetralone. The tetralone was reacted with lithium t-butylacetate to give 2-methyl-1-hydroxy-1-t-butyl acetyltetralin. This intermediate was hydrogenated and saponified to produce α-1-(2-methyl-1,2,3,4-tetrahydronaphthyl)-acetic acid. The acid was cyclized to the ketone with thionyl chloride and aluminum chloride and the ketone reduced with lithium aluminum hydride and aluminum chloride to 3-methyl-2a,3,4,5-tetrahydroacenaphthene.

The 4-methylindan was produced using the reaction sequence shown below. The scheme involves an interesting synthesis of o-tolylpropionic acid which is usually obtained by Perkin condensation of o-tolualdehyde followed by reduction.



2.2.10 Catalyst Analyses

In the CPU liquefaction test program two ores (Rubena pyrite and magnetite) were evaluated as disposable catalysts. To aid in understanding the effects of these two materials on liquefaction, both were analyzed by x-ray diffraction and x-ray fluorescence to determine purity.

X-ray diffraction analyses of the Rubena pyrite showed two forms of FeS_2 to be present; the major form was yellow iron pyrite while the minor constituent was marcasite. The magnetite sample was found to be predominately Fe_3O_4 and was quite pure, with only one or two minor peaks not identified in the XRD spectrum.

X-ray fluorescence (XRF) analyses of the two materials are shown in Table 2-11. The elements are expressed as their oxides on a weight percent basis of the raw sample, because the computer program to analyze the XRF spectrum was designed for the more common coal ash samples. The XRF analyses show there are small quantities of silica and aluminum present in both the Rubena pyrite and magnetite samples and that there are minor amounts of titanium in the magnetite and phosphorus in the pyrite.

TABLE 2-11

X-RAY FLUORESCENCE ANALYSES
OF MAGNETITE AND RUBENA PYRITE ORES

	Weight Percent	
Sample	Rubena Pyrite	Magnetite
Silica, SiO_2	4.6	7.3
Aluminum Oxide, Al_2O_3	2.0	9.7
Ferric Oxide, Fe_2O_3	10.6	77.1
Titanium Oxide, TiO_2	0.1	4.4
Phosh. Pentoxide, P_2O_5	2.5	0.0
Calcium Oxide, CaO	0.4	0.8
Magnesium Oxide, MgO	0.5	0.0
Sodium Oxide, Na_2O	0.8	0.0
Potassium Oxide, K_2O	0.0	0.2
Sulfur Trioxide, SO_3	78.0	0.2

2.2.11 Kinetics of Beulah-3 Lignite Pyrolysis

Uncatalyzed coal liquefaction results from both rapid and slow reactions. Thermal decomposition reactions of low-rank coal are generally thought to be rapid, while the hydrogenation and hydrocracking reactions of solvent are relatively slower. The disparity becomes important because coal decomposition begins occurring in liquefaction at temperatures as low as 360°C, while hydrogenation and hydrocracking do not become important until temperatures exceed 400° or 420°C. To better understand the coal decomposition reactions, coal samples were pyrolyzed to determine product distributions and rates of production of gaseous products. The data reported in this section were obtained under contract with Advanced Fuel Research.

Samples of a North Dakota lignite (Beulah-3) were heated on a wire mesh at 19 different temperatures (350° to 500°C in 10°C increments and at 700°, 800° and 900°C). After rapid heating the gaseous products were observed with time using FTIR. The lignite was originally dried under vacuum to remove extraneous moisture. The data obtained permitted a comparison of the relative production rates for CO_2, H_2O, CH_4, paraffins, and olefins and also permitted an estimate of the activation energies required in each case.

The kinetic data reported by Advanced Fuel Research for the pyrolysis of Beulah-3 lignite are listed in Table 2-12. The natural logarithm of the rate constant was plotted against the inverse of absolute temperature for all species as illustrated in Figures 2-3 through 2-8. The variation of the rate constant with temperature was studied over three temperature ranges:

1) 350° - 500°C
2) 700° - 900°C
3) 350° - 900°C

All plots were linear with the general equation:

$$\mathrm{Ln}\ K = -E/RT + \mathrm{Ln}\ A \qquad [1]$$

Where K is the rate constant in sec^{-1}, -E/R is the slope of the line, T is the absolute temperature in °K, and the LnA term is the y-intercept. Equation [1] may be written as:

$$K = Ae^{-E/RT} \qquad [2]$$

The slope and y-intercept were determined for each plot using linear regression. The results are presented in Table 2-13 and are compared to the rate equations reported by Advanced Fuel Research for the temperature range 350° - 900°C.

The differences in the rate equations exhibited when considering the temperature ranges separately suggest that there may be two reactions responsible for coal decomposition, one dominant at the lower temperatures with the other increasing in importance as temperature increases. To see how these reactions may differ, the activation energy for each temperature range, as well as for the total range, was calculated using Arrhenius equation:

$$\mathrm{Ln}K = -Ea/RT + \mathrm{Ln}A \qquad [3]$$

TABLE 2-12

PYROLYSIS RATE DATA FOR BEULAH-3 SAMPLES (RATE CONSTANT K IN SEC^{-1})

Temp.		CH_4		Paraffins		Olefins		CO		CO_2		H_2O	
°C	1000/T	K	ln K	K	ln K	K	ln K	K	ln K	K	ln K	K	ln K
350	1.61							0.0027	-5.91	0.020	-3.91	0.029	-3.54
360	1.58							--		0.018	-4.02	0.036	-3.32
370	1.56			0.0067	-7.31			--		0.016	-4.14	0.036	-3.32
380	1.53	0.00157	-6.46	0.0012	-6.73			0.0048	-5.34	0.025	-3.69	0.036	-3.32
390	1.51	0.0022	-6.12	0.0018	-6.32			0.0054	-5.22	0.031	-3.47	0.04	-3.22
400	1.49	0.00294	-5.83	0.0034	-5.68			0.0093	-4.68	0.027	-3.61	0.032	-3.44
410	1.46	0.0052	-5.26	0.0058	-5.15	0.0023	-6.07	0.0069	-4.98	0.045	-3.10	0.048	-3.04
420	1.44	0.0059	-5.13	0.0040	-5.52	0.002	-6.21	0.0045	-5.40	0.042	-3.17	0.029	-3.54
430	1.42	0.00417	-5.48	0.0047	-5.36	--		--		0.100	-2.30	0.1	-2.30
440	1.40	0.0065	-5.04	0.0070	-4.96	0.0022	-6.12	0.0056	-5.18	0.026	-3.65	0.038	-3.27
450	1.38	0.0087	-4.74	0.011	-4.51	0.0049	-5.32	0.014	-4.27	0.058	-2.85	0.1	-2.30
460	1.36	0.00602	-5.11	0.0081	-4.82	0.004	-5.52	0.0083	-4.79	0.070	-2.66	0.077	-2.56
470	1.35	0.0398	-3.22	0.025	-3.69	0.0069	-4.98	0.02	-3.91	0.085	-2.47	0.125	-2.08
480	1.33	0.0184	-4.00	0.016	-4.14	0.0039	-5.55	0.024	-3.73	0.082	-2.50	0.0556	-2.89
490	1.31	0.028	-3.58	0.017	-4.07	0.0077	-4.87	0.016	-4.14	0.075	-2.59	0.0588	-2.83
500	1.29	0.047	-3.06	0.045	-3.10	0.011	-4.51	0.023	-3.77	0.15	-1.90	0.111	-2.20
700	1.03	0.75	-0.29	0.76	-0.27	0.11	-2.21	0.22	-1.51	0.62	-0.48	0.77	-0.26
800	0.93	0.91	-0.094	1.43	0.36	0.48	-0.73	0.56	-0.58	1.08	0.077	1.67	0.51
900	0.85	2.0	0.69	1.67	0.51	1.5	0.41	1.43	0.36	2.70	0.99	2.22	0.80

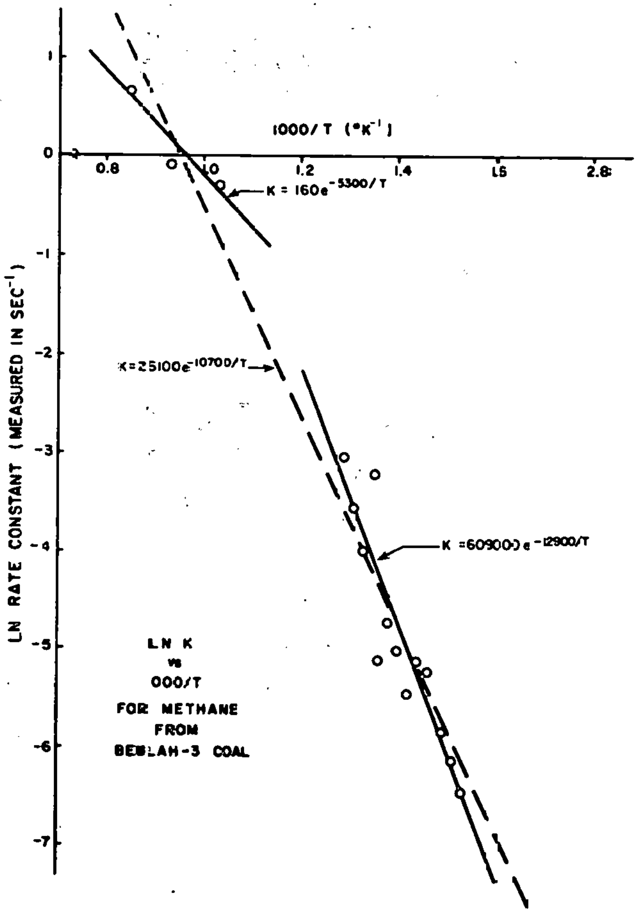


FIGURE 2-3. Natural logarithm of the rate constant versus the inverse of the absolute temperature for methane production during the pyrolysis of Beulah-3 lignite.

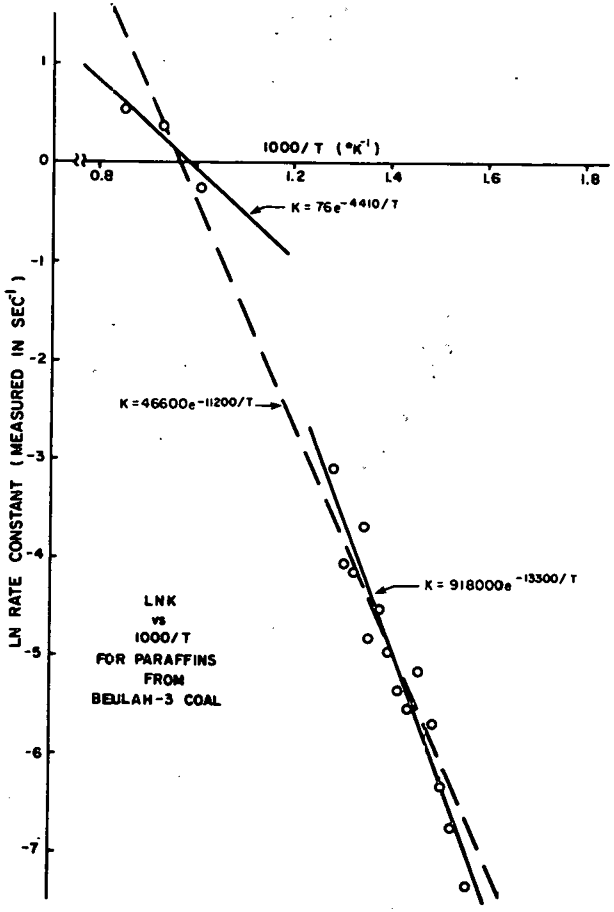


FIGURE 2-4. Natural logarithm of the rate constant versus the inverse of the absolute temperature for paraffin production during the pyrolysis of Beulah-3 lignite.

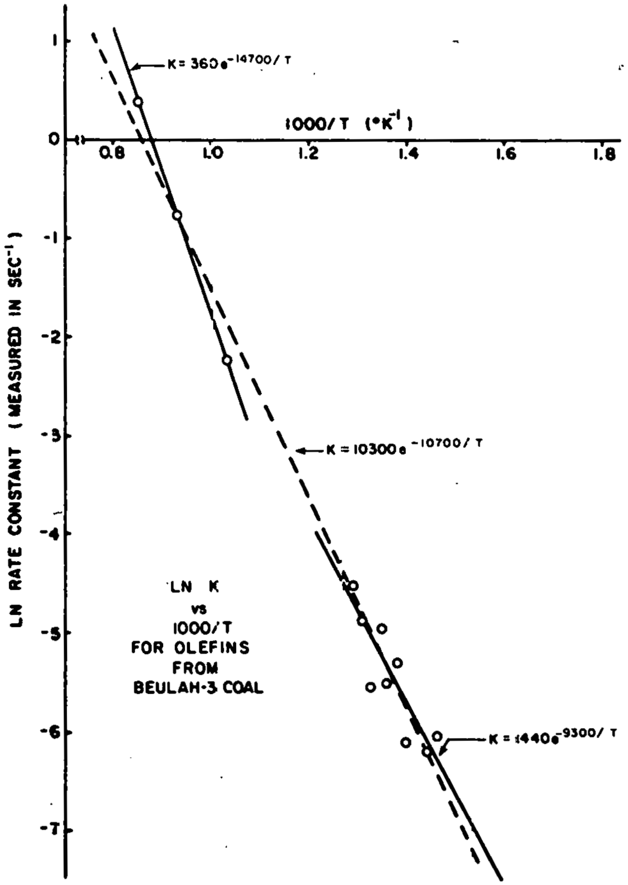


FIGURE 2-5. Natural logarithm of the rate constant versus the inverse of the absolute temperature for olefin production during the pyrolysis of Beulah-3 lignite.

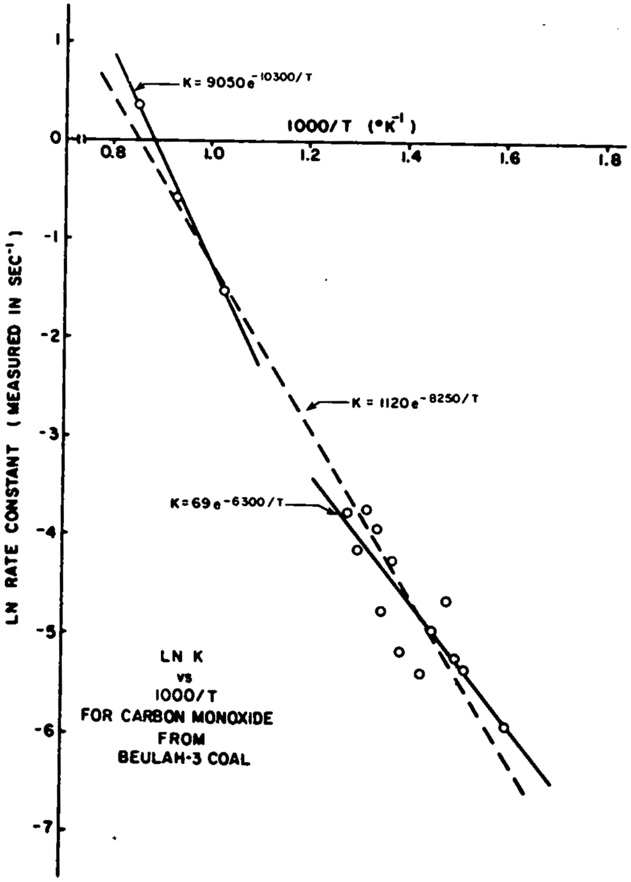


FIGURE 2-6. Natural logarithm of the rate constant versus the inverse of the absolute temperature for carbon monoxide production during the pyrolysis of Beulah-3 lignite.

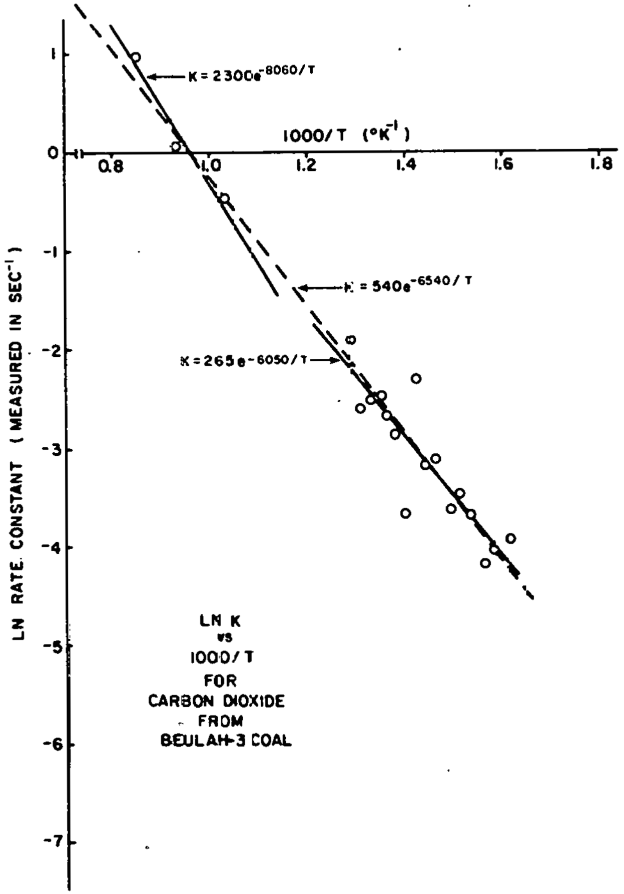


FIGURE 2-7. Natural logarithm of the rate constant versus the inverse of the absolute temperature for carbon dioxide production during the pyrolysis of Beulah-3 lignite.

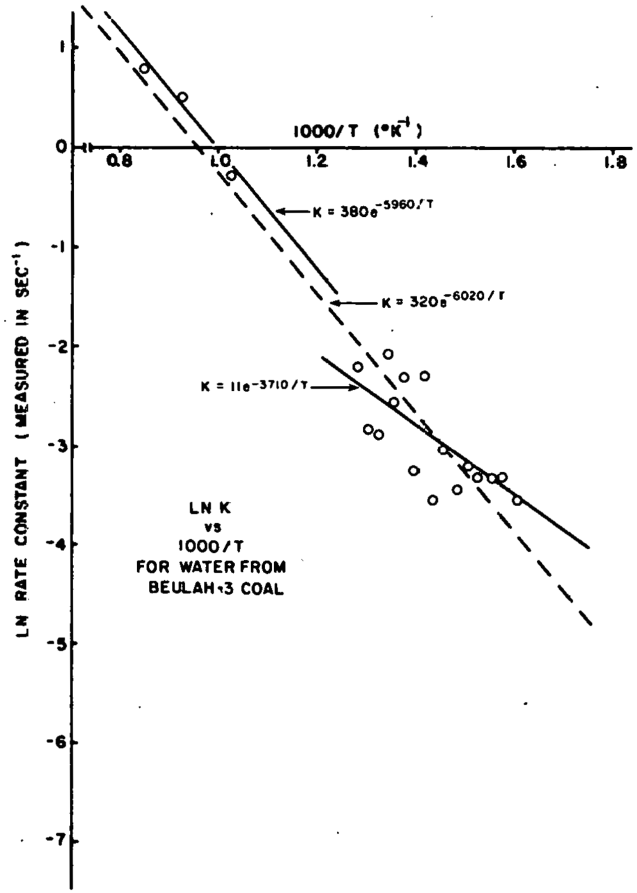


FIGURE 2-8. Natural logarithm of the rate constant versus the inverse of the absolute temperature for water production during the pyrolysis of Beulah-3 lignite.

TABLE 2-13

VARIATION OF RATE CONSTANT WITH TEMPERATURE FOR THE PYROLYSIS OF BEULAH-3 LIGNITE

Species	Rate Equation For 350°-500°C	Rate Equation For 700°-900°C	Rate Equation For 350°-900°C	Rate Equation Reported by Advanced Fuel Research
Methane	$K=609000\ e^{-12900/T}$	$K=160\ e^{-5300/T}$	$K=26100\ e^{-10700/T}$	$K=34000\ e^{-11000/T}$
Paraffins	$K=918000\ e^{-13300/T}$	$K=76\ e^{-4410/T}$	$K=46600\ e^{-11200/T}$	$K=34000\ e^{-11000/T}$
Olefins	$K=1440\ e^{-9300/T}$	$K=360\ e^{-14700/T}$	$K=10300\ e^{-10700/T}$	$K=15000\ e^{-11000/T}$
Carbon Monoxide	$K=69\ e^{-6300/T}$	$K=9050\ e^{-10300/T}$	$K=1120\ e^{-8250/T}$	$K=1950\ e^{-8100/T}$
Carbon Dioxide	$K=265\ e^{-6050/T}$	$K=2300\ e^{-8060/T}$	$K=540\ e^{-6540/T}$	$K=700\ e^{-6700/T}$
Water	$K=11\ e^{-3710/T}$	$K=380\ e^{-5960/T}$	$K=320\ e^{-6020/T}$	$K=700\ e^{-6700/T}$

Where Ea is the activation energy and R is the gas constant. The results are recorded in Table 2-14. It would seem logical that the reaction dominant at higher temperatures would have a higher activation energy. While such a relationship is exhibited for olefins, CO, CO_2 and H_2O, it was not found for methane and the paraffins, although there is scatter in the data and far more points at the lower temperatures.

TABLE 2-14

ACTIVATION ENERGIES IN KCAL/MOLE FOR THE PYROLYSIS OF BEULAH-3 LIGNITE

Species	350°-500°C	700°-900°C	350°-900°C	Advanced Fuel Research
Methane	25.7	10.5	21.3	21.9
Paraffins	26.4	22.2	22.2	21.9
Olefins	18.5	29.1	21.3	21.9
Carbon Monoxide	12.5	20.5	16.4	16.1
Carbon Dioxide	12.0	16.0	13.0	13.3
Water	7.4	11.8	12.0	13.3

An alternate method of interpreting the pyrolysis data obtained by Advanced Fuel Research is to plot a species half-life versus temperature. The half-life is the time required for half of the material to react as calculated from $\ln(0.5) = -kT_{1/2}$. The results of this exercise are shown in Figure 2-9. Two notable features of the graph are: 1) water production was found to be produced at a rate similar to that of CO_2; and 2) the extremely low temperature at which CO_2 and H_2O production was observed.

Earlier pyrolysis data obtained in the batch autoclave (DOE/GFETC/QTR-80/4) and reported for Beulah-3 lignite conflict with the heated screen pyrolysis data reported here. Comparing the two sets of data, the pyrolysis temperatures seem to disagree by 100°C based on CO_2 production from coal. In batch autoclave studies the rate of CO_2 production became significant beginning at 360°C in slow heat-up studies with timed gas sampling. At 360° - 380°C approximately half the CO_2 produced from the Beulah-3 lignite was observed in 5 minutes. In the heated screen pyrolysis, the 5-minute half-life for CO_2 occurred at about 260°C. Two significant differences be-

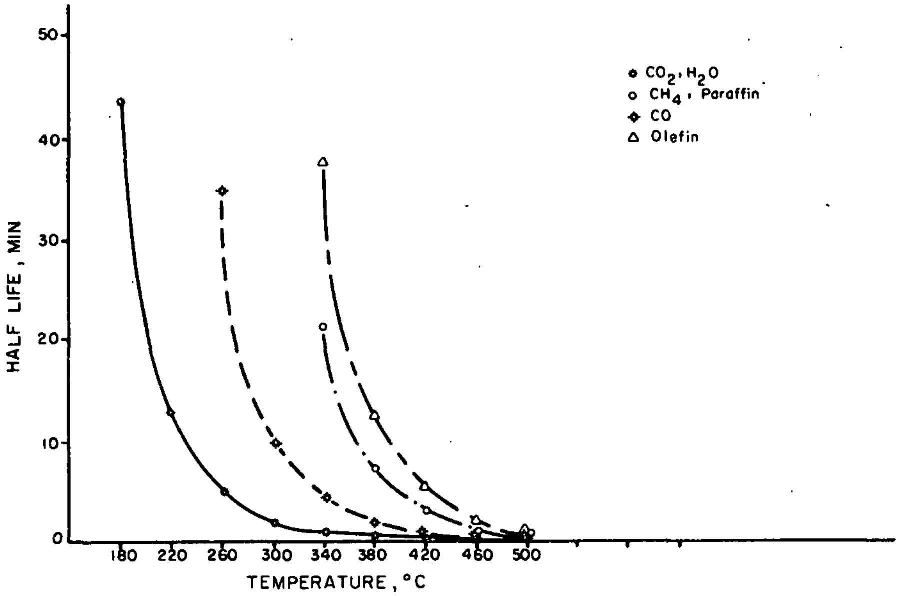


FIGURE 2-9. Thermal degradation of Beulah-3 lignite expressed as half-life in minutes of observed products.

tween the systems may explain the disparity in temperatures. First, temperature measurement for the batch reactor may be more accurate than that for a heated screen; and second, the coal used in the batch studies was much finer than the 40- to 60-mesh lignite used in the heated screen studies (95% minus 200-mesh). Still another disparity was that the total yield of CO_2 from the Beulah-3 lignite observed in the heated screen studies was lower than that obtained in the batch autoclave studies.

The low temperature formation of CO_2 and H_2O, as indicated by the Advanced Fuel Research kinetic data, is consistent with the thermal bond energies and stability of "leaving" groups (Tables 2-15 and 2-16) of possible functional groups present in the original coal. The carboxylic acid radical is an extremely good "leaving" group (ΔH_f of ·COOH is -53.3 kcal/mole at 298°C) and also forms relatively weak bonds, such as in benzyl carboxyl acid (68.1 kcal/mole), which can account for the low temperature formation of CO_2. Water production at low temperatures (even after vacuum drying) could be partially due to residual clay water of hydration. However, water production due to the dehydration of activated aliphatic hydroxyl groups (glycols) or benzylic hydroxyl groups is also possible. Phenolics and aliphatics with only a single hydroxyl group would be thermally stable at low temperatures (bond energies of 110 and 91 kcal/mole respectively). Aliphatic hydroxyl decomposition rates, however, could be greater than indicated by the bond energies since the products are water and olefins:

TABLE 2-15

BOND ENERGIES OF POTENTIAL COAL, SOLVENT OR ADDITIVE COMPOUND TYPES[a]

Compound	ΔH_f@298°k kcal/mole	Compound	ΔH_f@298°K kcal/mole
$CH_3O\text{-}COCH_3$	36.9	$H\text{-}CH_2OH$	94
$PhCH_2\text{-}SCH_3$	53.8	$H\text{-}C_2H_5$	98
$PhS\text{-}CH_3$	60	$Ph\text{-}OCH_3$	98
$PhCO\text{-}COPh$	66.4	$Ph\text{-}CH_3$	100
$PhCH_2\text{-}OOCCH_3$	67	$H\text{-}OCH_3$	103.6
$PhCH_2\text{-}COOH$	68.1	$H\text{-}H$	104
$PhCH_2\text{-}C_2H_5$	69	$CH_3\text{-}H$	104
$PhCH_2\text{-}CH_3$	72	$H\text{-}NH_2$	110
$PhCH_2\text{-}OH$	77	$Ph\text{-}OH$	110.7
$CH_3(CH_2)_m\text{-}CH_3$	81	$Ph\text{-}H$	110.2
$H\text{-}CHO$	87	$CH_2CH_2\text{-}Ph$	113
$H\text{-}COCH_2 = CH_2$	87.1	$Ph\text{-}Ph$	117
$H\text{-}OPh$	88	$H\text{-}OH$	119
$H_3C\text{-}CH_3$	88		
$H\text{-}SCH_3$	≥ 88		
$PhCH_2\text{-}H$	85		
$H\text{-}SH$	90		
$CH_3(CH_2)_m\text{-}OH$	91		

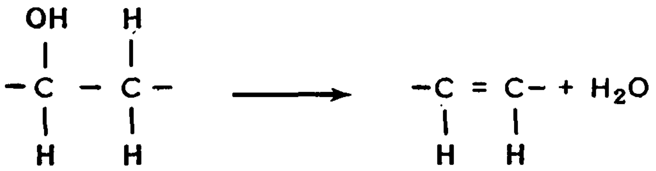
[a] From Handbook of Chemistry and Physics, 56th Ed, pp F 224-227.

TABLE 2-16

FREE RADICAL HEATS OF FORMATION[a]

Radical	ΔH_f @298°C kcal/mole
$\cdot COOH$	-53.3
$CH_3CO_2\cdot$	-49.6
$\cdot COOCH_3$	-40.3
$PhCO_2CH_2\cdot$	-16.7
$\cdot CH_2OH$	- 4.2
$CH_3O\cdot$	3.5
$\cdot CH=O$	7.7
$HO\cdot$	9.2
$PhO\cdot$	13
$Ph\dot{C}=O$	26
$CH_3S\cdot$	30.5
$HS\cdot$	33
$CH_3\cdot$	34
$PhCH_3\cdot$	45.1
$\dot{N}H_2$	47.2
$PhS\cdot$	49.5
$H\cdot$	52.1
$ph\cdot$	77.7

[a] From the Handbook of Chemistry and Physics; 56th Ed.
$D\ (R\text{-}X) = \Delta H_f\ (\dot{R}) + \Delta H_f(\dot{X}) - \Delta H_f\ (RX)$
Reactivity of the radical increases with the heat of formation



$$-\overset{\overset{\text{OH}}{|}}{\underset{\underset{\text{H}}{|}}{\text{C}}}-\overset{\overset{\text{H}}{|}}{\underset{\underset{\text{H}}{|}}{\text{C}}}- \longrightarrow -\underset{\underset{\text{H}}{|}}{\text{C}}=\underset{\underset{\text{H}}{|}}{\text{C}}- + H_2O$$

The olefin appearance at higher temperatures could represent a product of this dehydration reaction. Carbon monoxide production was only 2 pct of the maf coal and could originate from methoxy or aliphatic esters. IR analysis of coal before and after pyrolysis has indicated the disappearance of methoxy groups at lower temperatures. It is unlikely, however, that these were removed from aromatic rings, as the phenyl methoxy bond is very stable (98 kcal/mole). The appearance of paraffins and olefins at higher temperatures is more complex and may involve diffusion out of the coal matrix. Only a small amount of methane was produced from the coal coming from possibly two sources: aliphatics and methoxy groups. Previous batch autoclave pyrolysis data indicate about one weight pct methane is produced rapidly at under 400°C; while at temperatures of 440°C and above, methane is produced more rapidly, presumably from aliphatics in the coal. Another explanation for higher rates of methane production at elevated temperatures is that in batch autoclave pyrolysis studies all products remained in the reactor and therefore could continue to react.

In summary the pyrolysis kinetic data indicate that a two-step sequence of liquefaction could be important for coals containing CO_2 and water-producing functional groups. At lower temperatures (under 400°C) the Beulah-3 lignite thermally decomposes, producing up to 0.34 moles of CO_2 and 0.28 moles of water per 100 grams maf coal. Without hydrogenation during this decomposition process, extensive aromatization and subsequent decrease in conversion can occur. The need for hydrogen donating compounds of greater ability than hydrogen gas becomes apparent. Hydrogen donor solvents, CO + H_2O, H_2S and phenolics can donate hydrogen (based on bond energies) better than hydrogen gas. Thus it may be possible for liquefaction yields to be improved by two-stage reactions using donors such as CO + H_2O or H_2S at low temperatures followed by hydrogen at higher temperatures. High-temperature hydrogen reactions would also serve to desulfurize the liquefaction products.

2.2.12 Errors Introduced by Sulfur During Coal Analyses

One aspect of coal liquefaction research involves experimentally determining yield structures for individual feed coals and making subsequent comparison between coals. Ash content used in material calculations is usually determined by high-temperature ashing at 800°C following ASTM procedures. Due to the simplicity of the analysis, the technique with its inherent errors is still widely accepted and used in calculating product yields. As fundamental studies in the areas of coal liquefaction and gasification progress, kinetic models, mechanisms and detailed yield structures are being developed, and greater accuracy is required than is possible when using simple high-temperature ashing. Of special concern is the fate of some volatile elements, such as sulfur and their ultimate end needs to be considered.

To determine the amount of sulfur retained in the ash and subsequently counted twice, once as elemental sulfur by the LECO sulfur analysis and once as part of the ash, both the total coal and coal ash sulfur contents were determined for a number of liquefaction feed coals. These were calculated to a comparable dry coal basis and are tabulated in Table 2-17. Two techniques were used to determine the ash sulfur content: LECO sulfur analysis and x-ray fluorescence (XRF). The XRF analysis was duplicated and sulfur content was calculated from the as-measured SO_3 content. In general the two techniques resulted in sulfur ash values with a deviation of less than ±5 pct of the average value. The agreement between LECO and XRF analyses means that the simple LECO analysis can be used to determine ash sulfur content with a good degree of certainty. The results for the various analyses listed in Table 2-17 and labeled as Library Values are averages for all analyses on file for a particular coal sample. The number of analyses on a particular coal depends upon the frequency of use in the CPU or batch autoclave tests and ranges from a high of 36 for Beulah-3 lignite to only one for Usibelli subbituminous coal (Alaska). Typically 2 to 9 analyses have been performed on each coal.

Data concerning the sulfur forms found in each coal (Table 2-18) were obtained by the Pittsburgh Energy Technology Center or the State Electricity Commission of Victoria, Australia. Mineral analyses on a number of the tabulated coals were determined using an IR pellet technique by Advanced Fuel Research (calcite content is listed).

The sulfur retention values listed in Table 2-18 represent the sulfur found in the ash as a percentage of the total sulfur analyzed in that particular coal. Eight of the coals had sulfur retention values of 74 to 89 pct, while six of the coals had higher or lower values. Three of the coals that contained very low total sulfur contents (0.5 wt %) had retention values of over 97 pct, while at the other extreme, three coals (total sulfur > 3 wt %) had retention values under 46 pct. An extremely low sulfur retention value of only 5 pct was observed for the Powhatan #6 bituminous coal.

Attempts to correlate the amount of sulfur retained with the form of the sulfur in the coal (organic, pyritic, or sulfate) or with the coal ash content were unsuccessful. Measured values for sulfate were generally low and in most cases could account for only 25 pct or less of the retained sulfur. Pyrite content also did not correlate. In some cases the pyrite content was much higher than the retained sulfur, while in other instances it was much lower. For all but two of the twelve coals, the sum of pyritic- and sulfate-sulfur is less than the amount of sulfur retained in the ash, indicating that sulfur in some other form must be retained. To account for this sulfur retention, the most obvious source of cations is the ion exchangeable calcium found in these coals. During heat-up in the ashing process organic sulfur reactions with calcium, sodium, potassium, and/or magnesium could occur to form some oxides of sulfur which would be stable at the higher ashing temperatures. This is especially true for reactions with calcium.

Sulfur retention in the ash was found to correlate with calcium content as shown in Figure 2-10. The sulfur retained was found to be nearly linear, with the calcium-to-sulfur molar ratio in the dry coal for Ca/S molar ratios under 0.8 or when excess sulfur was present. For molar ratios between 0.8 and about 1.5, 85 to 89 pct of the total sulfur was retained, while at ratios over 2 nearly all of the total sulfur was retained with the ash.

TABLE 2-17

SULFUR ANALYSES OF COAL AND COAL ASH

Coal Source	Abbrev.	Coal Type	Ash[a] Library Value	Ash This Analysis	Sulfur Content of the Ash by LECO[b]	XRFA[c] 1	XRFA[c] 2	Average	Coal Total Sulfur Library Value	Coal Total Sulfur This Analysis
Absaloka, MT	ABS1	Sub.	22.2±1.2	21.7	0.74	1.00	0.86	0.87	3.41±0.55	3.53
Big Brown, TX	BB1	Lig.	12.6±0.5	13.1	0.77	--	0.85	0.81	0.96±0.05	0.86
Beulah, ND	B3	Lig.	16.6±0.6	17.2	1.68	1.88	1.76	1.77	2.38±0.14	2.56
Decker, MT	DEC 1	Sub.	5.6±0.4	5.2	0.42	0.36	0.42	0.40	0.53±0.02	0.53
Gascoyne, ND	GAS 1	Lig.	11.9±0.2	10.7	1.23	--	1.16	1.19	1.44±0.06	1.60
Larson, ND	LAR 1	Lig.	10.7±0.3	10.0	0.53	0.44	0.54	0.50	0.56±0.02	0.67
Martin Lake, TX	ML1	Lig.	16.9±0.1	18.5	1.23	1.57	1.36	1.39	1.79±0.01	1.78
Morwell, Australia	MOC	Brn	3.6±0.0	3.6	0.28	0.33	0.28	0.30	0.31	0.20
Powhatan #6, OH	POW1	Bit.	10.6±0.1	10.3	0.19	0.20	0.21	0.20	3.85±0.06	4.22
San Miguel, TX	SM1	Lig.	45.4±1.0	45.4	0.87	1.25	1.18	1.10	2.40±0.21	3.16
Velva, ND	VEL1	Lig.	11.0±0.5	8.3	0.60	0.65	0.65	0.63	0.37±0.06	0.52
Wyodak, WY	WYO1	Sub.	8.1±0.2	7.7	0.56	0.63	0.61	0.60	0.51±0.03	0.29
Indian Head, ND	ZAP1	Lig.	11.2±0.0	11.3	1.01	1.07	1.01	1.03	1.19	1.20
Usibelli, Alaska	USI1	Sub.	11.1	11.1	0.37	--	0.39	0.38	0.48	0.37

[a] Library values are averages of all analyses on file. Ash was determined by ashing at 800°C following ASTM procedures.

[b] Determined with a LECO sulfur analyzer.

[c] X-ray fluorescence analysis of the ash. The as-measured SO_3 content was used to calculate sulfur.

TABLE 2-18

COMPARISON OF COAL TOTAL SULFUR AND SULFUR FORMS TO ASH SULFUR CONTENT

Coal	Coal[a] Total Sulfur, Library Value	Ash Sulfur Content, Average	% of Total Sulfur Retained In the Ash[b]	Sulfur Forms As % Sulfur in Dry Coal[c]			Calcite[d]	Ca/S[e] Molar Ratio
				Sulfate	Pyritic	Organic (Diff.)		
ABS1	3.41	0.87	25	0.26	1.62	1.53	1.0	0.21
BB1	0.96	0.81	84	0.00	0.16	0.80	--	1.51
B3	2.38	1.77	74	0.03	0.64	1.71	0.9	0.55
DEC1	0.53	0.40	75	0.03	0.09	0.41	0.6	0.79
GAS1	1.44	1.19	83	0.19	0.25	1.00	0.9	0.85
LAR1	0.56	0.50	89	0.02	0.08	0.46	1.2	1.44
ML1	1.79	1.39	78	0.00	0.53	1.26	--	0.60
MOC	0.31	0.30	97	--	--	--	--	3.40
POW1	3.85	0.20	5	0.04	0.91	2.90	--	0.05
SM1	2.40	1.10	46	0.00	0.37	2.03	--	0.39
VEL1	0.37	0.63	170	0.03	0.07	0.27	1.1	2.58
WYO1	0.51	0.60	118	0.10	0.08	0.33	1.2	3.29
ZAP1	1.19	1.03	86	0.15	0.57	0.47	1.1	0.81
USI1	0.48	0.38	79	--	--	--	--	4.32

[a] Library values are averages of all analyses on file.

[b] The percentage of total coal sulfur found in the ash.

[c] Determined by the State Electricity Commission of Victory, Australia and/or the Pittsburgh Energy Technology Center.

[d] Determined by Advanced Fuel Research using an IR technique.

[e] Calculated from (moles Ca/100 gm dry coal)*32/(gms. S/100 gm dry coal).

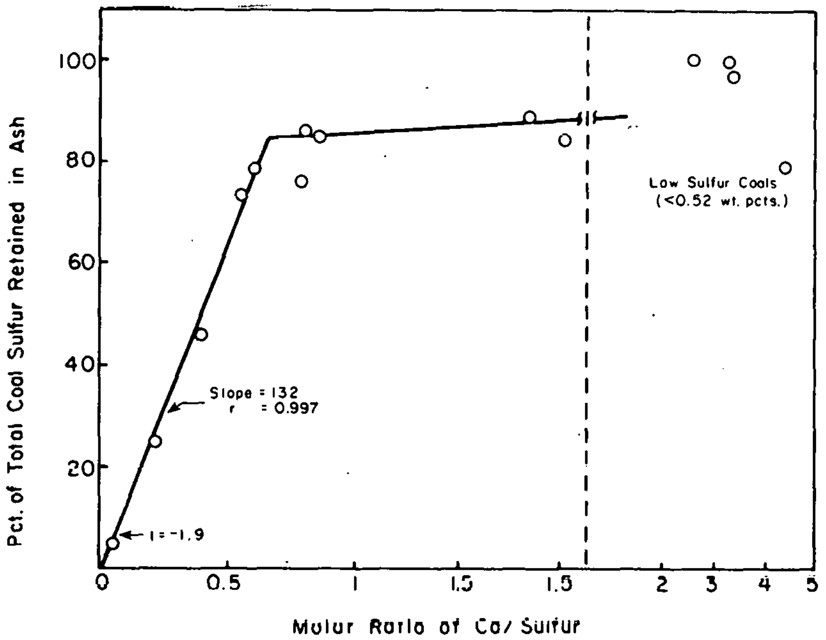


FIGURE 2-10. Effect of calcium content of the coal on retention of sulfur in the ash.

It should be noted in these discussions that the coals which had high Ca/S molar ratios were low-sulfur coals (less than ½ wt pct total sulfur), and experimental error could account for the wider retention range reported. For the coals with Ca/S ratios of under 1.5, total coal sulfur varied from 0.6 to 4.2 wt pct of the dry coal. It should also be noted that other alkali metal cations such as Na^+, K^+, and Mg^{2+} may be contributing; however, since the slope of the line in Figure 2-10 is nearly one-to-one for Ca/S molar ratios under 0.7, their contribution to the retention of sulfur appears to be minimal and within the realm predicted by the calcium content alone.

The previous discussion showed that some organically-bound sulfur was retained in the ash; this would, in turn, introduce some error into the material balance calculations for liquefaction experiments. The use of the ash value determined by high-temperature ashing would directly affect the dry coal oxygen content, which is typically determined by difference. Since the ash content is also used to determine the maf coal content of a sample, these values will also be in error depending on the amount of sulfur retained in the ash. Low sulfur retention for a higher-sulfur coal or a high retention for a low-sulfur coal will have the least effect. The error is appreciable for a coal such as Beulah-3 lignite, which contains 2.4 wt pct total sulfur and has an ash sulfur retention of 74 pct.

Table 2-19 presents the averaged data for Beulah-3 lignite and the calculations to adjust the inorganic content to account for sulfur retention and also calcite decomposition. Calcite decomposition to CaO and CO_2 at 800°C would decrease the amount of ash observed. As seen in Table 2-18, the

TABLE 2-19

EFFECT OF USING ASH OR INORGANIC CONTENT TO DETERMINE COAL ELEMENTS FOR BEULAH-3 LIGNITE[a]

Component	Wt Pct mf Coal (mf)	Wt Pct mf Coal Using HTASH (mf)	Wt Pct mf Coal Using CASH	Wt % maf Coal Using HTASH (maf)	Wt Pct maf Coal Using CASH (mif)	% Error between maf & mif
Carbon[b]		58.69±1.58	58.69	70.33	67.51	4.2
Hydrogen[b]		3.74±0.20	3.74	4.49	4.30	4.4
Nitrogen[b]		0.86±0.04	0.86	1.04	0.99	5.1
Oxygen[c]		17.77±1.86	22.33	21.29	25.46	16.5
Sulfur[d]		2.38±0.14		2.85		44.6
Organic Sulfur[c]	1.71		1.71		1.97	
Pyritic Sulfur[e]	0.64					
Sulfate Sulfur[e]	0.03					
Inorganic			13.07[i]			26.6
Ash[f]		16.55±0.66				
Ash Sulfur[g]	1.77					
Calcite[h]	0.9					
Total		100.00	100.00	100.00	100.00	

[a] Analysis with standard deviations represent a minimum of 37 analyses made over a two-year time frame.

[b] Determined by a Perkin Elmer 240 C, H, N analyzer.

[c] Determined by difference.

[d] Determined by LECO sulfur analyzer.

[e] Determined at PETC or by the SEC in Australia.

[f] Determined by Ashing at 800°C following ASTM procedures.

[g] Determined by X-ray fluorescence and LECO analyzer.

[h] Determined by direct I.R. analysis (Advanced Fuel Research).

[i] Inorganic = 16.55 - (Ash S) (MW_{SO_3}/MW_S) + (Sulfate S) (MW_{SO_3}/MW_S) + pyrite sulfur + calcite (MW_{CO_2}/MW_{CACO_3}).

amount of calcite in the eight coals for which analyses are available is small and relatively constant. Seven of the eight have calcite values between 0.9 and 1.2 wt pct dry coal. Using:

$$\text{Calcite Ash loss} = (\text{wt pct calcite})\ (MW_{CO_2}/MW_{CaCO_3})$$

the observed ash value would be 0.4 wt pct low for Beulah-3 lignite.

The amount of organic sulfur in the ash can be calculated and corrected for pyritic and sulfate sulfur using:

$$\begin{gathered}\text{Ash sulfur error} = (\text{Ash Sulfur})(MW_{SO_3}/MW_S) + \\ (\text{Sulfate S})(MW_{SO_3}/MW_S) + (\text{Pyritic S})\end{gathered}$$

For the Beulah-3 lignite a value of 3.8 wt pct is obtained, which is significant. The actual inorganic content of the coal would be:

$$\begin{gathered}\text{Inorganic} = \text{High Temperature Ash} + (\text{Calcite ash loss}) - \\ (\text{Ash sulfur error})\end{gathered}$$

or 13.1 wt pct for Beulah-3 lignite, which is 21 pct lower than the high-temperature ash value. The dry coal oxygen content increases from 17.8 to 22.3 wt pct. The calculation of the liquefaction yields on an maf coal basis is also affected in that a yield of 35 wt pct distillable oil derived from calculations using the high-temperature ash to calculate the amount of maf coal fed would be 33.6 wt pct using the sulfur and calcite corrected ash value in these calculations. Correcting the high-temperature ash value for these coals would not drastically affect the reported liquefaction yields; however, when dealing with oxygen elemental balances and especially inorganic or ash balances the errors are more significant. When determining the amounts and types of oxygen functionality of a coal such as Beulah-3 lignite, which has a large ash sulfur retention, corrections would be necessary to arrive at the true coal oxygen content. In ash balancing calculations for liquefaction or other systems where coal is processed, the necessity for correction becomes important. During coal liquefaction the organic matrix is made more volatile, sulfur is reduced to H_2S, pyrite goes to phyrrotite, and ion exchangeable alkali metals agglomerate principally as carbonates. The net result is an apparent ash loss during liquefaction.

In conclusion, the data indicate that for the coals studied, the quantity of sulfur retained in the ash during high-temperature ashing depends on the amount of calcium and, to a lesser extent, on the total sulfur present. In general, material balance calculations using ash would be more accurate and valid if sulfur-free ash data were used. For detailed elemental balancing, the ash sulfur content, as well as coal pyritic- and sulfate-sulfur contents are required to obtain accurate coal oxygen values. Liquefaction product distributions, on an maf coal basis, are affected by sulfur retention in the ash, but not to such an extent that correction would normally be necessary.

3. - SLAGGING FIXED-BED GASIFICATION

PTPA No.: 624,626,641,642,643

B&R Nos: SFBG - AA8510100
SFBG Environmental
Studies - AA8525050
AA1515000

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3.1 GOALS AND OBJECTIVES

The goal of the GFETC Slagging Fixed-Bed Gasification (SFBG) Project is to develop data to support commercial and demonstration applications of coal gasification technology. Due to the nature of the GFETC pilot plant equipment process and the Center's mission to pursue applications to low-rank coals, the primary focus of the GFETC project has been on the SFBG of lignites and subbituminous coals. Emphasis was placed on the development of environmental data and on by-product and effluent treatment and utilization studies because these are the most pressing needs. The project now includes the additional goals of generating data to validate the adequacy of various combinations of alternative physical, chemical, and biological wastewater treatment methods to meet criteria for reuse of wastewater and disposal of contaminants; to develop or improve select aspects of treatment technology; and to characterize slag and waste treatment sludges and their leachates to ensure safe disposal under RCRA guidelines. A joint venture will be undertaken with Argonne National Laboratory to assess occupational health issues, starting with biomedical assessment of all primary and secondary effluent streams that could involve the exposure of workers.

The four major activities in the Slagging Fixed-Bed Gasification Project during FY 1981 have the following objectives:

1. Demonstrate the capability to operate the SFBG continuously (up to 5 days) on lignite and to collect representative samples of effluents, especially wastewater, for subsequent treatment tests.

2. Separate and characterize organic constituents in gasifier effluents (especially wastewater) and relate them to coal-specific properties and process conditions.

3. Design and test alternate or advanced wastewater treatment techniques.

4. Obtain PDU-sized treatment equipment, including a cooling tower, and test proposed treatment methods to determine environmental and process efficiency.

3.2 ACCOMPLISHMENTS

3.2.1 Summary of Operations

The most successful SFBG test in GFETC history was completed on April 3, 1982, with over 120 hours of continuous slagging operation. This one-time goal of five days' continuous operation, once rejected as being impractical due to the small gasifier diameter, was accomplished on the same North Dakota lignite that will be used in the Great Plains Gasification Project commercial plant. Two major gasifer modifications largely responsible for this success were the enlargement of the gasifier I.D. to its maximum of 22" and the use of a ring-type methane burner in the taphole. Run termination was voluntary after five days of operation, during which two rail car loads of lignite were gasified and over 11,000 gallons of wastewater were collected. Post-run inspection revealed no internal gasifier damage, indicating that the test could have proceeded indefinitely.

Another highly successful SFBG test was completed on April 23 with 80 hours of trouble-free slagging operation on Indian Head (same as GPGA) lignite. This was followed by 2.5 hours of slagging operation on mildly-caking Emery, Utah, bituminous coal (free swelling index of 1.5), during which the water-cooled stirrer was successfully operated. Some caking of the bed was encountered, causing coal feeding problems just prior to termination of the run.

The third and last test under this operating contract was initiated with Indian Head lignite and switched to a 50:50 mixture with Emery. Although only six hours of slagging operation were obtained on the mixture, the lessened tendency toward caking, as evidenced by bed dps and stirrer torque, offers promise for this method for overcoming caking problems.

The recent series of three- to five-day runs on lignite (Table 3-1) has verified the fact that the slagging fixed-bed gasifier as currently configured is a reliable machine capable of producing large amounts of steady state effluents for environmental studies. Over 30,000 gallons of wastewater were collected before the end of the contract and stored in a rail freezer car for testing in the wastewater treatment train when installed.

3.2.2 Analyses of Gasifier Effluents

3.2.2.1 Development of a Fast Class Separation Method

A very fast method was devised for effecting the separation of compound classes (aliphatics, aromatics, and polars) in the same manner as the modified EPA-610 procedure. The 610 procedure open column chromatography on activated silica gel is very useful but requires approximately one hour to complete.

TABLE 3-1

OPERATING PARAMETERS FOR EXTENDED SFBG RUNS

Run No.	119	120		121	
Coal Used:					
Indian Head Lignite	X	X		X	X
Emery Bituminous			X		X
Slag Flow Hours	121.4	68.35	3.6	32.25	5.5
Operating Parameters:					
Oxygen Rate, scfh	6551	6823	6836	6563	6563
Oxygen/Steam Mole Ratio	0.90:1	0.9:1	0.9:1	0.80:1	0.86:1
Operating Pressure, psig	300	300	300	300	300
Causes Of Shutdown:					
Loss of Slag Flow					X
Fuel Bed Problems			X		
Voluntary Shutdown	X	X		X	
Mechanical Dimensions:					
Water-cooled Stirrer		X	X	X	X
Hearth plate Level, inches	4.65	3.675	3.675	3.675	3.675
Vessel Diameter, inches	22	22	22	22	22
Tuyere Angle, degrees	8°	18°	18°	18°	18°
Tuyere Insert, I.D.	0.269	0.269	0.269	0.269	0.269
Mass Balance:					
% IN: Steam	10.8	10.8	NC	12.0	NC
Oxygen	18.0	17.7	NC	17.3	NC
Fuel	65.6	64.9	NC	63.5	NC
Purge Gas	6.5	6.7	NC	7.2	NC
% OUT: Product Gas	66.6	66.3	NC	66.5	NC
Slag	2.6	3.3	NC	2.7	NC
Tar	2.3	1.7	NC	1.4	NC
Liquor	29.4	28.8	NC	24.3	NC
% Accounted For -	100.9	100.1	NC	94.8	NC

Highly volatile compounds can be lost in the solvent evaporation steps. Since Aldrich-Davidson #12 silica gel had always effected a good separation with open columns, a short tube (13 x 1 cm) was filled with the silica gel activated at 518°F and an end cap made from a Waters Associates' "sep-pak" was attached so that a syringe could be used to force the eluting solvents through the column. The device is shown in Figure 3-1.

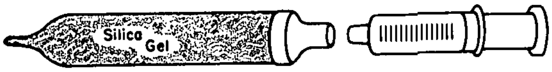


FIGURE 3-1. Homemade device for rapid separation of compound classes in SFBG light organic by-products.

Using this tube with pentane, methylene chloride, and methanol as eluents, clean separation of aliphatics, aromatics, and polars was obtained on 50-μl samples of gasifier light oil. Solvents were evaporated from the three fractions, and gas chromatographic analysis was performed on each fraction. Future experiments will be aimed at reducing the size of the tube, thus reducing column dead volume and giving fractions suitable for on-column injection gas chromatographic analysis without evaporation of the solvent.

3.2.2.2 Analysis of Time-Sampled Light Oils

Light oils from the sidestream sampler (Gasifier Run RA-119) were examined using the separation method described in the preceding section. Samples obtained on the first, third, and fifth days of Run RA-119 were shown to have identical compositions. Gas chromatograms of the aliphatic, aromatic, and polar fractions were compared. The only difference was in the amounts of the highly volatile aromatics, which could have been caused by variation in the vacuum distillation conditions or evaporation during sampling. This is significant since it indicates that steady state conditions were achieved early in the run (before 6 hours). Figure 3-2 provides a comparison of the chromatograms of the aromatic fractions of samples from the first and fifth days of the run.

A sample from an earlier run, RA-87, using the same coal was analyzed by the same method. The chromatograms of the RA-87 sample were identical in every detail to the third day's sample from Run RA-119.

3.2.2.3 Guaiacols in Light Oils

Five guaiacols have been identified in gasifier light oil phenolics by normal phase HPLC and GC/MS: guaiacol, 6-methylguaiacol, 4-methylguaiacol, 4-ethylguaiacol, and 4-n-propylguaiacol. One other methoxymethylphenol was present in the unseparated phenolics but was found in the o-phenol fraction

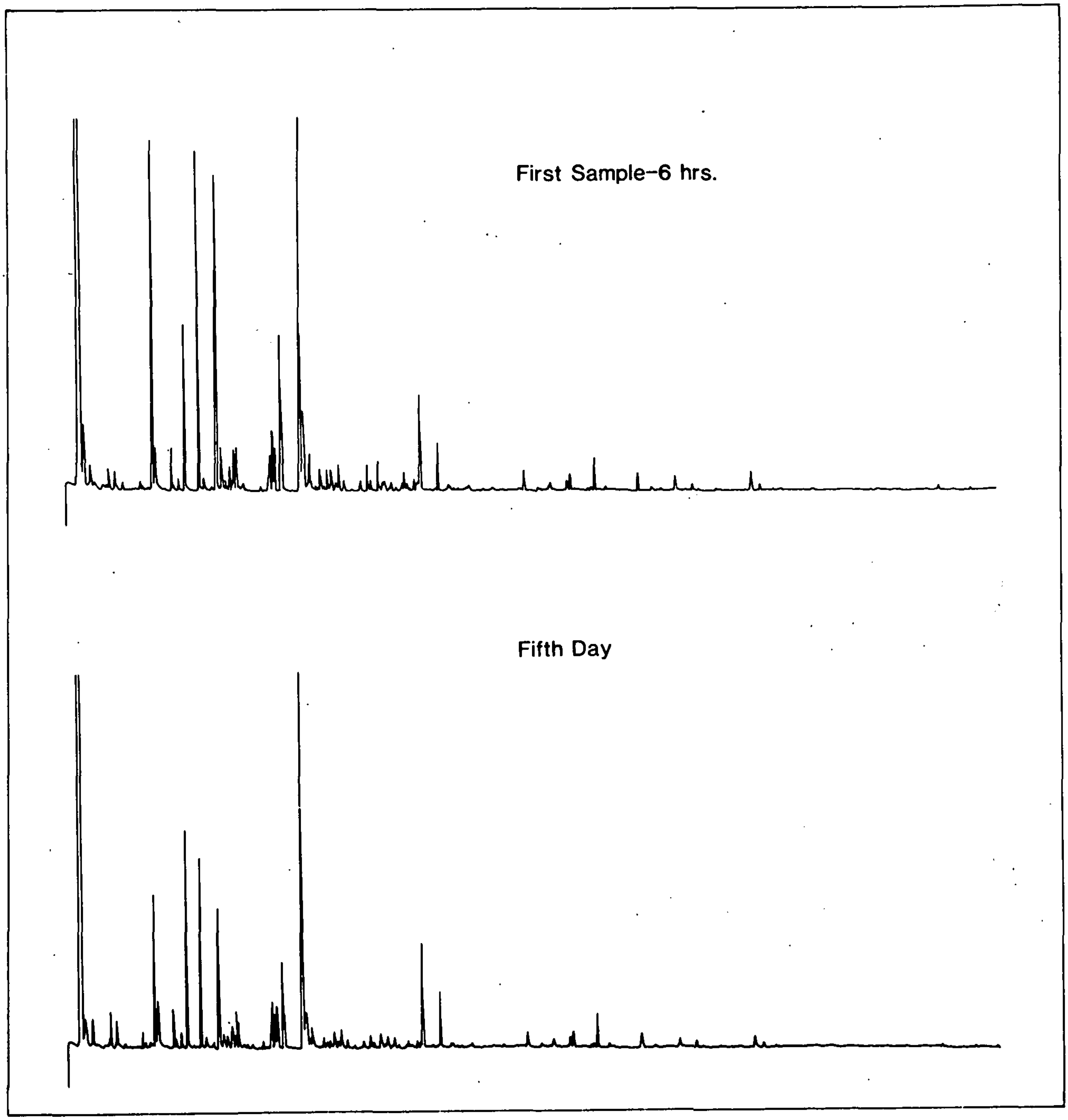
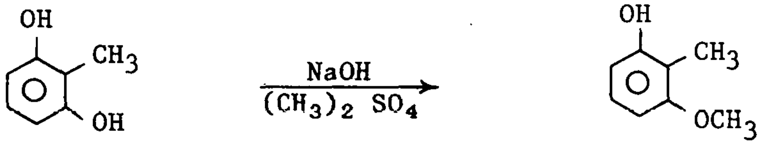


FIGURE 3-2. Comparison of aromatic fractions of light oils. Samples collected at different time periods. RA-119 (Indian Head); first sample: 6 hours.

rather than with the guaiacols; hence, it must be either the 3-, 4-, or 5-methoxy-2-methylphenol. None of the appropriate compounds were available as standards, so a synthesis of 3-methoxy-2-methylphenol was carried out, as shown:



The other two standards will be synthesized by Clemmensen reduction of the corresponding salicylaldehydes.

3.2.2.4 Hydantoins in Gasifier Effluents

Hydantoins were obtained by charcoal treatment of gasifier condensate water which had been extracted with methylene chloride. Gas chromatography with DB-5 columns gave very broad, distorted peaks for these compounds. Gas chromatography on a 60-meter SE-54 column was not successful; forming the methyl derivatives gave no major improvement. A 25-meter Alltech Superox-FA was installed with an on-column injector, and produced excellent resolution with good peak shape. This is the first time a polar capillary column has proven superior over the SE-54, indicating that Superox may have other uses in future wastewater analysis. The Superox-FA column was then installed on the GC/MS.

Several methylation experiments were carried out to convert the hydantoins to their N,N-dimethyl derivatives. It was hoped that these derivatives would give more intense molecular ions than the underivatized compounds. (Without derivatization, the molecular ions of some of the smaller hydantoins are obscured by those of other hydantoins with larger alkyl groups.) The best conversion of the hydantoins to the N,N-dimethyl derivatives was obtained by stirring the hydantoin with methyl iodide in acetone with a pH 13 buffer.

These derivatives were resolved easily on the DB5 column and gave good molecular ions. The following hydantoins were identified by fragmentation patterns and molecular ions: 5,5-dimethylhydantoin, 5-ethyl-5-methylhydantoin, 5,5-diethylhydantoin, 5-methyl-5-propylhydantoin, and 5-methyl-5-isopropylhydantoin.

The most likely source of these hydantoins is the reaction of ketones in the condensate water with cyanide and ammonia. None of the monosubstituted hydantoins, which would have come from aldehydes, were found. No phenylhydantoins were found.

3.2.3 Slag Viscosity

3.2.3.1 Prediction of Viscosity by the Dolomite Ratio

A continuing activity in the slag viscosity project is the testing of empirical data from the viscosity measurements made by Bituminous Coal Research against predictive models in the literature. A spot check was made of the dolomite ratio method* of predicting slag viscosity. The dolomite ratio is calculated from

$$\frac{100\ (CaO + MgO)}{CaO + MgO + Fe_2O_3 + Na_2O + K_2O}$$

where the chemical formulae represent the weight percentage of the respective components on an SO_3-free, P_2O_5-free basis. The dolomite ratio method was tested by comparing the temperature at which the viscosity is predicted to be 250 poises, based on the composition of the slag, against the observed temperature for five slags. The results are summarized in Table 3-2.

TABLE 3-2

COMPARISON OF PREDICTED AND OBSERVED TEMPERATURES FOR 250 POISES VISCOSITY

Slag	Dolomite Ratio	T_{calc}, °F	T_{obs}, °F	Error, °F
Atlantic Richfield	87.8	2170	2170	0
Baukol-Noonan	73.7	2100	2210	110
Big Horn	56.0	2025	2195	170
Colstrip	92.0	2160	2440	280
Decker	59.7	2050	2160	110
Average Error				134

Based on this rather limited sample, it appears that the dolomite ratio method generally predicts temperatures that are too low. The theoretical implications of this underprediction, in terms of likely processes in the melt, have not been explored as yet, nor has the spot check reported here been extended to more than five slags.

3.2.3.2 Activation Energy for Flow

The activation energy for molecules to move into holes in the liquid structure during viscous flow can be calculated from the well-known equation

$$-\Delta\varepsilon \left(\frac{1}{T_1} - \frac{1}{T_2}\right) = R\ell n \frac{(\emptyset_1)}{(\emptyset_2)} + \tfrac{1}{2}\ \ell n \frac{(T_1)}{(T_2)},$$

where $\emptyset_1$ is the fluidity or reciprocal viscosity at temperature T_1. Values of $\Delta\varepsilon$ were calculated for 14 slags using the empirical viscosity-temperature curves determined by BCR. Values of T_1 and $\emptyset_1$ were taken from the Newtonian

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* Duzy, A.F. "Fusibility-Viscosity of Lignite-Type Ash". ASME Paper #65-WA/FU-7 (1965).

region of the curve, roughly equidistant from the midpoint and spanning as wide a range as seemed reasonable. For this set of slags $\Delta\varepsilon = 76 \pm 10$ kcal/mole. It is interesting to note that the Pauling single bond energy for an Si-O bond is 88 kcal/mole. This result suggests that flow in these slags arises from rupture of some fairly strong bonds, probably in the aluminosilicate polymers.

The range of observed values of $\Delta\varepsilon$ was 58.7 to 95.6 kcal/mole. As yet no attempt has been made to determine whether $\Delta\varepsilon$ can be correlated with some other property of the slag, such as extent of polymerization, or whether the range is simply due to experimental scatter.

3.2.3.3 Partition Coefficients--Carnegie-Mellon University

A review of the literature concerning estimation of partition, or distribution, coefficients (K_D) revealed two approaches by which K_D values may be predicted: 1) thermodynamic approaches, which derive from the definition of K_D expressed as the ratio of solute mole fraction activity coefficients in the aqueous and solvent phases, respectively, and 2) correlation analysis, which is based on the observation that partitioning processes are similar in similar solvent systems and that substitution for replacement of a hydrogen atom on a solute molecule has an additive effect on the distribution coefficient.

Previous progress reports have described the use of a thermodynamic model based on the concept of regular solutions. It was shown that this approach was accurate only for systems that do not include hydrogen bonding. However, the approach is suitable for a relative ranking of solutes for extraction of a particular solute. New efforts have expanded the analysis of this model with nonhydrogen-bonded systems, and additional work has also included an analysis of solvent mixtures. These results have confirmed the applicability of regular solutions to nonpolar-solvent, polar-solvent systems. Preliminary work with solvent mixtures has shown that accurate estimates of K_D for phenol extracted with a mixture of octanol-cyclohexane can be obtained over the range of octanol volume fractions 0.2 to 0.9. The same approach was not suitable for a polar-polar solvent mixture of octanol-butyl acetate.

Previous quarterly reports have shown the use of Linear Free Energy Relationships (LFER) for correlation of solute K_D values in a particular solvent with distribution of substituent constants; some numerical examples are given below.

The substituent constant is defined as

$$\pi_X = \log P\ (x) - \log\ (p(H)$$

where P(x) is the partition coefficient of a derivative and P(H) is that of a parent compound. For example, the SC value for NO_2 substitution of benzene with octanol as the solvent is

$$\pi\ NO_2 = \log P(\text{nitrobenzene}) - \log\ (P(\text{benzene})$$
$$= 1.85 - 2.13 = -0.28$$

This can then be used to estimate log P for 1,3-dinitrobenzene

$$\begin{aligned} \log P(\text{1,3-dinitrobenzene}) &= \log P(\text{benzene}) + 2\,\pi_{NO_2} \\ &= 2.13 + 2(-0.28) \\ \log P(\text{1,3-dinitrobenzene}) &= 1.57 \\ \text{observed } \log P &= 1.49 \end{aligned}$$

When phenol is taken as the parent compound, the SC for NO_2 in octanol increases to 0.50 for para and meta substitution but has a value of only 0.30 for ortho substitution. The SC value for NO_2 substitution on phenol with n-butyl actetate as solvent is 0.60, 0.72, and 0.62 in the ortho, meta and para positions, respectively.

3.2.4 Anaerobic Treatment Wastewater--Georgia Institute of Technology

Research is being performed to assess the feasibility of using anaerobic treatment of coal gasification wastewater by the Activated Carbon filter method. The process, shown in previous quarterly reports, consists of a first-stage reactor containing Raschig Rings and a second-stage reactor containing granular active carbon. The effluent is treated by nitrification-denitrification to remove residual ammonia and other nitrogen compounds. Three parallel systems are being operated to minimize losses in data collection due to upsets.

Systems I and II have been operated for 266 days. During this time they received identical feed substrates of diluted wastewater and phosphates. The concentration of the wastewater was $\sim$10 pct (1,000 ppm TOC) for a period of 20 days (day 175-196). On day 196 of operation the concentration of raw wastewater in the influent was increased to $\sim$15 pct (1,500 ppm TOC) and the system was operated for an additional 40 days (day 126-236). During this latter period, performance of both Systems I and II decreased markedly. In order to improve the efficiency of the system performance, $FeC1_3$ was added to the feed substrate on day 209 to either precipitate, in the case of S^{-2}, or complex in the case of CN^- and SCN^-, potentially inhibitory species. No improvement in operation was noted. Therefore, on day 237 the influent raw wastewater concentration was reduced to $\sim$10 pct (1,000 ppm TOC) and the systems were operated an additional 17 days under these conditions. Lack of biological activity, as evidenced by extremely low TOC and COD removal coupled with a lack of gas production, indicated the systems were either severely inhibited or had failed. Therefore, on day 254 both Systems I and II were drained, reseeded with sludge from a municipal anaerobic sludge digester, and reacclimation of these two systems was initiated. In the meantime, the concentration of wastewater feed to System III was increased to $\sim$10 pct which appears to be the upper limit for raw wastewater.

Gas production from the two Systems is shown in Figures 3-3 and 3-4. Average daily gas production for the period day 147-194 for both systems was 1.2 ℓ/day CO_2 and 4.5 ℓ/day CH_4, with System I showing more variability in daily gas production than System II. Upon increasing the raw wastewater concentration to 15 pct, System I showed a decrease in gas production to a value of zero on day 202, while System II showed an increase in gas production to 5.5 ℓ/day on day 202 and then decreased to zero on day 209. These decreases in gas production indicated a loss of bacterial activity either due to inhibition or toxicity.

During the period day 147-195, both Systems continued to show good phenol removal (as shown in Figures 3-3 and 3-4) with ranges of removal efficiencies of 79-93 pct and 84-95 pct for Systems I and II, respectively. The average removal efficiency for both systems for this period was 90 pct.

Operation of the nitrification system continued at a hydraulic residence time of 18 hours and a sludge age of approximately 22 days. The feed solution to the system consisted of increasing concentrations of effluent from the anaerobic filters, as indicated in Table 3-1. The nitrification system showed extremely good removal of NH_3 as well as residual TOC and COD in the wastewater. NH_3-N, NO_2^--N, NO_3^--N influent and effluent concentrations are given in Table 3-3 for the five anaerobic effluent concentrations that have been treated. As can be seen from the data, essentially complete nitrification occurred at all concentrations with conversion of the NH_3-N to NO_3^--N. However, it should be noted that the level of NO_2^--N has started to increase in Phase 2, indicating a possible inhibition in the conversion of NO_2^--N to NO_3^--N at this concentration of wastewater.

3.2.5 Solid Waste Disposal--University of Pittsburgh

The overall objective of this research is to evaluate compliance with RCRA guidelines for landfill disposal of representative sludges produced during the treatment of process effluents from the SFBG. In order to accomplish this objective, wastewater produced at GFETC has been shipped to the University of Pittsburgh where laboratory-scale treatment facilities will be used to process the wastewater. A linkage of unit operations incorporating solvent extraction, free and fixed ammonia stripping, judicious pH adjustment, and biological oxidation (illustrated in Figure 3-5) is operational within the Environmental Engineering laboratories of the University of Pittsburgh. Some combination of these processes is thought to represent the way in which best available technologies will be used in commercial-scale coal conversion operations.

Raw wastewater, received in drum-sized quantities from GFETC, is aerated at a temperature of about 150°F to simulate the free leg of the ammonia stripping operation, as reported in DOE/FC/QTR-82/1. Lime is added after free-leg ammonia stripping to raise the pH to about 11. A dark-brown lime sludge containing phenolic odors is produced during this phase of operation. The filtered liquid is then transferred to the fixed leg ammonia stripper and air-stripped at a temperature of about 150°F. Contents of the fixed-leg ammonia stripper are discharged to a container where sodium carbonate is added to precipitate excess calcium as calcium carbonate. Effluent after carbonate addition is filtered to remove "recarbonation sludge", and pH depressed to the range of 5 to 6 with sulfuric acid. Alum is then added to enhance removal of any of the polymerized organics that were not removed in the recarbonation sludge. This liquid is filtered, giving yet another sludge, and the effluent pH is adjusted to 7 with sodium hydroxide before being fed to the biological reactors, which also yield a sludge.

Sludges produced are leached using the EPA and ASTM methods and a method developed by the University of Pittsburgh. Sludge samples, along with the leachants, are then tested for mutagenicity using the Ames test, and for toxicity using Daphnia Magna.

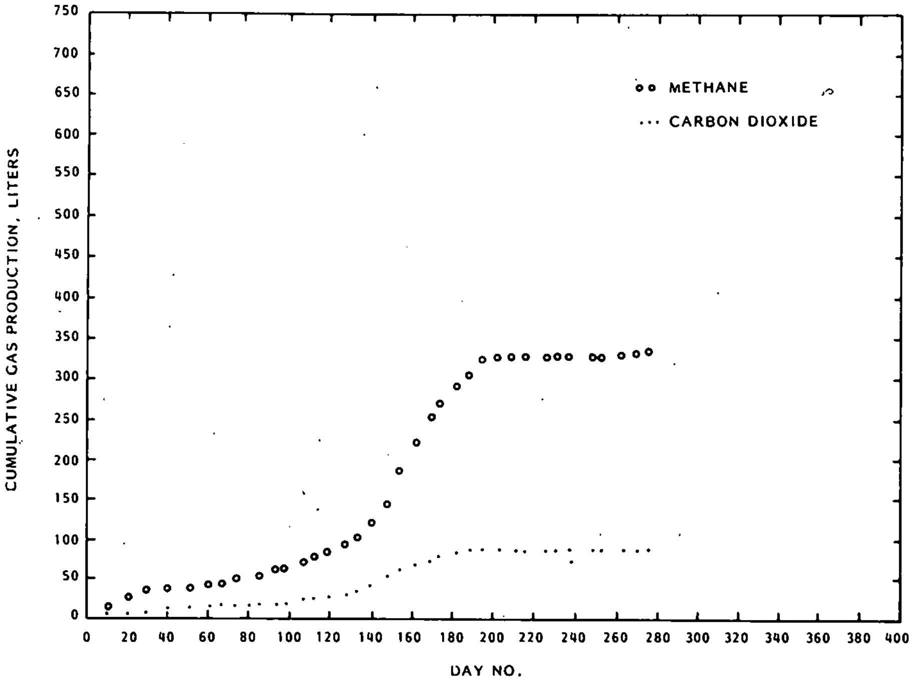


FIGURE 3-3. Gas production for System I.

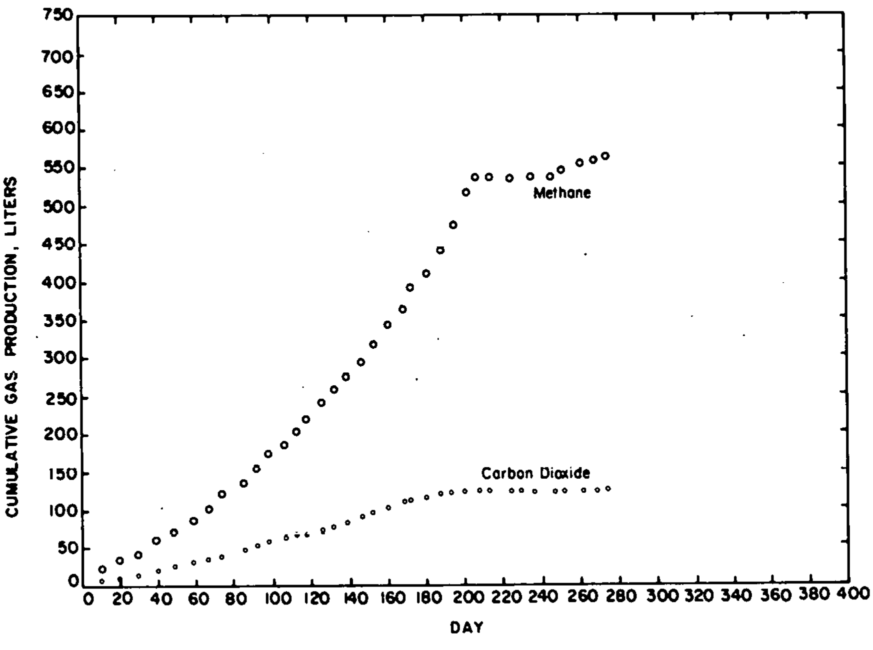


FIGURE 3-4. Gas production for System II.

TABLE 3-3

OPERATIONAL PARAMETERS AND REMOVAL RATES FOR NITRIFICATION SYSTEM

Parameters	Phase 1-a		Phase 1-b		Phase 1-c		Phase 1-d		Phase 2 (up to 7/1)	
Dilution ratio	1:9		1:3		1:1		3:1		No dilution	
NH_3-N loading (kgNH_3-N/kgMLSS/d)	0.054		0.076		0.129		0.125		0.154	
COD loading (kgCOD/kgMLSS/d)	0.083		0.125		0.126		0.194		0.277	
MLSS (mg/ℓ)	1560		1900		2655		3393		3130	
	Inf.	Eff.	Inf.	Eff.	Inf.	Eff.	Inf.	Eff.	Inf.	Eff.
NH_3-N (mg/ℓ)	65	0.7	111	0.4	269	1.8	425	1.6	482	5.0
NO_3^- -N (mg/ℓ)	0.5	57	0.3	101	0.8	221	2.1	354	3.1	402
NO_2^- -N (mg/ℓ)	ND[a]	ND	0.02	0.3	0.02	0.2	ND	0.3	ND	30.8
TOC (mg/ℓ)	50	30	111	30	227	46	466	56	640	132
COD (mg/ℓ)	100	51	182	48	263	91	659	91	867	192
Alkalinity mg/ℓ)	425	50	975	310	1868	313	2798	386	3430	745
pH	7.8	6.9	8.0	7.9	8.0	7.6	8.1	7.7	8.2	8.0

[a] = Not determined

Ames tests that have been performed in this reporting period are as follows:

1. A 200-ml sample of mixed liquor from a biological reactor that was fed solvent-extracted wastewater was found to be slightly mutagenic.
2. A 200-ml sample of lime sludge was found to be mutagenic.
3. A 200-ml mixture of carbonation sludge and wastewater was not mutagenic.
4. A 20-gm sample of bio sludge made from wastewater that was ammonia stripped and solvent extracted was not mutagenic.

3.2.6 Pilot-Scale Wastewater Treatment

Based on the laboratory studies reported earlier and the knowledge that the required level of wastewater treatment is dictated by end use, the most logical end use for treated wastewater, and the only one proposed to date for gasification projects, is as feed to a cooling tower. Laboratory-scale tests with fixed-bed wastewater have indicated that solvent extraction and ammonia stripping are the two necessary and sufficient pretreatment steps prior to activated sludge (AS) processing. Commercially available technology for these pretreatment steps exists, and no processing anomolies were uncovered in bench-scale tests. Further basic research is needed in this area only if a totally different pretreatment technology is substituted; e.g., anaerobic reduction in place of solvent extraction.

The major area of uncertainty where research activities should be focused centers around the cooling tower itself. This view is shared by American Natural Resources, sponsor of the Great Plains Coal Gasification Project (GPGA). The extent of wastewater treatment needed to produce a satisfactory feed to the cooling tower is unknown, and the environmental and economic risks are substantial. The most cost-effective approach is to feed water directly from the extraction/stripping units to the cooling tower, without intermediate biological treatment. However, this wastewater contains several thousand mg/ℓ of COD--after phenolics and other organics are reduced to low levels. The behavior of these previously uncharacterized species in a cooling tower with respect to drift, further biological activity, and associated fouling, and their effects on the solubility of dissolved solids is unknown. Another ill-documented source of concern is the fate of these organics after concentration in the cooling tower blowdown, and their behavior on lime or biological sludges from wastewater treatment in a landfill. Many of the above questions can be answered by bench-scale tests on fixed-bed wastewater after pretreatment. However, the principal question--what is the minimum treatment necessary to prepare feed for a cooling tower?--can only be answered by a cooling tower simulation unit sized to obtain scaleable data and operated for sufficient periods of time to measure fouling rates, both chemical and biological.

A design for a pilot-scale wastewater treatment train was completed in 1978 by engineers from the Center and Stearns-Roger, Inc., but funding was never obtained for acquisition of the systems. During this quarter a pilot-scale wastewater treatment train, sized at nominally 1 GPM, which was the property of the Environmental Protection Agency, was made available to

GFETC on an interdepartmental loan basis. Since the end use for GFETC wastewater was as discharge after biological treatment and polishing, there was no cooling tower with the EPA train. However a small cooling tower was located at Resources Conservation Co. (RCC), Seattle, Washington, that could be leased at a nominal rate. Thus a decision was reached to obtain the use of this equipment and install a pilot-scale treatment facility using commercially available technology.

The wastewater treatment train (shown in Figure 3-5) was received from the Holston Army Depot and consists of rough filtration, solvent extraction, and ammonia stripping. A lease agreement has also been arranged with Resources Conservation Company for use of a small commerical cooling tower which will complete the unit operation for the first phase of the test program. Also shown in Figure 3-5 is an alternative treatment scheme using biological treatment to prepare a higher quality makeup for the cooling tower. A contract has been written with the University of North Dakota for installation, operation, and analysis of the wastewater treatment train. Hydrotechnic Corp., fabricators of the treatment train, have been contracted to supervise installation and provide startup assistance beginning on June 7.

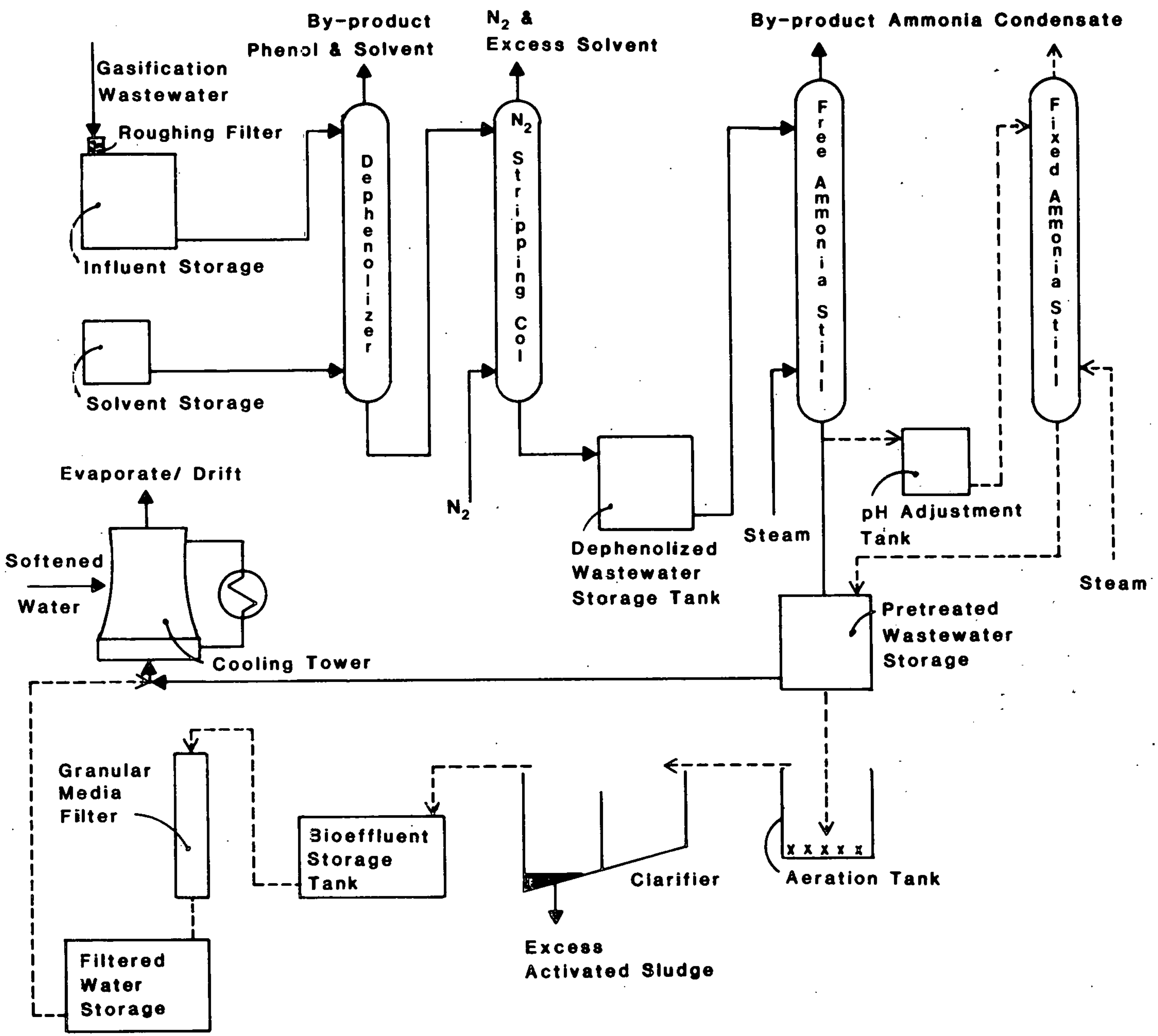


FIGURE 3-5. Flow diagram depicting wastewater treatment pilot plant.

4. - ATMOSPHERIC FLUIDIZED-BED COMBUSTION OF LOW-RANK COAL

PTPA No.: 604 B&R No.: AA3505300

Submitted by: G.A. Wiltsee, Jr., Manager, Project Management Division

Prepared by: G.M. Goblirsch, Project Manager, AFBC

Assigned GFETC Personnel: Stanley J. Miller
Douglas R. Hajicek

4.1 GOALS AND OBJECTIVES

The goal of the Atmospheric Fluidized-Bed Combustion (AFBC) Project at the Grand Forks Energy Technology Center (GFETC) is to provide the necessary data base for utilizing low-rank coals that will enable the technology to move into the private sector. Five major activities ongoing during FY 1982 will contribute to this overall goal:

1. Prepare a comprehensive topical report on the performance of low-rank coal in the AFBC.
2. Develop a data base on the formation of bed material agglomerates, including analytical studies to formulate a mechanism, and define the role of sodium in the formation of these agglomerates.
3. Characterize the particulate emitted from the AFBC burning low-rank coal and evaluate the performance of particulate control devices.
4. Evaluate the performance of heat transfer surfaces immersed in the bed burning low-rank coal.
5. Complete the data base on the retention of coal sulfur by the inherent coal ash alkali.

4.2 ACCOMPLISHMENTS

4.2.1 2.25-Ft^2 AFBC Testing

Five tests were performed on the 2.25-ft^2 AFBC at GFETC during the period April 1 through June 30, 1982. One test completed the series on low-sodium Beulah lignite which began last quarter. The purpose of this series of tests was to investigate the effects of various bed conditions on agglomeration; provide baseline information on the performance of the low-sodium sample; test the operability of a direct screw feed system for the fuel; evaluate the performance of the ESP as a collection device for low-rank coal AFBC fly ash; and evaluate the performance of the baghouse as a collection device for low-rank coal AFBC fly ash using felted fiberglass and woven fiberglass bags. The last test, BW9-9582, was conducted for the specific purpose of evaluating the effect of nahcolite addition on sulfur capture and bed material agglomeration.

The other four tests conducted this quarter were performed to evaluate the effects of ion exchange on the performance of Beulah lignite in the AFBC. Table 4-1 shows the operating conditions and the important results.

4.2.2 Agglomeration Results

The last of the low-sodium Beulah lignite tests was performed with a low rate of nahcolite injection to evaluate the effect of sodium in the form of sodium bicarbonate on sulfur capture and bed agglomeration. The nahcolite was added to the combustor at a rate of 3.4 lbs/hr or 0.02 lbs/lb coal. This is an added alkali-to-sulfur ratio of 0.28.

The sulfur retention under these conditions was 53 pct compared with about 47 pct without any added sorbent. This is only a utilization of about 21 pct for the added sodium, much lower than other tests have indicated. The test lasted for a duration of 42 hours, and was shut down at that time because of a coal feed problem, which was attributed to a deposit on the distribution plate, just below the coal feed pipe. No other agglomeration of any significance was found in the fluid bed after the run was complete.

The purpose of the ion-exchange test series was to identify the regime of operability of the AFBC as a function of sodium level with all other coal-specific effects remaining constant.

The Beulah high-sodium lignite, which had an analysis as shown in Table 4-2, was ion-exchanged with a sulfuric acid solution to a level of 6.4 pct Na_2O in the ash. Run BI1-0682 was made with this sample of lignite in the 2.25-ft^2 AFBC using a quartz sand bed under the conditions shown in Table 4-1. On post-test inspection, no agglomerates of any significance were found. The overall heat transfer coefficient, however, did decrease from 44.6 to 37.7 Btu/hr-ft^2-°F over the 74-hour run period, indicating a growth in bed particle size.

Test BI2-0782 was run with the parent Beulah lignite with a sodium content of approximately 9.6 pct Na_2O in the ash. This run was terminated early at 62 hours because of severe agglomeration of the bed material. This run was made under essentially the same conditions as Run BI1-0682 except for the coal feed stock. Approximately 75 pct of the bed material was contained in a single, large agglomerate. The condition, temperature, fluidization, etc., deteriorated rapidly toward the end of the test, likely accelerating the formation of the large agglomerate. The agglomerated bed is shown in Figure 4-1.

The lack of agglomeration in Run BI1-0682 indicated that the ion-exchange process changed the coal in some way, other than just removing sodium, because past experiences have indicated that some agglomeration would be noted after a 74-hour run on a coal with a 7 pct sodium level in the ash.

A second run on the ion-exchanged Beulah lignite was made under a more severe set of conditions, high temperature, and maximum recycle. The average Na_2O content in the coal ash for this test was 6.7 pct. Run BI3-0882 was run to 72 hours and underwent a normal shutdown. No agglomeration of bed material was noted on inspection of the bed after the combustor was opened. This test also indicated a decrease in overall heat transfer

TABLE 4-1

RUN CONDITIONS AND RESULTS FROM THIRD QUARTER AFBC RUNS

Run No.	BW9-0582	B11-0682	B12-0782	B13-0882	B14-0982
Purpose of Test	Agglomeration and Sulfur Capture With Nahcolite	Agglomeration With Ion-Exchanged Coal, 6.4% Na_2O	Agglomeration With Parent Coal, 9.6% Na_2O	Agglomeration With Ion-Exchanged Coal, 6.7 % Na_2O	Agglomeration With Ion-Exchanged Coal, 9.5% 110 hr. Run
Average Bed Temp., °F	1562	1553	1541	1647	1641
Velocity, ft/sec	6.4	6.2	6.0	5.9	5.9
Excess Air, %	24.4	20.2	21.0	20.7	20.4
Sulfur Retention, %	53	67	76	54	48
Heat Transfer Coefficient, Btu/hr-ft^2-°F	42	43	40	52	48
Oxides Of Nitrogen, lbs/10^6 Btu	0.51	0.49	0.51	0.46	0.59
Additive Type and lbs/hr	Nahcolite 3.4	N/A	N/A	N/A	N/A
Alkali/ Sulfur Ratio	0.80	0.63	0.84	0.73	1.04
Recycle Rate, lbs/hr	8.1	7.1	11.1	14.3	4.6

TABLE 4-2

COAL AND COAL ASH PROPERTIES OF BEULAH HIGH- AND LOW-SODIUM SAMPLES

Coal Type:	Beulah High-Sodium N. Dak. Lignite		Beulah Low-Sodium N. Dak. Lignite	
Coal Property:	Dry Basis	As Rec'd	Dry Basis	As Rec'd
Proximate Analysis:				
Moisture, %	N/A	21.0	N/A	20.9
Ash, %	11.9	9.4	14.1	11.1
Volatile matter, %	39.7	31.4	38.7	30.6
Fixed carbon, %	48.4	38.2	47.2	37.4
Heating value, Btu/lb	10,497	8,293	10,406	8,231
Ultimate Analysis, %:				
Carbon	62.6	49.4	61.5	48.7
Hydrogen	3.4	5.0	3.6	5.2
Nitrogen	0.9	0.7	0.8	0.7
Sulfur	1.4	1.1	2.8	2.2
Ash	11.9	9.4	14.1	11.1
Oxygen	19.8	34.4	17.2	32.1
Elemental Ash Analysis, %:				
SiO_2	16.5		27.9	
Al_2O_3	11.7		9.0	
Fe_2O_3	11.1		8.8	
TiO_2	0.8		1.0	
P_2O_5	0.9		0.9	
CaO	16.5		14.9	
MgO	6.1		5.7	
Na_2O	9.1		4.1	
K_2O	0.1		0.3	
SO_3	27.2		27.4	

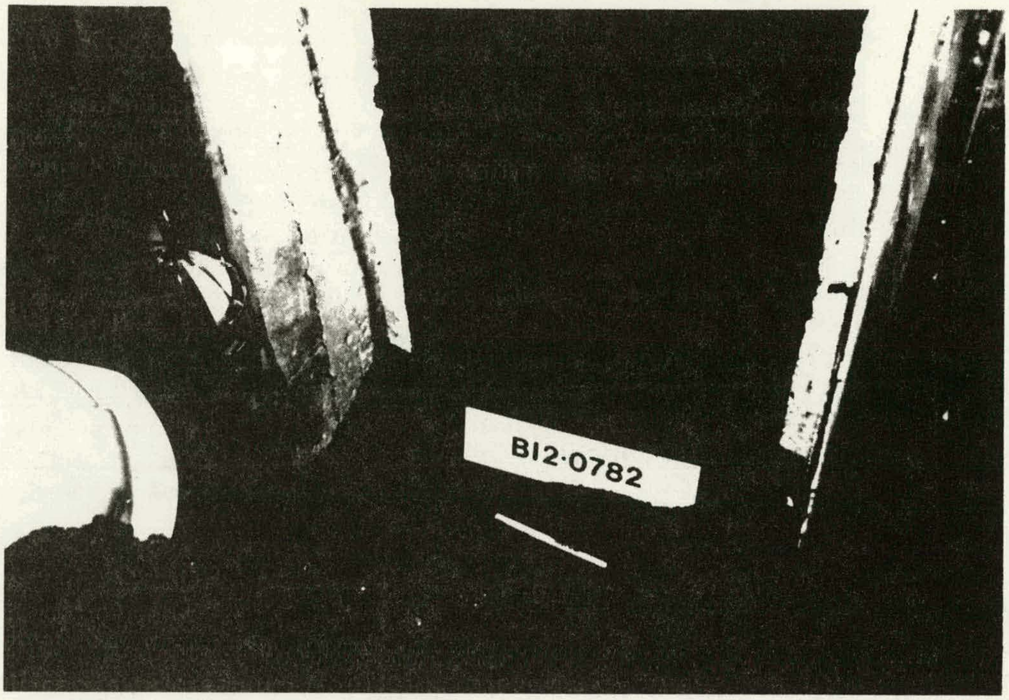


FIGURE 4-1. Quartz bed after 58 hours using high-sodium Beulah lignite.

coefficient from about 55.3 to about 49.3 Btu/hr-ft^2-°F over the run duration. The lower sulfur capture obtained in this test as compared to Run B11-0682 reflects the effect of temperature. The lower sulfur capture in Runs B11-0682 and B13-0882 compared to Run B12-0782 is an indication of the effect of sodium on sulfur capture.

The last run of this series was performed under the same conditions as B13-0882 except the coal was ion-exchanged only to an average level of 9.5 pct Na_2O in the ash. Run B14-0982 lasted a total of 110 hours and was shut down at that time because of schedule conflicts, not operational problems. After the run some agglomeration was found. About a 1-inch layer of agglomerated material was formed on the wall of the combustor, and several small agglomerates were found in the removed bed material. The heat transfer coefficient decreased from about 54 to 45 Btu/hr-ft^2-°F over about 62 hours of operation and then increased again as time went on to an average of about 49 Btu/hr-ft^2-°F at 110 hours. The reason for the slight increase at the end of the run is not clear at this time.

The concentration of sodium recorded as Na_2O in the bed at the end of the run was highest at 6.0 pct for Run B12-0782, which was performed with the parent coal sample. The lowest concentration found in an end-of-run bed material sample was from Run B13-0882, 2.4 pct in the ash. The concentration in the bed material sample after the 110-hour run with the ion-exchanged lignite was 5.4 pct, comparable to that found after the 62-hour run with the parent coal sample.

4.2.3 Contract Activities

EG&G submitted two test series final reports during the third quarter FY 1982, one for the Sarpy Creek heat transfer coefficient determination series, and a second from the Beulah low-sodium test series.

The Sarpy Creek series was a short, two-test series performed to evaluate the effect of position of the heat transfer surface in the bed on overall coefficient. For Test SC1-2881 a heat transfer tube with thermocouples mounted on the top and bottom outside surfaces was installed low in the bed in the third of seven positions. The overall coefficient for all tubes was 49.66 Btu/hr-ft^2-°F. The overall coefficient for the special tube in position 3 was 52.83 Btu/hr-ft^2-°F. For the second test the special tube was moved to the seventh position. The overall coefficient calculated for all tubes was 49.48 Btu/hr-ft^2-°F, and for the special tube, 52.48 Btu/hr-ft^2-°F. The total overall coefficient and the overall coefficient for the special tube were very close in both tests, indicating the position has little effect on overall coefficient for the conditions under which this test was performed.

The outside coefficient was determined for the top and bottom sides of the special tube by the direct measurement of surface temperature. These coefficients are not accurate, because they are calculated using the average heat flow over the tube; however, they do give relative values of heat flux. The top side of the tube showed a higher coefficient in both tests; an average of 60.58 Btu/hr-ft^2-°F was calculated. The difference between the two tests was less than 2 pct. The coefficient calculated for the bottom of the tube was an average of 55.38 Btu/hr-ft^2-°F and the difference was about 5 pct. The coefficient varied very little over the duration of the tests.

The second final report for the low-sodium Beulah lignite test series indicated that this fuel had an average Na_2O concentration in the coal ash of 4.1 pct see (Table 4-2). The purpose of this test series was to evaluate the effects of several additives and process modifications on the tendency for bed material agglomeration. Table 4-3 shows the test conditions and results of this series of nine tests.

The UND agglomeration analysis final report was completed and submitted. Only minor changes were requested to the second draft copy; these are currently being made by UND. The report proposes a mechanism for the agglomeration of quartz bed material, which takes place in four stages:

A. Stage 1 - Initial Ash Coating

Samples of bed material collected early in the run have a fine coating, about 50 microns thick, consisting of sulfated aluminosilicate particles (Figure 4-2a). The coatings contain some coarser ash materials in the outer parts, and the inner parts have penetrated the quartz grains slightly along gently curved or cuspate embayments. The quartz grains are extensively fractured, apparently as a result of thermal stresses.

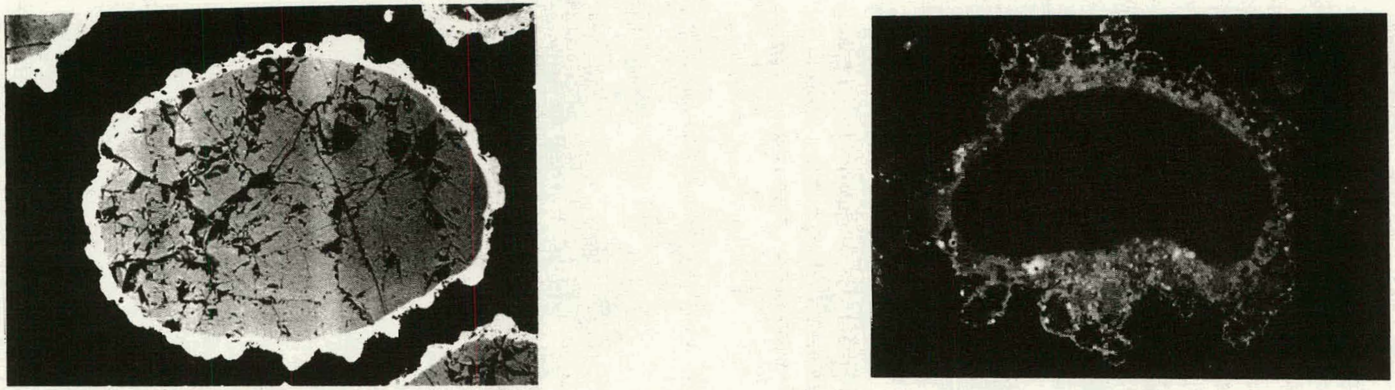
B. Stage 2 - Thickened Nodular Coatings

Longer bed usage results in the development of thicker ash coatings (about 100 - 300 microns thick) with distinct nodular outer surfaces resulting from incorporation of larger ash particles (Figure 4-2b). Sulfating, shown by lighter-colored areas in the SEM photographs, is common within both the finer and coarser ash particles of the coating. Extensive reaction penetrating quartz grains may occur (Figure 4-2c).

TABLE 4-3

BEULAH LOW-SODIUM TEST SERIES CONDITIONS AND RESULTS

Run No.	Purpose Of Test	Average Bed Temp. °F	Velocity ft/sec	Excess Air °F	Sulfur Retention °F	Heat Transfer Coefficient Btu/hr ft^2°F	Oxides Of Nitrogen lb/10^6 Btu	Addictive Type and Rate lb/hr	Alkali/ Sulfur Ratio	Recycle Rate lb/hr
BW1-3081	Agglomeration and Sulfur Capture Baseline	1553	6.2	18	59	46	0.38	N/A	0.49	35.7
BW2-3181	Agglomeration and Sulfur Capture Rerun	1533	6.6	20	48	42	0.41	N/A	0.48	44.7
BW3-3381	Sulfur Capture with Limestone	1501	6.5	21	91	40	0.36	Linwood limestone 11.4	1.72	40.1
BW4-3481	Agglomeration and Sulfur Capture with NaCL	1531	6.4	19	75	42	0.29	NaCL 5.9	1.01	19.5
Screw Feed BW5-0182	Feed System Effect On Agglomeration and Sulfur Capture	1558	5.8	18	55	43	0.44	N/A	0.47	0
Pneumatic			6.1	20	39	41	0.46			0
BW6-0282	Particulate Test/ESP Performance	1537	6.0	15	46	40	0.40	N/A	0.52	16.4
BW7-0382	Particulate Test Baghouse Performance	1546	6.2	16	48	44	0.37	N/A	0.52	40.5
BW8-0482	Agglomeration and Sulfur Capture With Trona	1522	5.5	21	93	35	0.56	Trona 12.7	1.47	0
BW9-0582	Agglomeration and Sulfur Capture With Nahcolite	1562	6.4	24	53	42	0.51	Nahcolite 3.4	0.80	8.1



2a Initial ash coating on quartz bed material. SEM/BEI image. Run BA1- 2181, 40 hrs.

2b Thickened nodular ash coating on quartz bed material. SEM/BEI image. Run BA1-2181, 40 hrs.

2c Extensive penetration of end of quartz grain by reaction with ash coating. Nodular material in the quartz grain may indicate growth of nodules in place. PLM photomicrograph, plane polarized light. Length of field = 1.2 mm. Run BA1-2181

2d Quartz bed grains loosely cemented by sulfate aluminosilicate ash. SEM/BEI image. Run BA1-2181

FIGURE 4.3. SEM photomicrographs of non-agglomerated and agglomerated quartz bed materials.

C. Stage 3 - Sulfated Ash-Cemented Agglomerates

In this stage, the quartz grains are loosely held together by a cement of sulfated aluminosilicate ash (Figure 4-2d). Penetration of quartz grains by fine-grained ash is more extensive.

D. Stage 4 - Glass-Cemented Agglomerates

In the final stage, quartz grains are bound by sulfated ash which has partly melted and crystallized through reaction of the hot ash and the quartz grains. Resultant cooled agglomerates consist of quartz grains of the bed material bonded by a mixture of sulfated ash and calcium-rich, sulfur-poor glass (Figure 4-2e), with an intermediate reaction zone made up of a sulfur-depleted, silicon-enriched ash portion with a fringe of melilite or augite crystals projecting into the glass (Figure 4-2f). Some quartz grains are partly melted and/or recrystallized to the high temperature polymorph, cristobalite or other phases.

A similar mechanism has been proposed for the formation of an agglomerate in a limestone bed. The limestone grains undergo the following reactions.

1. The limestone was calcined by loss of CO_2, and conversion to CaO with subsequent increases in S, Fe, Na, and other elements. These reactions produced concentric alteration zones, high Ca and S contents, and the reddish color that characterized typical grains (Figure 4-3).

2. Continued reaction produced thicker sulfated ash coatings and more thoroughly altered bed grains.

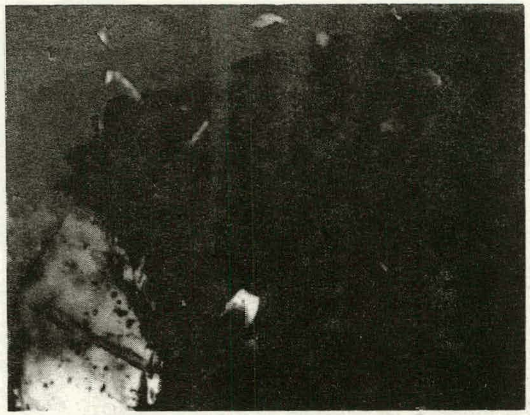
3. Bed grains were observed to disintegrate extensively and become mixed with ash coatings, producing a weakly bonded agglomerate consisting of masses of sulfated ash and altered limestone bed grains and fragments. The altered limestone appeared to recrystallize to coarse crystals of anhydrite in a fine-grained matrix containing abundant Ca, S, and Si. Other phases, not yet identified, occurred in the limestone agglomerates including crystalline Fe-Ca oxides and other iron-rich zones and coatings.

The contract with UND to continue the agglomeration work has been awarded. This work basically involves the determination of the role of sodium, and the identification of the phase relationships between involved compounds.

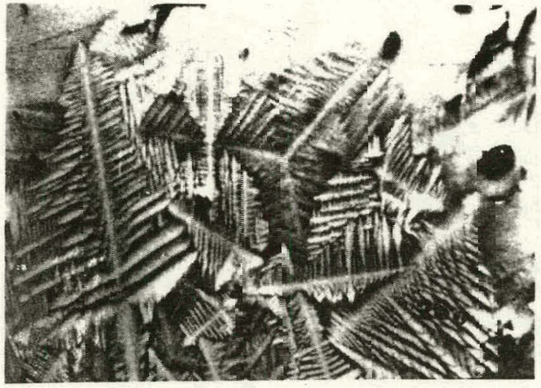
The contract to evaluate the heat transfer data from the 2.25-ft^2 AFBC obtained over the last year has been awarded to Dr. Grewal at UND. The work on designing the heat transfer tubes to determine the radiative component of the overall coefficient has been completed. Some problems in constructing the tubes have been encountered. The surface coatings necessary to obtain high- and low-emissivity surfaces have not been identified because of potential erosion problems. Work to identify surface coatings is continuing.

Combustion Power Company has started to reduce data and prepare sections of the topical report on Low-Rank Coal AFBC. Some work on sections of the topical report have been started by both EG&G and GFETC personnel.

2e Quartz bed agglomerate bonded by altered sulfated ash, to the right of the dotted boundary; Ca-rich, S-poor glass, to the left of the dashed boundary; and intermediate fringe of melilite or augite crystals. SEM/BEI image. Run BA1-2181, 69 hrs.



2f Closer inspection of lower center of Figure 3e showing light quartz grain, gray glass, and crystals of melilite or augite projecting into the glass. PLM photomicrograph, partially crossed polars. Run BA1-2181, 69 hrs.



2g Detail of lower center of Figure 3f showing dendritic crystal form of melilite or augite. SEM/SEI image. Run BA1-2181, 69 hrs.

FIGURE 4.2. SEM photomicrographs of non-agglomerated and agglomerated quartz bed materials (continued).

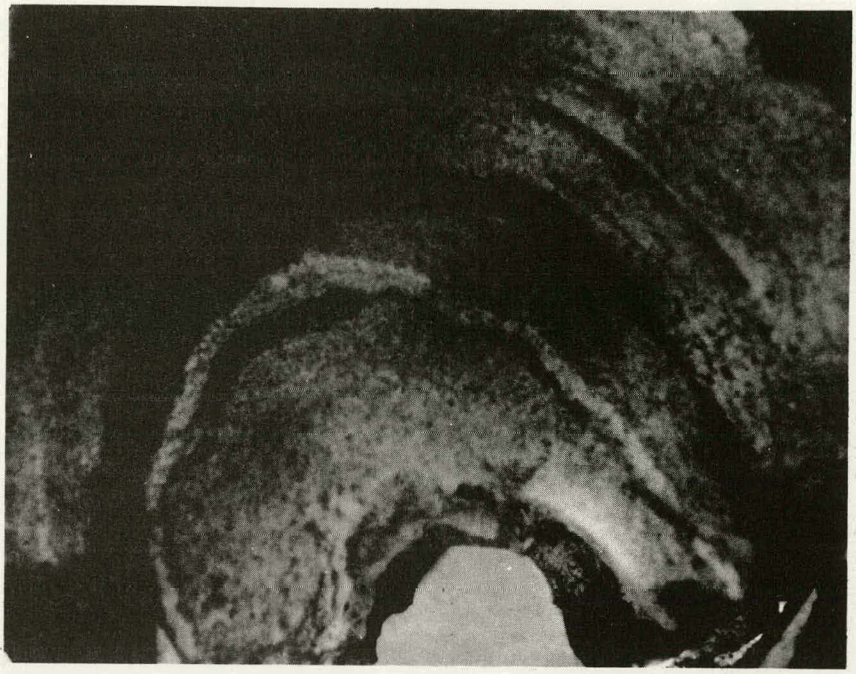


FIGURE 4-3. Concentric alternation zones and reacted limestone bed material. SEM/BEI image. Run BA4-2481, 169 hrs.

5. - ASH FOULING AND COMBUSTION MODIFICATION FOR LOW-RANK COALS

PTPA No.: 605 B&R No.: AA1505000

Submitted by: G.A. Wiltsee, Jr., Manager, Project Management Division

Prepared by: M.L. Jones, Project Manager, Ash Fouling and Combustion Modification of Low-Rank Coals

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A.L. Severson

5.1 GOALS AND OBJECTIVES

The goal of the Ash Fouling and Combustion Modification Project at the Grand Forks Energy Technology Center (GFETC) is a greater understanding of the combustion process in low-rank coal. Particular interest is given to the fate of the inorganics in coal in an attempt to decrease or eliminate the ash fouling problems associated with combustion of low-rank coals.

The specific objectives of the project in FY 1982 are to:

1. Establish and define the benefits of limestone addition for reducing the effects of boiler tube fouling in utility boilers.
2. Extend pilot plant studies using the GFETC ash fouling unit to characterize selected coals.
3. Consolidate all technical information generated at GFETC into a topical report on ash fouling.
4. Obtain experimental data on the reactions of alkali species in low-rank coal flames.
5. Design and construct experimental apparatus to optically examine the combustion of individual coal particles.

The planned activities in the third quarter to support the FY 1982 objectives include the following:

1. Evaluate the success of phase one of the additive program.
2. Complete combustion testing of Morwell and Esperance lignites.
3. Complete outline for ash fouling topical report.

5.2 ACCOMPLISHMENTS

5.2.1 Field Test to Demonstrate the Benefits of Additives Use in Preventing Ash Fouling in Utility Boilers

The test program to evaluate additives in boilers using high-fouling low-rank coals was divided into four parts to alternate between operation with and without additive use. Each segment was scheduled to be approximately three months in duration.

Collection of data for the first segment was been completed. During this time the boiler was operated without any additive being used. These data were collected between March 14 and May 7, 1982, on a Babcock and Wilcox opposed-wall, pc-fired unit with a gross rating of 216 MW. This unit operated on a high-fouling North Dakota lignite and experienced considerable fouling during normal operation.

A major problem developed with the use of this unit in completing the scheduled test program. Due to the low power demand experienced by the station in question, the load level was very low. For the period in questions, the average load level was only 65 pct of rated value. At these low load levels, appreciable fouling was not experienced, thus limiting the value of these data to establish the economic benefits.

Since no change in load requirements for the Leland Olds Station is expected in the near future, the decision was made to discontinue collecting data at this station. An interim report is being completed and an alternate site is being considered.

5.2.2 Combustion Testing of Morwell and Esperance Lignite

Combustion testing of Morwell and Esperance coals from Australia have been completed in the ash fouling unit located at GFETC. Results for the tests are found in Table 5-1.

The results of the Esperance burns show some very interesting results. It should be noted that the Esperance lignite is a high-ash, high-moisture, and high-sodium coal. In this case much of the sodium is present as NaCl. As would be expected, the coal rates as a high-fouling fuel on GFETC's relative fouling index. In addition, the deposits exposed to 2000°F flue gas appeared totally fused, with an appearance very much like wall slag seen in the combustion section of the unit.

5.2.3 Ash Fouling Topical Report

GFETC is planning to complete a monograph covering the almost twenty years of work on ash fouling of low-rank coals. This document is intended to include data generated from field and pilot-plant testing, analytical studies, and engineering/economic studies. Progress to date has involved generation of a detailed outline which will lead to a completed report by June 1983.

TABLE 5-1

ASH FOULING PILOT PLANT TEST RESULTS FOR MORWELL AND ESPERANCE COALS

Coal	Deposit at 1st probe (g deposit) / kg coal	Deposit Strength Results			
		SRF[a]	Duct Index (%)	Friability	MM Dia
Beulah CPC	2.43	5.5	26	76.8	1.8
Morwell	0.32	1	ND[b]	ND	ND
Esperance Sample B	1.37	10	ND[c]	ND	ND
Esperance Sample C	4.52	10	ND[c]	ND	ND
Esperance A	6.11	10	ND[c]	ND	ND
Esperance B	3.70	10	ND[c]	ND	ND

[a] SRF = Strength rating factor

[b] Values not determined due to small amount of material available.

[c] Values not determined since the material was so hard that the procedure normally used was not valid.

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

PTPA NO.: 2-634 B&R NO.: AA0505100

Submitted by: G.A.Wiltsee, Jr., Manager, Project Management Division

Prepared by: H.M. Ness, Project Manager, Combined Flue Gas Cleanup/
Simultaneous SO_x-NO_x Control

Assigned GFETC Personnel: G.L. Schelkoph
D.K. Rindt

6.1 GOALS AND OBJECTIVES

The goals of the Flue Gas Cleanup Project at the Grand Forks Energy Technology Center (GFETC) are to: 1) investigate alternative methods for simultaneous control of SO_x/NO_x emissions when burning low-rank western coals; and 2) complete activities characterizing fly ash alkali Flue Gas Desulfurization (FGD) wet scrubber systems.

To accomplish these objectives, the FY 1982 Flue Gas Cleanup Project consists of the following major elements: 1) dry sorbent studies using a 75-lb/hr coal-fired combustor and a 130-scfm propane-fired combustor; 2) analytical characterization of dry sorbent reactants and spent reactants; and 3) characterization of fly ash alkali FGD wet scrubber systems.

6.2 ACCOMPLISHMENTS

6.2.1 Simultaneous SOx/NOx Control

The GFETC Simultaneous SO_x/NO_x Flue Gas Cleanup Project consists of controlling SO_x emission by furnace injection techniques using primarily calcium compounds. The SO_x sorbents are collected by a high-temperature chemical reactor such as a ceramic filter. Control of NO_x emissions will be investigated using ammonia-catalytic reduction methods, and by throw-away sorbents that may be collected by ceramic filters operated at high temperatures (up to 1000°F) or low temperatures (down to 200°F).

Experiments investigating simultaneous SO_x/NO_x emission control are conducted using a 130-scfm propane-fired combustor equipped with a baghouse capable of operating on flue gas at temperatures up to 1000°F. A schematic of the combustor-baghouse is presented in Figure 6-1.

Several experiments were performed to determine morphological changes in limestone particles as a function of temperature. Limestone, screened to provide three particle size ranges, was injected into flue gas at temperatures ranging from 1200°F up to about 3000°F. Samples were collected at isokinetic conditions at the inlet to the baghouse. Baghouse operating temperature averaged 741°F. The three limestone particle size ranges were -325 mesh, -100+200 mesh, and -20+42 mesh. The surface area of the limestone samples was measured using B.E.T. techniques, and the results as a function of injection temperature are presented in Figure 6-2.

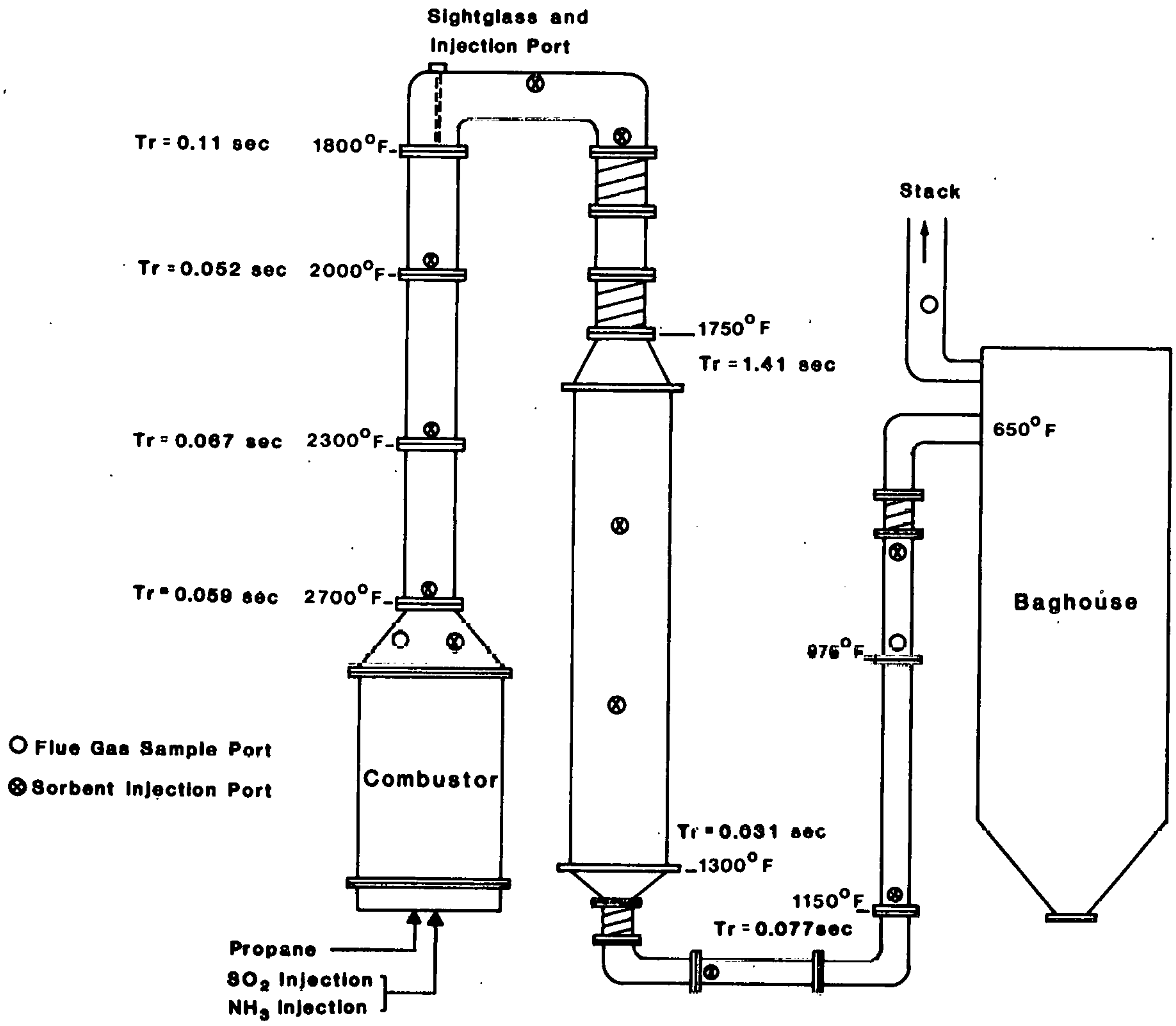

FIGURE 6-1. Schematic of 130-scfm combustor/baghouse PDU; baghouse can operate up to 1000°F.

The data indicate a general increase in surface area with increasing temperature. No significant differences were observed between -325-mesh particles and -100+200-mesh particles. Results for -20+42-mesh particles indicate less surface area development than the other two particle size ranges. In general, all three size ranges produced relatively low surface area development, despite complete calcination at high temperatures.

The conversion of -325-mesh $CaCO_3$ to CaO at various temperatures is shown in x-ray diffraction spectra presented in Figure 6-3. The limestone was injected into hot flue gas without SO_2, and collected isokinetically at the baghouse inlet using a high-volume sampler. The data indicate that conversion of $CaCO_3$ to CaO did not begin until injected into flue gas at a temperature of 1800°F. The percent conversion as a function of flue gas temperature (at the point of injection) is presented in Figure 6-4. The data indicate that about 90 to 95 pct conversion occurs at approximately 2800°F.

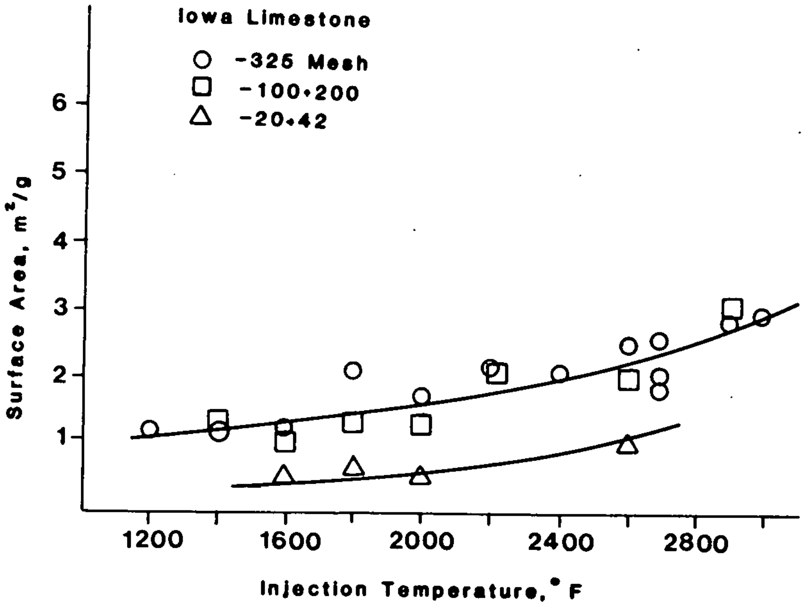

FIGURE 6-2. Surface area of Iowa limestone after injection into flue gas (without SO_2) at various temperatures.

However, sorbent utilization values do not significantly exceed 10 pct, and are nominally consistent with low surface area development. The relatively low reactivity of the limestone is thought to be due to inadequate exposure time at high temperatures required for good calcination to occur, and is therefore characteristic of GFETC's PDU apparatus.

The x-ray diffraction spectra for -100+200-mesh particles indicates less conversion when compared with -325-mesh particles; however, the surface area development is similar, as shown in Figure 6-2. The development of a porous structure for -325-mesh particles was examined using SEM techniques; results are presented in Figures 6-5 through 6-9. The data showing minimal pore development are generally consistent with surface area measurements and the x-ray diffraction data.

6.2.2 Reactivity of Western Fly Ash in a Spray Dryer FGD Process

Work on this contract is being conducted by the University of Tennessee. Specific project objectives are to: 1) characterize SO_2 removal in a pilot plant spray dryer FGD process due to addition of western alkaline fly ashes; and 2) investigate chemical techniques of enhancing fly ash reactivity so as to increase SO_2 removal efficiencies in a spray dryer FGD unit.

Twenty-two fly ash materials have been collected and tested using a 1000-scfm spray dryer pilot plant to characterize SO_2 removal capacity. The ash materials are derived from low-rank coals primarily representative of the Gulf Coast, Rocky Mountain, and the Northern Great Plains Provinces. Five fly ash materials were derived from combustion of bituminous eastern coal. The power plants providing the fly ashes are presented in Table 6-1.

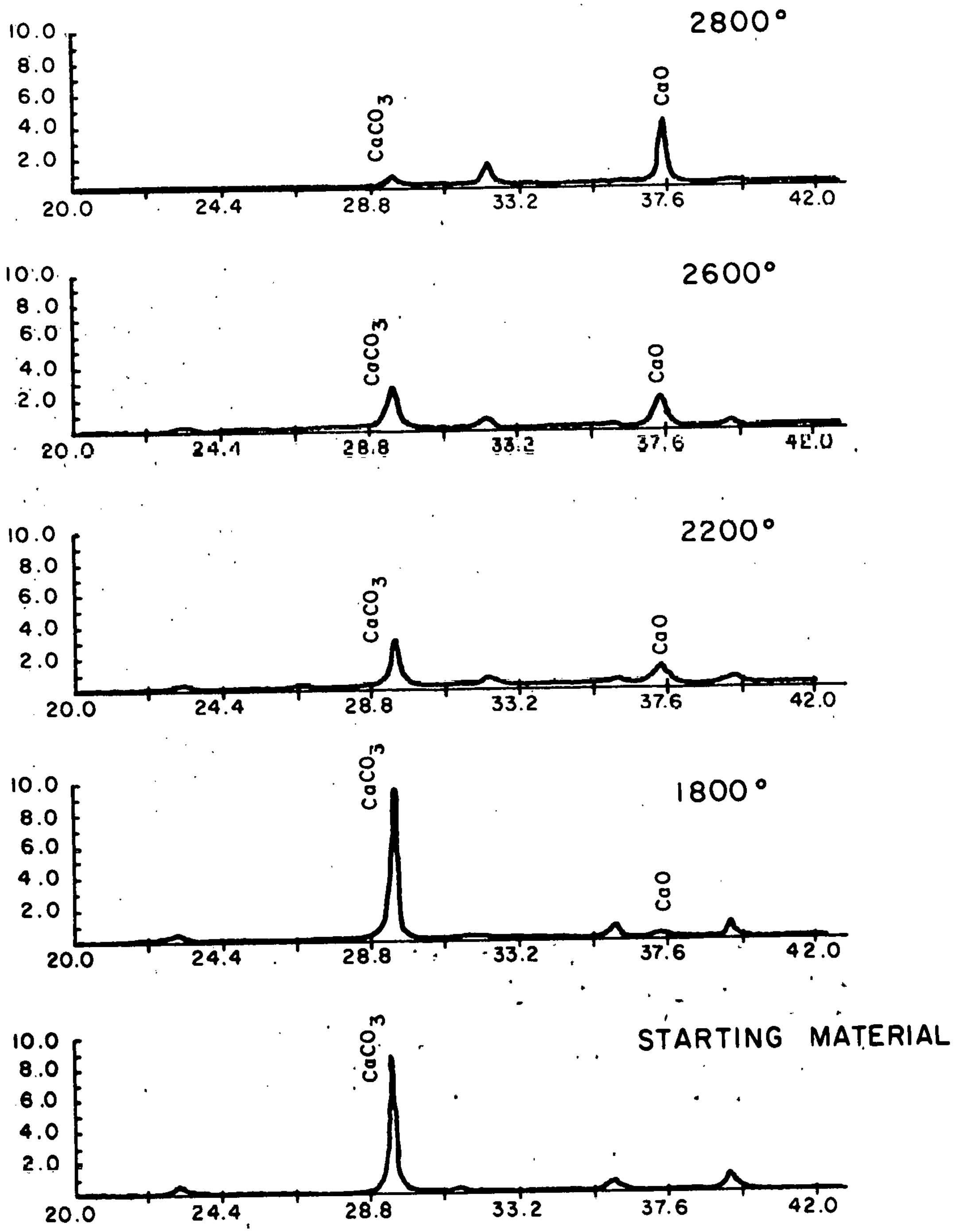

FIGURE 6-3. X-ray diffraction spectra showing conversion of $CaCO_3$ to CaO with increasing temperature for Iowa limestone (-325 mesh).

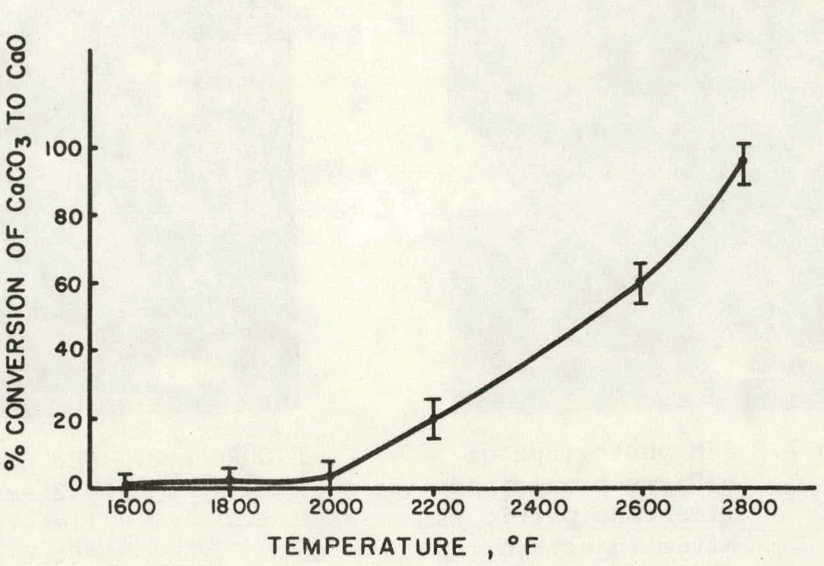

FIGURE 6-4. Percentage conversion of $CaCO_3$ to CaO as a function of flue gas temperature for -325-mesh Iowa limestone.

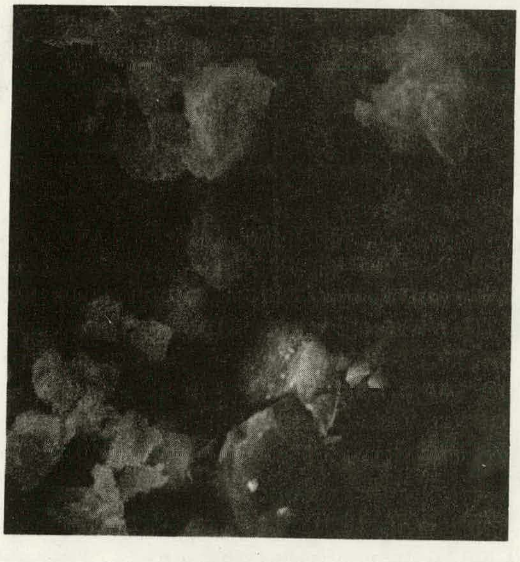

FIGURE 6-5. SEM photograph of -325-mesh limestone feed material before injection into hot flue gas.

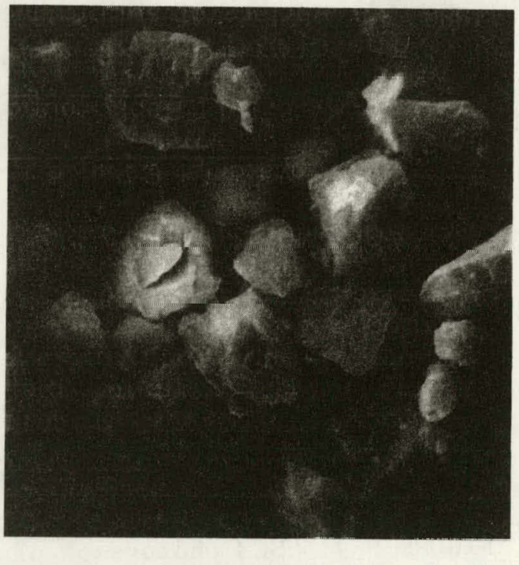

FIGURE 6-6. SEM photograph of -325-mesh calcined limestone particles after injection into flue gas at 1400°F.

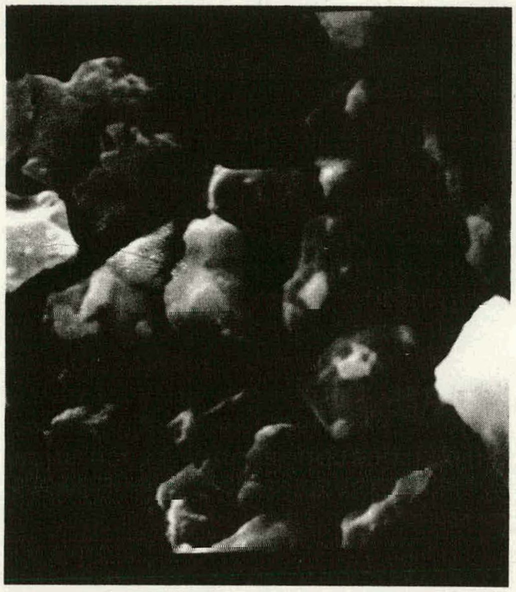

FIGURE 6-7. SEM photograph of -325-mesh calcined limestone particles after injection into flue gas at 2000°F.

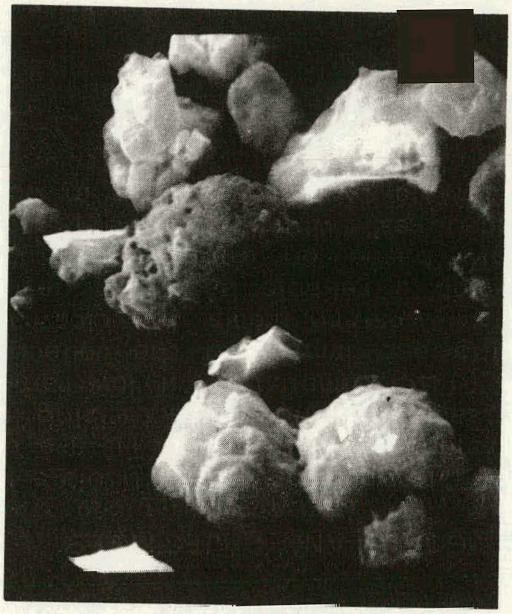

FIGURE 6-8. SEM photograph of -325-mesh calcined limestone particles after injection into flue gas at 2600°F.

FIGURE 6-9. SEM photograph of -325-mesh calcined limestone particles after injection into flue gas at 2700°F.

TABLE 6-1

ORIGIN OF THE FLY ASHES INVESTIGATED

Fly Ash No.	Power Plant of Origin	Type of Fuel (approximate)	Source
1	Belews Creek Steam Station	bituminous	Low sulfur eastern coal
2	Bowen Steam Plant	bituminous	Eastern Kentucky
3[a]	Clay Boswell Unit 4	subbituminous	Big Sky Mine-Colstrip Montana
4	Nebraska Public Power Station Gerald Gentleman Station	subbituminous	Black Thunder Mine Campbell Co., Wyoming
5	Pacific Power and Light Wyodak Plant	subbituminous	Wyodak Resources-Wyodak Mine
6	Hunter Steam Plant	bituminous	Wilberg Mine-Emery Co., Utah
7	Cherokee #4	bituminous	Colorado Western Slope
8	Gallagher Station II Public Service of Indiana	bituminous	Amax Aryshire
9	Texas Utilities Generating Co., - Big Brown	lignite	Freestone County
10	New Madrid Power Plant #2	bituminous	Southern Illinois, Seam #6
11	Ohio Edison-Gorge	bituminous	Ohio strip mine
12	Harrington Station : Southwestern Public Service Co.,	subbituminous	Black Thunder Mine near Gillette, Wyoming
13	Laramie River Station	subbituminous	Cordero Mine
14	Basin Electric Power Cooperative-Unit 1	lignite	Consolidated Coal Co., Stanton, North Dakota
15	Milton R. Young Station Center Unit 1	lignite	Baukol-Noonan Mine Center, North Dakota
16	United Power Assoc. Cooperative Power Assoc.	lignite	Falkirk Mine Underwood, North Dakota
17	Black Hills Power and Light Company	subbituminous	Wyodak Mine-Wyoming
18	Otter Tail Power Hoot Lake Station Unit #2	lignite	Knife River Coal Mining Co., Beulah, North Dakota
19[a]	Minnesota Power and Light Co., Clay Boswell Station	subbituminous	Big Sky Mine Colstrip, Montana
20	Monifer Resources San Antonio Public Service	subbituminous	Cordero Mine, Wyoming
21	University of Tennessee Steam Plant	bituminous	Eastern Kentucky
22	Marshall Steam Station	bituminous	Low sulfur eastern coal

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[a] Fly ashes obtained from the same station, however, their production resulted from different combustion conditions.

Sulfur dioxide removal efficiencies due to addition of a fly ash slurry were determined by measuring the inlet and outlet SO_2 levels from the spray dryer and from a fabric filter baghouse. Operating conditions for all tests are presented in Table 6-2.

TABLE 6-2

SPRAY DRYER OPERATING CONDITIONS

Spray dryer:	
Inlet temperature	300°F
Outlet temperature	138°F
Approach to dew point	20°F
Fly ash slurry	1.45 lb/gal
Flue gas SO_2	600-800 ppm

The preliminary SO_2 removal efficiencies are presented in Table 6-3 for the spray dryer, the baghouse, and the combined spray dryer-baghouse system.

Future work will examine correlations of the SO_2 removal efficiencies with fly ash properties such as coal rank, alkali content, and surface area, in an attempt to develop equations predicting performance in a spray dryer system.

TABLE 6-3

SULFUR DIOXIDE REMOVAL EFFICIENCY BY A FLY ASH SLURRY IN A SPRAY DRYER-BAGHOUSE SYSTEM

	SO_2 Removal Efficiency		
Fly Ash No.	Spray Dryer	Baghouse	System[a]
1	0.	3.9	0.9
2	12.0	-	6.9
3	7.0	13.7	17.4
4	35.0		29.6
5	21.7	2.5	21.4
6	25.7		23.0
7	3.7	0.3	1.8
8	7.4	1.5	6.5
9	3.1	4.1	4.8
10	5.6	2.3	5.6
11	2.4		0.
12	26.8	13.6	25.6
13	19.5	10.5	25.7
14	13.1	4.9	15.1
15	19.1	4.8	20.7
16	10.1	1.1	8.9
17	23.5	6.2	26.0
18	16.7	1.4	17.9
18[a,b]	16.9	38.0	46.2
19	13.3	15.2	24.2
20	14.2	0.8	12.6
21	13.0	21.3	29.3
22	1.9	1.0	0.6

[a] Efficiency data corrected for SO_2 removal by water feed without fly ash.

[b] Particles were reduced in size by ball milling.

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

PTPA Nos.:	2-634 and 2-612	B&R Nos.:	AA0505100 AA0515000

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7.1 GOALS AND OBJECTIVES

The goals of the Particulate Control and Hydrocarbons and Trace Element Emissions Projects at GFETC are to: 1) develop, evaluate, and apply methods for sampling and characterizing particulate matter generated in conventional for AFBC combustion of low-rank western coals; 2) develop means for evaluating and improving the collectability of high-resistivity fly ash from low-sulfur western coals by electrostatic precipitation, and other means; 3) develop a reliable basis for designing and sizing particulate control equipment, based on information obtained from laboratory and pilot plant test procedures, which can be performed on reasonably small samples of coal obtainable by core drilling in advance of mining; and 4) characterize and measure the organic and trace element emissions from pc-fired and AFBC furnaces.

The specific objectives for FY 1982 are to:

1. Sample, size, and characterize particulates.
2. Collect and analyze low-rank coal flue gas and fly ash samples for organics and trace elements before and after particulate control devices.
3. Develop advanced sampling and characterizing methods.
4. Field test particulate control devices (for example, baghouses and ESPs).
5. Test advanced, high-efficiency particulate equipment.
6. Collect samples and perform material balance on selected trace elements emitted from an AFBC unit burning low-rank coal.

7.2 ACCOMPLISHMENTS

7.2.1 Material Balance in AFBC

7.2.1.1 Background

The GFETC 2.25-ft^2 AFBC pilot plant has been operational since January 1980. A variety of subbituminous coals and lignites have been burned in this equipment. Performance, retained ash and fly ash analyses, post-run bed characteristics, and flue gas analyses have been performed as functions of operating parameters. Sulfur oxide capture by retained (recycled) alkaline fly ash and by injected limestone has been studied extensively.

Current interest in and regulatory attention to gaseous and particulate emissions and hazardous solid waste disposal requires an understanding of the fate of several inorganic species introduced to an AFBC in the various feedstocks, which include fuel and combustion air, bed material, and injected FGD agents. Therefore, GFETC contracted with GCA/Technology Division, GCA Corporation, Bedford, Massachusetts, to perform a material balance study on GFETC's AFBC during a specific test burn of Beulah, North Dakota, lignite with a limestone bed (1,2).

In addition to the material balance investigation performed by GCA, other studies performed during this specific test burn (FB2-BA5-2581) included:

- o Trace element concentrations in post-run baghouse ash composite, using x-ray fluorescence (XRF) and neutron activation analysis (NAA).
- o Investigation of fly ash mutagenicity performed by DOE's Laboratory for Energy Related Health Research (LERHR) at University of California-Davis.
- o GFETC analyses of polycyclic organic matter in this fly ash.
- o Bed aggregation studies, fly gas emissions, and sulfur retention (2,3).

Because of the diversity and breadth of studies arising from this test burn, and the latter's relation to other studies in the AFBC project, this particular AFBC run may well be one of the most thoroughly investigated of all fossil-fueled AFBC runs.

7.2.1.2 Description of AFBC

The GFETC 2.25-ft^2 AFBC is a square, refractory-lined steel shell with a flat, drilled distributor plate. Nominal feed rates are 180 lbs coal/hr with a superficial air velocity of 9 ft/sec at 20 pct excess air. In contrast to combustion zone temperatures in pc-fired furnaces, AFBC bed temperatures are quite low: ∿1450°-1650°F. As a consequence, fly ash particle size distributions, morphology, and mineral composition tend to differ dramatically from those observed in pc-fired combustion.

Particulate emissions are controlled by two cyclones and a baghouse in series. The secondary cyclone is designed to be 65 to 71 pct efficient for 4-5 μm particles at 250 scfm and 1200°F.

The pulse jet baghouse contains eighteen 6" x 108" bags of woven fiberglass fabric with silicon graphite coating. Baghouse face velocities (air-to-cloth ratios) were ∿ 1.6 ft/min, and average $\Delta p \cong 2$ inch W.G.

Figure 7-1 is a schematic of the AFBC showing ash and fly ash sampling points.

7.2.1.3 Flue Gas Sampling

During the nine-day test burn, seven flue gas samples were collected using an Acurex Source Assessment Sampling System (SASS Train), illustrated schematically in Figure 7-2. The SASS Train is a high-volume (4-6 ACFM) sampling configuration of cyclones and impingers designed to collect size-fractionated particulate matter and volatile metals.

The flue gas sampling point (Figure 7-1) downstream from the baghouse was located 3.7 duct diameters upstream and 1.9 diameters downstream from flow disturbances. This is not an ideal location; however, none other was available. Particulates are collected in the sequence of 3 cyclones (10, 3, and 1μm cutoffs) and a back-up filter. Volatile inorganics are captured in the impingers which contain, variously, 30 pct H_2O_2, 0.1N nitric acid, desiccant, or are empty.

Very low dust loadings necessitated extraordinarily long sampling periods, the longest of which corresponded to 7000 dry scfm.

7.2.1.4 Solid Sampling

Coal was sampled periodically from the feeder, and a run composite was created. In addition, coal samples were collected to correspond to the fuel combusted during each flue gas sampling period. Limestone feed material was collected at intervals and composited in a manner similar to the coal samples. Bed drain (spent bed material) was sampled periodically throughout the run to track accumulation or depletion of elements in the bed. Fly ash sampling was performed at several locations and intervals: primary and secondary cyclones, baghouse, and residues between heat exhangers.

Tables 7-1, 7-2, and 7-3 summarize the sampling and sample preparation schemes and ICAP detection limits.

7.2.1.5 Analytical Results

Results of analyses of coal and limestone feeds, cyclone and baghouse catches, and bed drain appear in Tables 7-4 to 7-9. Fly ash (particulate matter) analyses and gas phase (volatile metal component) analyses are in Tables 7-10 and 7-11.

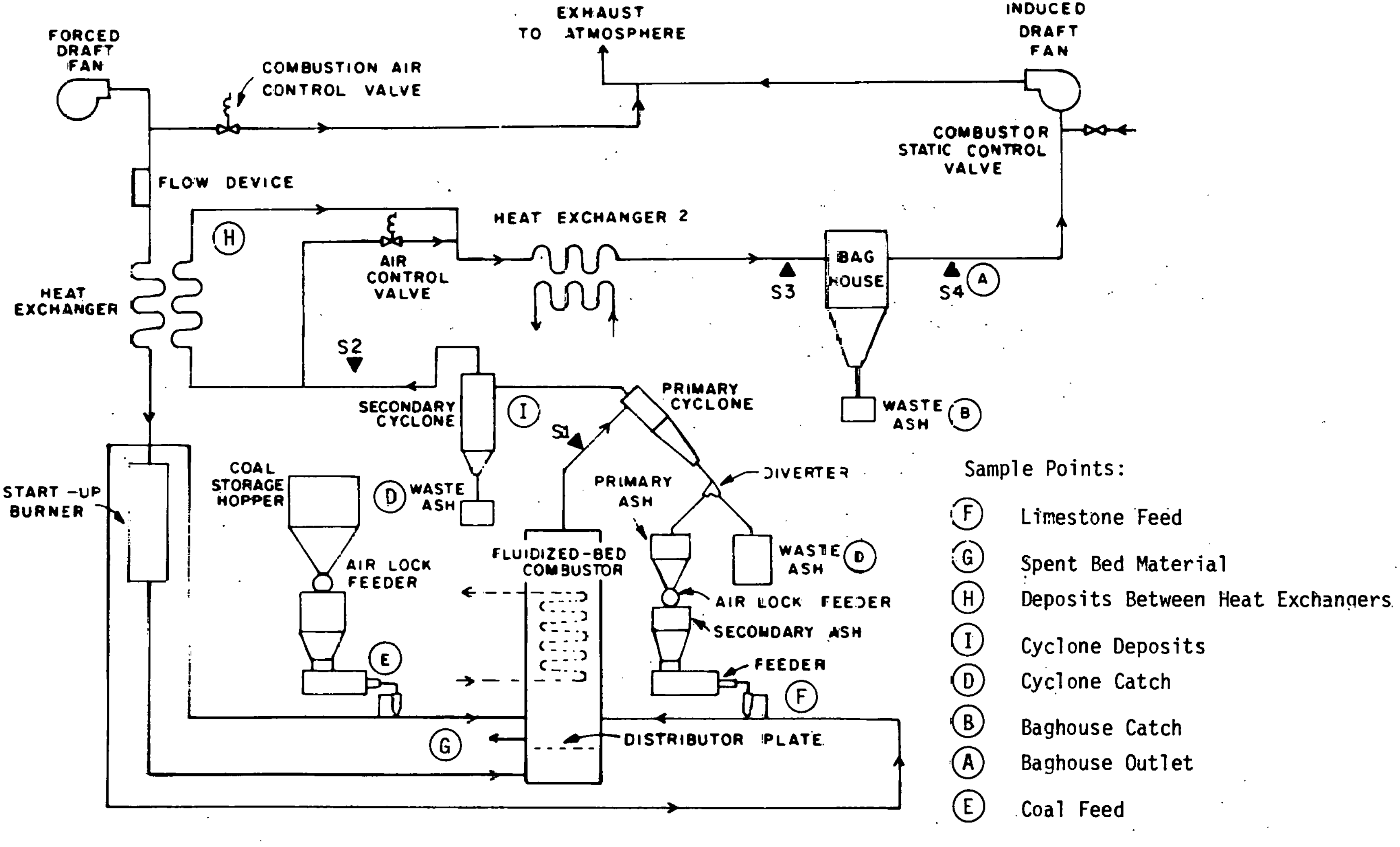

FIGURE 7-1. Schematic of AFBC showing sampling points (From Reference 1).

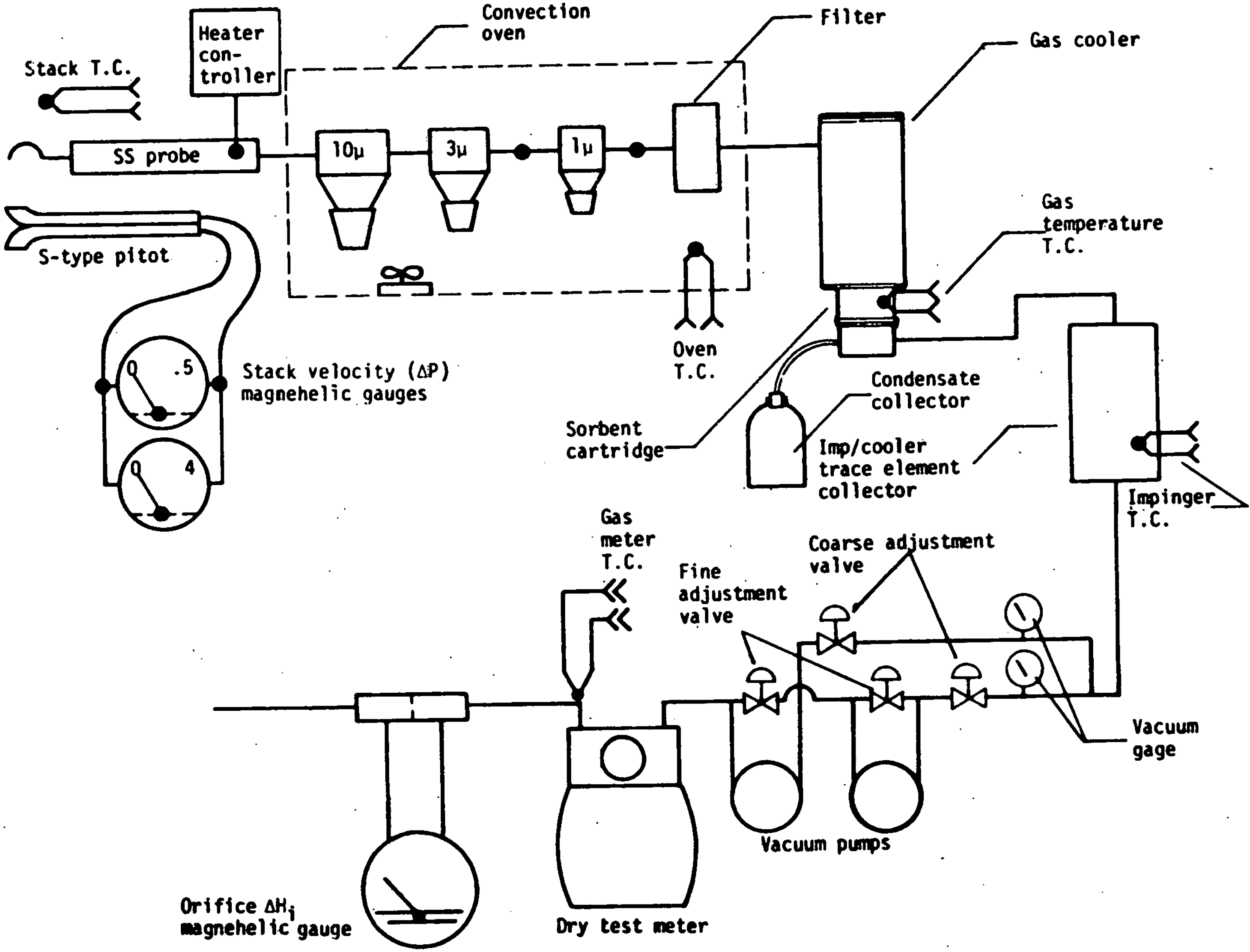

FIGURE 7-2. SASS-Train flow diagram. (From Reference 9).

TABLE 7-1

SAMPLE SUMMARY (Ref. 1)

		Samples	Samples Collected
Flue Gas			
	SASS Train -	10 µm cyclone dry catch	2
		3 µm cyclone dry catch	2
		1 µm cyclone dry catch	2
		Particulate filter	2
		Particulate filter blank	3
		Acetone rinse	2
		Acetone blank	1
		0.1 N HNO_3 impingers	12
		0.1 N HNO_3 blank	3
		30% H_2O impingers	12
		30% H_2O blank	3
Solid Stream			
	Coal -	Total run as-fired composite	1
		Total run hopper composite	1
		SASS run composite	6
		Daily composite	12
	Limestone -	Total run composite	1
		Daily composite	12
		SASS run composite	6
	Bed Material -	SASS run samples	23
		Daily samples	18
		Virgin bed sample	1
		Spent bed composite	19
Fly Ash			
	Primary cyclone -	Total run composite	1
		SASS run sample	6
		Daily sample	12
	Secondary cyclone -	Total run composite	1
		SASS run sample	6
		Daily sample	12
	Baghouse -	Total run composite	1
		SASS run sample	6
		Daily sample	12
	Heat exchanger -	Deposits	1

TABLE 7-2

SUMMARY OF SAMPLE COLLECTION SCHEDULE (Ref. 1)

Sample	Frequency/duration	Date-August 11	12	13	14	15	16	17	18	19
Flue gas	0800 to 1600			•	•	•		•	•	•
Coal	0800, 1600, 2400. Additional sample from each new hopper	•	•	•	•	•	•	•	•	•
SASS train samples	0800, 1200, 1600, 2000			•	•	•		•	•	•
Limestone feed	0800, 1600, 2400	•	•	•	•	•	•	•	•	•
	SASS Run 0800, 1200, 1600, 2000 Samples			•	•	•		•	•	•
Bed drain	0800, 1600, 2400			•	•	•	•	•	•	•
	SASS Run 0800, 1200, 1600, 2000 Samples			•	•	•		•	•	•
Fly ash from primary and secondary cyclone, baghouse	0800 and 2000		•	•	•	•	•	•	•	•
Heat exchanger deposits		•								•
Virgin and spent bed composites		•								•

TABLE 3

SAMPLE PREPARATION METHODS AND DETECTION LIMITS FOR ICAP ANALYSIS (Ref. 1)

	Coal[a]	Fly ash[a]	Liquid detection limit,[b] ppb	Solid detection limit,[c] ppm
Aluminum	DA/LMF	LMF	9.0	1.0
Arsenic	PB	HF-AR	32	6.4
Barium	DA/HF-AR	LMF	0.6	0.1
Beryllium	DA/HF-AR	HF-AR	0.4	0.1
Cadmium	DA/HF-AR	HF-AR	0.8	0.2
Calcium	DA/LMF	LMF	10	2.0
Chromium	DA/HF-AR	HF-AR	2.6	0.5
Cobalt	DA/HF-AR	HF-AR	3.0	0.6
Copper	DA/HF-AR	HF-AR	1.6	0.3
Iron	DA/LMF	LMF	3.4	0.7
Lead	DA/HF-AR	HF-AR	--	--
Magnesium	DA/LMF	LMF	20	4.0
Manganese	DA/HF-AR	HF-AR	0.4	0.1
Mercury	PB	HF-AR	--	--
Molybdenum	DA/HF-AR	HF-AR	2.2	0.4
Nickel	DA/HF-AR	HF-AR	4.8	0.1
Potassium	DA/LMF	LMF	--	--
Selenium	PB	HF-AR	22	4.4
Silicon	DA/LMF	LMF	5.0	1.0
Silver	PB	HF-AR	1.0	0.2
Sodium	DA/LMF	LMF	10	2.0
Titanium	DA/LMF	LMF	1.2	0.2
Vanadium	DA/HF-AR	HF-AR	5.4	1.1
Zinc	DA/HF-AR	HF-AR	0.8	0.2

[a] Abbreviations:
DA = Dry ashed
LMF = Lithium metaborate fusion (ASTM D3682-78)
HF-AR = Hydrofluoric acid-aqua regia digestion (ASTM D3683-78)
PB = Parr bomb combustion (ASTM D3684-78)

[b] Detection limit applicable to liquid solution.

[c] Detection limit applicable to 250-mg sample with standard sample preparation techniques.

TABLE 7-4

COAL FEED METAL ANALYSIS, μg/g (Ref. 1)

	SASS Runs					
	2	3	4	5	6	7
Aluminum	6,630	6,900	6,360	7,110	5,280	6,410
Arsenic	<3.2	4.2	4.55	3.8	3.2	5.3
Barium	448	342	198	413	597	51.3
Beryllium	1.4	1.5	1.7	2.6	0.89	1.8
Cadmium	0.12	0.12	0.14	0.21	0.08	0.16
Calcium	14,400	12,600	14,100	19,500	12,400	13,900
Chromium	2.5	1.9	2.0	2.5	1.8	2.2
Cobalt	1.7	1.3	1.7	1.5	2.15	1.4
Copper	2.8	1.3	2.4	16.9	1.4	1.9
Iron	7,210	4,460	6,910	18,900	5,070	11,200
Lead	<1	<1	<1	<1	<1	<1
Magnesium	3,730	3,310	3,540	6,020	3,300	3,400
Manganese	26.2	19.9	26.0	25.7	27.8	21.9
Mercury	<0.05	0.12	<0.05	<0.05	<0.05	<0.05
Molybdenum	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Nickel	1.5	1.1	19.6	1.2	1.0	7.2
Potassium	426	430	440	349	233	625
Selenium	<2.2	<2.2	<2.2	<2.2	<2.2	<2.2
Silicon	8,630	10,600	7,970	9,110	6,030	7,620
Silver	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Sodium	7,760	6,530	7,380	7,970	6,560	6,770
Titanium	254	274	231	279	172	230
Vanadium	3.1	3.75	2.8	3.25	3.35	3.45
Zinc	3.0	1.2	1.4	2.2	1.5	0.98

TABLE 7-5

LIMESTONE FEED METAL ANALYSIS, μg/g (Ref. 1)

	SASS Runs					
	2	3	4	5	6	7
Aluminum	3,910	3,000	2,650	2,790	3,140	3,210
Arsenic	<16	<16	<16	<16	<16	<16
Barium	20	48	0.6	19	25	16
Beryllium	2.2	3.0	1.3	2.3	2.2	2.7
Cadmium	0.6	<0.4	0.6	<0.4	<0.4	<0.4
Calcium	197,000	199,000	208,000	208,000	207,000	205,000
Chromium	10	11	7.6	9.7	11	11
Cobalt	10	8.1	12	9.2	9.5	12
Copper	99	1.4	131	1.8	1.4	1.7
Iron	16,400	15,700	15,800	15,200	15,800	15,400
Lead	<8	<8	<8	<8	<8	<8
Magnesium	113,000	113,000	118,000	117,000	116,000	117,000
Maganese	1,620	1,655	1,540	1,640	1,550	1,600
Mercury	<0.025	<0.025	<0.025	<0.025	<0.025	<0.025
Molybdenum	<1	<1	<1	<1	<1	<1
Nickel	5.1	4.9	5.9	4.2	3.8	4.2
Potassium	3,480	2,710	2,330	2,710	2,880	2,870
Selenium	<11	<11	<11	<11	<11	<11
Silicon	96,600	89,400	47,200	73,900	72,600	84,700
Silver	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Sodium	124	126	106	79.8	128	69.2
Titanium	159	113	115	94	127	120
Vanadium	11	9.2	9.4	8.9	9.2	7.8
Zinc	9.2	10.1	20.3	10.3	9.0	9.2

TABLE 7-6

PRIMARY CYCLONE CATCH METAL ANALYSIS, µg/g (Ref. 1)

	SASS Runs					
	2	3	4	5	6	7
Aluminum	27,500	38,200	54,100	40,100	39,000	44,200
Arsenic	<16	<16	<16	<16	<16	<16
Barium	2,070	3,230	4,150	3,660	3,630	4,070
Beryllium	6.5	10.2	12.1	10.9	10.9	13.8
Cadmium	<0.2	0.9	1.0	1.0	0.5	<0.5
Calcium	250,000	226,000	193,500	237,000	240,000	212,000
Chromium	29	25	18	41	31	112
Cobalt	4.0	4.9	6.4	6.4	8.2	6.8
Copper	22	18	7.6	7.6	36	10.3
Iron	48,200	65,100	74,200	51,700	56,400	66,800
Lead	<8	<8	<8	<8	<8	<8
Magnesium	121,000	101,000	76,500	105,000	105,000	83,700
Manganese	1,530	1,130	790	1,310	1,350	1,050
Mercury	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Molybdenum	<1	<1	<1	<1	<1	<1
Nickel	57	10.1	7.6	8.1	7	68
Potassium	5,010	4,380	3,650	4,010	3,090	2,760
Selenium	<11	<11	<11	<11	<11	<11
Silicon	76,500	106,000	106,000	110,000	101,000	99,600
Silver	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Sodium	22,500	26,400	25,200	21,700	18,300	20,900
Titanium	190	1,260	1,710	1,630	1,290	1,670
Vandium	17	23	17	25	27	28
Zinc	14.4	13.1	13.1	13.8	14.9	13.6

TABLE 7-7

SECONDARY CYCLONE CATCH METAL ANALYSIS, μg/g (Ref. 1)

	SASS Runs					
	2	3	4	5	6	7
Aluminum	43,000	46,500	54,700	52,000	36,200	37,650
Arsenic	<16	<16	<16	<16	<16	<16
Barium	5,570	6,140	7,230	6,410	5,080	5,080
Beryllium	6.6	6.8	8.7	6.6	8.2	8.8
Cadmium	0.8	1.0	0.7	1.7	1.0	0.5
Calcium	163,000	247,000	241,000	242,000	266,000	254,000
Chromium	34	34	42	34	34	41
Cobalt	9.5	8.5	15	10	12	11
Copper	14	12	15	19	18	16
Iron	33,600	35,600	36,200	30,400	31,300	30,700
Lead	<8	<8	<8	<8	<8	<8
Magnesium	116,000	102,000	82,200	88,700	121,00	109,000
Manganese	1,470	1,120	1,070	1,270	1,580	1,530
Mercury	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Molybdenum	<1	<1	<1	<1	<1	<1
Nickel	11	11	12	13	13	12
Potassium	3,880	3,860	3,050	2,540	2,100	2,810
Selenium	<11	<11	<11	<11	<11	<11
Silicon	43,600	46,400	52,300	51,700	32,900	40,400
Silver	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Sodium	32,200	31,100	29,200	27,200	22,200	25,500
Titanium	1,920	2,030	2,610	2,400	1,910	1,830
Vandium	34	30	42	46	39	37
Zinc	12.2	9.4	9.5	9.0	9.1	13.6

TABLE 7-8

BAGHOUSE CATCH METAL ANALYSIS, μg/g (Ref. 1)

	SASS Runs					
	2	3	4	5	6	7
Aluminum	31,700	29,400	31,900	31,300	30,600	24,800
Arsenic	70	57	80	65	73	52
Barium	4,950	4,730	5,270	4,730	4,270	3,620
Beryllium	5.1	4.9	7.1	7.9	5.5	8.0
Cadmium	2.1	2.0	1.8	2.1	1.3	1.1
Calcium	270,000	190,000	78,800	194,000	211,000	177,000
Chromium	40	42	52	56	74	38
Cobalt	9.3	9	12	11	22	9
Copper	12	9	17	16	18	18
Iron	28,500	30,400	30,900	29,300	32,400	28,800
Lead	<8	<8	<8	<8	<8	<8
Magnesium	98,000	86,100	83,200	87,000	102,000	90,900
Manganese	1,180	952	1,250	1,210	1,460	1,270
Mercury	0.3	1.1	1.4	0.5	0.5	0.2
Molybdenum	<1	<1	<1	<1	<1	<1
Nickel	17	15	23	20	34	22
Potassium	7,670	8,470	8,450	6,990	6,800	8,260
Selenium	<11	<11	<11	<11	<11	<11
Silicon	24,000	23,200	24,700	24,600	26,200	19,700
Silver	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Sodium	108,000	101,000	90,800	89,200	71,300	115,000
Titanium	2,180	1,980	2,270	2,260	2,180	1,730
Vandium	24	26	39	42	42	34
Zinc	20.7	19.8	36.9	30.4	28.8	33.7

TABLE 7-9

BED DRAIN METAL ANALYSIS, µg/g (Ref. 1)

	SASS Runs					
	2	3	4	5	6	7
Aluminum	10,200	19,100	21,900	22,000	15,900	17,500
Arsenic	<16	37	49	16	<16	<16
Barium	1,460	3,210	3,650	3,700	2,570	3,050
Beryllium	6.4	9.9	8.3	10.9	2.2	15.9
Cadmium	1.1	0.7	1.8	0.9	<0.4	0.9
Calcium	264,000	220,000	216,000	206,000	231,000	204,000
Chromium	14	20	18	26	11	17
Cobalt	6.2	6	8.7	6.9	9.5	7.3
Copper	8.2	7.6	12	17.1	14	20.1
Iron	35,400	44,500	45,400	45,600	36,900	42,000
Lead	<8	<8	<8	<8	<8	<8
Magnesium	138,000	100,000	99,400	92,400	114,000	104,000
Manganese	2,260	1,350	1,610	1,380	1,820	1,500
Mercury	0.025	0.025	0.025	0.025	0.025	0.025
Molybdenum	<1	<1	<1	<1	<1	<1
Nickel	12	10	15	9.3	3.8	15
Potassium	3,930	2,840	2,470	2,800	3,300	2,450
Selenium	<11	<11	<11	<11	<11	<11
Silicon	61,600	62,500	57,800	59,400	21,300	70,400
Silver	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Sodium	10,300	28,400	33,600	38,600	25,900	39,900
Titanium	530	888	1,090	1,120	1,030	874
Vandium	22	22	27	21	9.2	25
Zinc	19.2	21	20.1	19	9.0	18.1

TABLE 7-10

PARTICULATE EMISSIONS METAL ANALYSIS (Ref. 1)

	SASS Runs 2-4		SASS Runs 5-7	
	μg/g	μg/scm	μg/g	μg/scm
Aluminum	34,000	16.0	31,400	8.54
Arsenic	<15	<0.0069	<4	<0.011
Barium	472	0.22	1,280	0.35
Beryllium	14.0	0.0066	11.6	0.0031
Cadmium	37.0	0.017	73.1	0.020
Calcium	55,600	26.2	46,200	12.6
Chromium	361	0.17	2,733	0.74
Cobalt	64.4	0.030	159	0.043
Copper	295	0.139	522	0.142
Iron	48,700	22.9	43,700	11.9
Lead	<60	<0.0275	<20	<0.0055
Magnesium	20,000	9.44	8,230	2.24
Manganese	652	0.308	540	0.147
Mercury	--	--	--	--
Molybdenum	164	0.077	289	0.079
Nickel	3,580	1.68	1,750	0.476
Potassium	3,541	1.67	4,620	1.26
Selenium	<10	<0.0049	<30	<0.0076
Silicon	66,500	31.3	99,000	27.0
Silver	279	0.13	411	0.11
Sodium	54,200	25.5	50,300	13.7
Titanium	3,090	1.46	5,840	1.59
Vandium	76.9	0.036	80.6	0.022
Zinc	6,460	3.04	8,700	2.37

TABLE 7-11

GAS PHASE VOLATILE COMPONENTS (IMPINGER SAMPLES), µg/scm (Ref. 1)

	SASS Runs					
	2	3	4	5	6	7
Aluminum	<0.73	<1.26	<0.32	<0.42	<0.65	<0.62
Arsenic	<3.14	<2.96	<2.88	<3.02	<2.89	<5.18
Barium	0.15	<0.09	<0.06	<0.02	<0.03	<0.05
Beryllium	<0.04	<0.04	<0.02	<0.04	<0.04	<0.06
Cadmium	<0.08	<0.08	<0.08	<0.08	<0.12	<0.11
Calcium	<2.63	<5.92	<0.73	<1.03	<0.94	<2.18
Chromium	4.39	3.39	4.75	5.49	5.57	7.33
Cobalt	<0.20	<0.13	<0.40	<0.19	<0.30	<0.49
Copper	3.30	<0.46	<0.14	<0.58	<0.33	<1.69
Iron	17.31	14.33	23.26	1.56	20.04	27.96
Lead	<1.58	<1.47	<1.46	<1.51	<1.45	<2.60
Magnesium	<1.79	<1.84	<1.80	<1.89	<1.87	<3.25
Manganese	1.08	0.43	0.89	<0.40	<0.37	<0.80
Mercury	--	--	--	--	--	--
Molybdenum	0.66	0.49	0.74	0.68	0.61	0.75
Nickel	2.22	2.17	3.36	3.58	3.44	4.95
Potassium	<4.92	<2.95	<2.82	<6.61	<4.67	<1.17
Selenium	<2.89	<2.37	<1.99	<1.94	<3.29	<2.91
Silicon	--	--	--	--	--	--
Silver	<0.25	<0.34	<0.09	<0.14	<0.09	<0.23
Sodium	16.20	13.92	9.71	11.94	15.71	28.84
Titanium	<0.10	<0.13	<0.09	<0.09	<0.21	<0.16
Vandium	<0.50	<0.46	<0.03	<0.46	<0.44	<0.78
Zinc	5.94	6.82	4.57	1.44	<0.48	<0.75

7.2.1.6 Atmospheric Emission Rates

Dust loadings at the baghouse outlet were extremely low. In Table 7-12 we summarize the particulates concentrations (dust loadings) as the flue gas stream progresses from furnace freeboard to baghouse outlet. Fabric filter inlet and outlet data are also presented in the form of emission factors (i.e., lbs/10^6 Btu), which is the form in which U.S. EPA New Source Performance Standards (NSPS) are currently espressed (4). For conventional pc-fired steam-electric boilers, the NSPS for particulate matter is now 0.03 lb/10^6 Btu.

TABLE 7-12

FLUE GAS PARTICULATE CONCENTRATIONS AND EMISSION RATES (REF. 1)

	SASS Runs 2-4	SASS Runs 5-7
Before Primary Cyclone,[a] g/scm	14.0	8.61
Before Secondary Cyclone,[a] g/scm	0.758	0.588
Before Fabric Filter,[a] g/scm	0.207	0.217
gr/scf	0.0905	0.0949
lb/10^6 Btu	0.178	0.204
After Fabric Filter,[b] g/scm	0.000471	0.000272
gr/scf	0.000206	0.000119
lb/10^6 Btu	0.000404	0.000256
Fabric Filter Efficiency, pct	99.772	99.875
Overall Particulate Control, pct	99.9966	99.9968

[a] Based on particulates collected in the control device hoppers and gas flow rates measured after the fabric filter.

[b] Measured with the SASS train.

Clearly the GFETC AFBC betters the NSPS by approximately two orders of magnitude. It also betters normal performance of conventional combustion systems by about one order of magnitude (5). Presumably this is due largely to the conservative sizing of the pulse jet baghouse.

A consequence of the very low particulate emission rates is that the corresponding elemental emission rates will be very low. These are presented in Table 7-13.

TABLE 7-13

COMPARISON OF MEASURED ELEMENTAL RATES TO CONVENTIONAL COMBUSTION SYSTEMS, µg/scm[a] (Ref. 1)

	Grand Forks	Controlled Conventional Industrial Boiler[b]		
	Lignite[c]	Coal[d]	Oil[d]	TLV (Ref. 6)
Aluminum	13	2,600	480	5,000
Arsenic	<3	220	30	200
Barium	0.2-0.4	--	--	500
Beryllium	<0.1	2	1	2
Cadmium	<0.1	1	66	50
Calcium	20	36	70	2,000
Chromium	6	13	18	50-500
Cobalt	<0.4	12	12	100
Copper	<1	20	7	1,000
Iron	35	2,400	280	1,000
Lead	<2	21	13	150
Magnesium	7	11	30	10,000
Manganese	0.8	15	4	5,000
Mercury	--	5	0.2	50
Molybdenum	0.7	27	25	5,000
Nickel	4.4	63	200	100-1,000
Potassium	2-3	--	--	2,000
Selenium	<2	4	6	200
Silicon	29	--	--	10,000
Silver	<0.3	--	--	10-100
Sodium	37	--	--	5,000
Titanium	1.6	--	--	10,000
Vandium	<0.5	58	820	500
Zinc	6	48	65	5,000

[a] For the Grand Forks unit. 1 µg/scm was equivalent to 9.0×10^{-7} lb/10^6 Btu. For the conventional boiler, 1 µg/scm was equivalent to 9.7×10^{-7} lb/10^6 Btu when firing coal and 7.3×10^{-7} lb/10^6 Btu when firing oil.

[b] Refrence 7. The steam capacity of this pulverized coal-fired boiler was 100,000 lb/hr.

[c] Emissions were controlled by cyclones and a fabric filter. Total particulate emissions were 0.00026 to 0.0004 lb/10^6 Btu.

[d] Emissions were controlled by multicyclone, a venturi scrubber and a dual alkali scrubber. Total particulate emissions for both coal and oil firing were 0.04 lb/10^6 Btu.

7.2.1.7 Material Balance

Partitioning of elements between the various process streams can be expressed as concentration ratios, or in terms of consumption or emission rates in units of mass/unit time. Because of rather large unsyncronized time-to-time variations in concentrations, the former method is not as instructive as the latter methods, which are presented in Table 7-14.

7.2.1.8 Aluminum-Normalized Enrichment Ratios

Aluminum compounds found in combustion products are both non-volatile and non-slagging. Therefore, aluminum concentrations have been used as normalizing factors in comparing various emission streams with feedstocks, and also with earth's crustal abundances. Consequently, it is instructive to examine aluminum-normalized enrichment and depletion ratios for some of the major and trace elements studied in this investigation. These aluminum-normalized enrichment and depletion ratios were calculated by comparing the appropriate concentration in the primary cyclone, secondary cyclone, baghouse, and heat exchanger catches and flue gas emissions to the concentration in the feed materials. Because some elements appear in the limestone, the total feed was used for this calculation instead of just the coal. The formula is:

$$\text{Al-normalized enrichment ratio} = \frac{(C_i/C_{Al})_{\text{emitted}}}{(C_i/C_{Al})_{\text{feed}}}$$

where: i indicates the element

$$C_i \text{ in the feed} = \frac{C_i \times \text{coal feed} + C_i \times \text{limestone feed}}{\text{coal} + \text{limestone feed}}$$

C_{Al} in the feed is calculated in the same manner as C_i.

Average aluminum enrichment/depletion ratios for the six SASS runs are presented in Table 7-15. The results show that cadmium, chromium, molybdenum, nickel, and zinc were greatly enriched in the flue gas emissions. Chromium and nickel were also greatly enriched in the heat exchanger deposits. Beryllium, cobalt, sodium, titanium, and vanadium were slightly enriched in the particulate emissions. The other enrichment/ depletion ratios are neither very high nor very low.

7.2.1.9 Summary of Material Balance Results

During the test burn of Beulah, North Dakota, lignite in the 2.25-ft^2 AFBC, analyses of 24 elements were performed in all significant process streams (feedstock, emissions and products, retained material). Flue gas particulate emission levels were lower than normal performance of conventional combustion systems and the current New Source Performance Standards for steam-electric boilers by 1 and 2 orders of magnitude, respectively. Particulate concentrations ranged from 0.00026 to 0.00040 lbs/10^6 Btu.

TABLE 7-14

MATERIAL BALANCE RESULTS FOR TOTAL RUN COMPOSITES, μg/sec. (Ref. 1)

	Feed		nput	Cyclone					Bed			
	Coal	Limestone	Total	Primary	Secondary	Baghouse	Heat Exchanger	Bed Drain	Buildup/ Depletion	Flue Gas	Output Total	Percent Closure
Aluminum	97,600	6,850	104,400	54,200	2,500	1,490	186	15,300	7,960	1.5	81,600	78
Barium	5,940	4.8	5,945	4,540	353	202	2.2	2,280	1,450	0.036	8,850	149
Beryllium	35.4	3.32	38.7	13.2	0.57	0.35	0.065	4.33	7.4	<0.005	25.9	67
Calcium	193,000	476,000	669,000	365,000	17,400	8,800	1,080	195,000	63,100	2.4	650,000	97
Chromium	31.0	26.2	57.2	51.5	2.24	1.64	8.25	22.0	6.5	0.61	92.8	162
Cobalt	23.6	14.8	38.4	8.69	0.84	0.31	0.17	18.7	2.47	0.03	31.2	81
Iron	189,000	35,200	224,000	91,200	2,140	1,310	174	30,700	17,400	4.1	142,900	64
Magnesium	52,300	266,000	318,000	166,000	7,630	3,840	452	138,000	29,500	0.79	345,000	109
Manganese	123	3,710	3,830	2,090	103	49.2	7.1	1,170	407	0.090	3,830	100
Nickel	39.8	18.1	57.9	14.6	1.0	0.6	9.2	5.9	5.9	0.48	37.2	64
Potassium	4,340	3,970	10,300	6,280	275	280	25.5	3,180	640	0.15-0.50	10,680	104
Silicon	132,000	199,000	331,000	142,000	2,480	1,310	191	46,300	27,400	3.4	219,700	66
Sodium	106,000	55	106,000	31,600	2,070	2,700	182	23,400	18,900	4.2	78,900	74
Titanium	3,750	275	4,020	1,900	129	84	8.6	670	392	0.18	3,180	79
Vandium	44.2	26.2	70.4	40.3	2.03	1.04	0 19	12.5	9.85	<0.05	65.9	93
Zinc	20.6	20.9	41.5	23.5	1.06	1.11	0 15	11.0	6.5	0.70	43.3	104

TABLE 7-15

AVERAGE ALUMINUM-NORMALIZED ENRICHMENT AND DEPLETION RATIOS FOR THE SIX SASS RUNS (Ref. 1)

	Primary Cyclone	Secondary Cyclone	Baghouse	Heat Exchanger	Particulate Emissions
Barium	1.4	2.2	2.6	2.7	0.45
Beryllium	0.97	0.63	0.74	0.94	1.4
Cadmium	--	--	--	0.42	>59
Calcium	0.91	0.86	0.86	0.86	0.24
Chromium	1.54	1.62	3.4	78	81
Cobalt	0.37	0.48	0.79	2.1	7.1
Iron	1.1	0.58	0.71	0.43	1.0
Magnesium	0.88	0.77	1.0	0.77	0.16
Manganese	0.84	0.79	1.1	1.0	0.50
Molybdenum	--	--	--	--	>130
Nickel	1.8	0.74	2.1	89	99
Potassium	0.68	0.55	2.2	1.3	0.99
Silicon	0.84	0.34	0.27	0.34	0.84
Sodium	0.56	0.63	2.4	0.96	1.6
Titanium	0.94	1.27	1.65	1.51	4.0
Vanadium	0.82	1.2	1.8	1.2	3.7
Zinc	0.66	0.53	2.2	1.9	430

Emissions of trace elements were very low, appearing to represent no environmental concern whatsoever. Material balances for 16 elements were performed for the entire 8-day run, with closures varying from 64 to 162 pct. (Chromium, a component of the stainless steel structure, was the element with the apparent 162% closure.) The primary cyclone catch was the major vehicle for release of most minor and trace elements.

7.2.2 Polycyclic Organics in Baghouse Ash

Baghouse ash from the high-sodium Beulah, North Dakota, lignite AFBC material balance run was subjected to polycyclic organic (POM) analysis. It was extracted with methylene chloride in a Soxhlet, subjected to the "EPA 610" clean-up procedure, and analyzed by HPLC and fused silica capillary GC analysis. Results are shown in Table 7-16. POMs were present in relatively large amounts by comparison with previously analyzed samples generated in the particulate test combustor, which is a pulverized coal pc-fired furnace. This was not surprising, because the combustion temperatures in AFBC are very much lower than in conventional pc-firing.

TABLE 7-16

POLYCYCLIC ORGANIC ANALYSIS OF BAGHOUSE ASH FROM RUN FB2-BA5-2581

POM	g POM/g Ash
Phenanthrene	5×10^{-7} g/g
Anthracene	5×10^{-8} g/g
Fluoranthene	5×10^{-7} g/g
Pyrene	3×10^{-7} g/g
Benzo (b) fluorene	1×10^{-7} g/g
Benzo (a) anthracene	1×10^{-7} g/g
Chrysene	8×10^{-7} g/g
Benzo (k) fluoranthene	7×10^{-7} g/g
Benzo (a) pyrene	1×10^{-7} g/g
Indenopyrene	3×10^{-7} g/g
Bibenz (a,h) anthracene	1×10^{-7} g/g
Benzo (ghi) perylene	2×10^{-7} g/g

We have also sampled flue gas organics during AFBC combustion of high-sodium Beulah lignite. This was during a different run (No. FB2-BU1-1182) for which bed temperature, excess oxygen, and superficial gas velocity differed (1631° versus 1445°F, 19 pct excess O_2 versus 24 pct, and 6.37 ft/sec versus 5.9 ft/sec for BU1-1182 versus BA5-2581). The analysis, also by HPLC and fused silica capillary GC, resulted in data for 25 polycycleis and heterocycleis, 13 of which were "EPA Priority Pollutants". The AFBC run was characterized by several periods of unstable operation during coal feed problems. This would be expected to increase the diversity of organics observed, and possibly their concentrations.

7.2.3 Mutagenicity in Extracts of AFBC Ash

In a cooperative effort with DOE's Laboratory for Energy Related Health Research (Univ. California-Davis), U.Cal's Dr. Wesley R. Harris reports the completion of tests on baghouse ash from the 110-hour, high-sodium Beulah FBC material balance run.

Ames tests (Salmonella mutagenesis assays) were completed without S-9 activation, using Salmonella strains TA1538, TA100, and TA98, as well as a nitroreductase-deficient variant of each of these strains. The results, which will be published in detail elsewhere, suggest that this North Dakota lignite AFBC ash is only modestly mutagenic - perhaps more so than observed with AFBC bituminous ash at Argonne National Laboratory. The results also suggest that the activity is due to nitro-aromatics.

LERHR is planning to perform two additional tests:

1. Using benzene-methanol extraction followed by fractionation of the extract on an HPLC column, they plan to perform Ames test prescreening on fractions, followed by a mammalian cell transformation test on especially potent fractions. This work has already begun.

2. LERHR has begun doing lymphocyte stimulation tests using canine serum extract.

When completed, these investigations will also be reported elsewhere.

7.2.4 Neutron Activation Analyses of AFBC Fuel, Bed, and Ash.

Neutron activation analysis (NAA) is applicable to a different selection of elements than that normally determined by inductively coupled argon plasma (ICAP) spectroscopy. The latter method was used for most of the elements studied by GCA in their material balance investigation reported in earlier sections of this report.

Composite samples of feed coal, virgin bed, and baghouse ash were submitted to North Carolina State University's Nuclear Engineering Department. We report in Table 7-17 those elemental analyses not performed by GCA as part of their material balance investigation. Mainly these are lanthanides, actinides, halogens, and transition metals.

NAA technology in fossil applications is discussed in a review by Weaver (8), who describes the sources of error in NAA and their relative contribution to overall precision. The standard errors listed in Table 7-17 are purely analytical (due chiefly to counting statistics and neutrons flux uncertainties). They do not include any measure of sampling errors. Although the coal, limestone, and ash samples were carefully blended composites, they were not replicated. Consequently, we have no estimate of how representative the selected composites were of the total respective materials. A conservative approach would require that the indicated errors be increased at least tenfold.

Even allowing for this caveat, it is noteworthy that certain elements are enriched in the fly ash. These include bromine, cesium, hafnium, thorium, and uranium. The latter two, which are heavy metals as well as radioactive, have elicited some published concern, but do not appear on the EPA priority pollutant list.

TABLE 7-17

NAA ANALYSES OF TRACE ELEMENTS AND AFBC RUN FB2-BA5-2581 ANALYSES (AND ∂'s) REPORTED IN μg/g

Sample	82-0567 High-Na Beulah		82-0568 Shakopee Ls.		81-4846 Baghouse Catch	
Antimony	0.14	(.007)	0.01	(.003)	1.11	(.01)
Bromine	0.81	(.04)	5.62	(.006)	173.6	(0.9)
Cerium	9	(2)	7	(1)	40	(4)
Cesium	0.06	(0.1)	0.04	(.01)	0.86	(.04)
Chlorine	<50		124	(6)	3479	(35)
Europium	0.16	(.008)	0.04	(.004)	0.72	(.007)
Gold	<0.0001		<0.0001		<0.0001	
Hafnium	1.12	(.03)	0.22	(.02)	4.66	(.05)
Iodine	<3		<3		<3	
Lanthanum	3.07	(.03)	2.09	(.02)	18.6	(.2)
Rubidium	8	(2)	3	(1)	34	(7)
Samarium	0.41	(.004)	0.31	(.003)	2.14	(.01)
Scandium	1.50	(.008)	0.27	(.005)	6.10	(.03)
Thorium	2.43	(.002)	0.28	(.003)	14.39	(.01)
Uranium	0.65	(.03)	0.64	(.03)	2.83	(.03)

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[a] ∂'s include analytical errors only, without contribution from sampling errors.

7.3 REFERENCES

1. Hall, R.R., M.M. McCabe, and D. McGrath. Material Balance in Atmospheric Fluidized Bed Combustion of North Dakota Lignite. DOE/FC/10281-1, March 1982.

2. Mann, M.D. Preliminary Experiment Data Report for the 2.25-ft^2 Atmospheric Fluidized Bed Combustor, Run FB-2-BA5-2581, EG&G, Inc., Grand Forks, ND, Sept. 2, 1981.

3. Mann, M.D. Final Experimental Data Report for the 2.25-ft^2 Atmospheric Fluidized Bed Combustor Beluah High-Sodium Lignite Series, Runs FB2-BA1-2181 through FB2-BA7-2781, EG&G Inc., Grand Forks, ND, April 20, 1982.

4. New Stationary Sources Performance Standards; Electric Utility Steam Generating Units. Federal Register Volume 44, No. 133, June 11, 1979.

5. Roeck, D.R., and R. Dennis. Technology Assessment Report for Industrial Boiler Applications: Particulate Collection. EPA-600/7-79-178h, December 1979, p. 115

6. Threshold Limit Values for Chemical Substances in Workroom Air Adopted by ACGIH for 1981. American Conference of Governmental Industrial Hygienists, Cincinnati, OH. 1981.

7. Leavitt, C. et al. Environmental Assessment of Coal- and Oil-Firing in a Controlled Industrial Boiler; Volume II. Comparative assessment. EPA-600/7-78-164b. August 1978.

8. Weaver, J.N. "Neutron Activation Analysis of Trace Elements in Coal, Fly Ash, and Fuel Oils," in Analytical Methods For Coal and Coal Products, Vol. 1, C. Karr, Jr., ed. (N.Y. Academic Press, 1978) pp 377 ff.

9. Anon. "Operating and Service Manual-Aerotherm Source Assessment Sampling System. Acurex Corp., March 1977.

8. - WASTE CHARACTERIZATION AND DISPOSAL

PTPA No.: 611 B&R No.: AA0515000

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8.1 GOALS AND OBJECTIVES

The goals of the Waste Characterization and Disposal Project at the Grand Forks Energy Technology Center (GFETC) are to characterize and develop suitable techniques for environmentally satisfactory disposal of waste materials derived from burning low-rank western coals. Specific project objectives for FY 1982 are to: 1) conduct laboratory studies on the chemical and physical characteristics of western FGD sludge materials; 2) determine leaching characteristics of western FGD sludge and fly ash materials; 3) evaluate hazardousness classification of reuse products containing low-rank coal waste material; and 4) characterize waste materials generated by fluidized-bed combustion of low-rank western coals.

8.2 ACCOMPLISHMENTS

8.2.1 Chemical and Physical Characterization of Western Low-Rank Coal Waste Material

Work on this project is being conducted by Radian Corporation. The project is designed to characterize the chemical and physical properties of 14 low-rank coal waste materials including: 1) sludge from utility wet scrubber FGD systems employing alkaline fly ash; 2) fly ash from a fluidized-bed combustor (FBC); 3) mixtures of fly ash and spent SO_2 duct injection dry sorbent materials such as nahcolite and trona; and 4) a mixture of fly ash and sodium-base waste material produced in a spray dryer GFD system.

8.2.1.1 Characteristics of AFBC Waste Materials

The chemical and physical properties of four AFBC waste materials were characterized. The waste materials were produced by GFETC's 2.25-ft^2 pilot plant AFBC, and were derived from a North Dakota lignite with and without supplemental limestone, a Texas lignite, and an Illinois bituminous coal.

The concentrations of the RCRA trace elements (As, Ba, Cd, Cr, Pb, Hg, Se, and Ag) in the AFBC fly ashes and the limestone additive are presented in Table 8-1. Concentrations of seven of the eight RCRA trace elements were higher in the ash material from North Dakota lignite with supple-

TABLE 8-1

CONCENTRATIONS OF EIGHT RCRA TRACE ELEMENTS IN AFBC FLY ASHES AND LIMESTONE USED IN FBC TESTS (Concentrations are given in μg/g)

Sample Type:	Shakopee Limestone Used in AFBC Tests	AFBC Fly Ash from North Dakota Lignite	AFBC Fly Ash from North Dakota Lignite, Limestone Added	AFBC Fly Ash from Texas Lignite	AFBC Fly Ash from Illinois Bituminous Coal Limestone Added	Cyclone Ash[a] Conventional Power Station III[b]	Precipitator Ashes, From Conventional Power Stations[c]
DOE Run Number:	3080 and 1680	0380	3080	3280	1680	---	---
Sample Number:	73	7	9	12	8	---	---
Arsenic	3.0	24	41	150	30 31	188	57-74
Barium	90	620	1600	290	290 300	7700	700-15,000
Cadmium	<1	0.20	3.7	<1	1.3 1.6	2.9	1.4-5.3
Chromium	6.0	160	140	100	120 100	86	3.6-28
Lead	5.5	35	85	46	30 33	8.2	4-27
Mercury	0.08	0.09	0.1	0.32	0.2 0.3	0.17	0.01-0.15
Selenium	<0.8	1.0	18	35	6.6 6.2	9.5	3.2-16
Silver	<0.3	0.2	0.9	<0.5	0.1	0.75	NR[d]

[a] For this program, concentrations were measured using the following analytical techniques: arsenic and selenium, atomic absorption, hydride generation; barium, inductively coupled argon plasma emission spectrometry; cadmium, chromium, lead and silver, atomic absorption, graphite furnace; mercury, atomic absorption, cold vapor.

[b] Radian Corporation, Coal-Fired Power Plant Trace Element Study, Volume IV, Station III, Environmental Protection Agency, Region VIII, Denver, Colorado, EPA Contract 68-01-2663, Sept. 1975, p.30. Power Station III burned North Dakota lignite.

[c] Holland, W.F., K.A. Wilde, J.L. Parr, P.S. Lowell, and R.F. Pohler. The Environmental Effects of Trace Elements in the Pond Disposal of Ash and Flue Gas Desulfurization Sludge, Research Project 202, Electric Power Research Institute, Palo Alto, California, September, 1975. Range for three stations burning high-sulfur coals.

[d] Not reported.

mental limestone than in North Dakota lignite without supplemental limestone. In the absence of other factors, one would expect lower trace element concentrations in the fly ash waste with supplemental limestone, because the Shakopee limestone would dilute trace elements found in higher concentrations in fly ash alone. One possible explanation is that some volatile elements (e.g., As, Cd, Se, and Pb) are retained more efficiently in the presence of calcined limestone than by fly ash alone. However, without complete mass balance information, explanations for the observed concentration relationships are speculative.

Concentrations of RCRA trace elements in AFBC fly ashes from the Illinois bituminous coal and the Texas lignite were generally in the same range as concentrations in AFBC fly ashes from North Dakota lignite.

Concentrations of the RCRA trace elements in a conventional fly ash from a conventional pulverized-coal-fired boiler using a North Dakota lignite and from three high-sulfur coals fed to conventional boilers are also presented in Table 8-1. In general, concentrations for ashes from a given geographic region were comparable, considering the expected variability of trace element concentrations. In the AFBC fly ash from the Illinois bituminous coal, arsenic and barium concentrations were low and chromium concentration were high relative to concentrations in conventional fly ashes from three high-sulfur coals.

Concentrations of Al, Ca, Fe, Mg, and Na in AFBC fly ash solids are listed in Table 8-2. As expected, concentrations of calcium and magnesium are higher in the AFBC fly ash from combustion of North Dakota lignite with limestone added than without limestone added. Iron concentration was markedly higher in ash from Illinois bituminous coal.

Concentrations of Cu, Mn, Mo, Ni, Sr, V, and Zn in AFBC fly ashes are listed in Table 8-3. These elements are of environmental interest since standards have been promulgated regarding their concentrations in some drinking water supplies and in irrigation water. Concentrations of manganese and vanadium were relatively high in AFBC fly ash from Texas lignite. Concentrations of copper and zinc were relatively high in ash from combustion of Illinois bituminous coal.

The four samples of AFBC fly ashes were subjected to the RCRA Extraction Procedure (EP), described in the May 19, 1980, Federal Register. The EP test is specified to determine whether or not wastes should be classified as hazardous according to the characteristics of EP toxicity. Concentrations of the eight RCRA trace elements in the extracts are listed in Table 8-4. All concentrations are well below levels at which waste is classified as toxic under current RCRA regulations. The relatively high concentration of selenium in the EP extract of AFBC fly ash from combustion of North Dakota lignite with limestone correlates with the high selenium concentration found in the solids.

TABLE 8-2

CONCENTRATIONS[a] OF MAJOR ELEMENTS IN AFBC FLY ASHES, LIMESTONE USED IN FBC TESTS, AND CYCLONE ASH FROM CONVENTIONAL POWER STATION

(Concentrations are given in percent)

Sample Type:	Shakopee Limestone	North Dakota Lignite	North Dakota Lignite, Limestone Added	Texas Lignite	Illinois Bituminous Coal, Limestone Added	Conventional Power Station, Cyclone Ash[b]
DOE Run Number:	3080 1680	0380	3080	3280	1680	---
Sample Number:	73	7	9	12	8	---
Element						
Aluminum	0.28	2.6	2.9 2.4[c]	7.9	5.1	7.4
Calcium	16.	5.0	8.6 8.2[c]	9.5	7.2	13.0
Iron	1.4	2.9	2.6 2.7[c]	5.2	12.	5.8
Magnesium	9.5	1.2	2.4 2.4[c]	0.65	0.41	3.6
Sodium	0.008	1.5	3.0 2.5[c]	4.1	0.88	NR[d]

[a] For this program, concentrations were measured using inductively coupled argon plasma emission spectrometry. Solids were brought into solution using a perchloric acid digestion.

[b] Radian Corporation, Coal-Fired Power Plant Trace Element Study, Volume IV, Station III, Environmental Protection Agency, Region VIII, Denver, Colorado, EPA Contract 68-01-2663, Sept. 1975, p. 30. Power Station III burned North Dakota lignite.

[c] Concentrations in blind duplicate digestion and analysis.

[d] Not reported.

TABLE 8-3

CONCENTRATIONS[a] OF ADDITIONAL ELEMENTS IN AFBC FLY ASHES, LIMESTONE USED IN FBC TESTS, AND ASHES FROM CONVENTIONAL POWER STATIONS (Concentrations are given in μg/g)

Sample Type:	Shakopee Limestone	North Dakota Lignite	North Dakota Lignite, Limestone Added	Texas Lignite	Illinois Bituminous Coal, Limestone Added	Conventional Power Station, Cyclone Ash[b]	Three Eastern Power Stations[c]
DOE Run Number:	3080 1680	0380	3080	3280	1680	---	---
Sample Number:	73	7	9	12	8	---	---
Element							
Boron	NR[d]	NR[d]	NR[d]	NR[d]	NR[d]	1600	270-1000
Copper	12	13	18 14[e]	41	82	145	60-240
Manganese	1400	400	410 390[e]	1,200	330	750	240-370
Molybdenum	<0.5	9.9	28 16[e]	46	21	61	5.9-12
Nickel	<0.8	40	66 40[e]	91	71	38	75-110
Strontium	23	1,650	2,300 2,000[e]	1,300	140	NR	NR
Vanadium	3.1	20	22 19[e]	150	66	86	<100
Zinc	31	21	66 59[e]	160	690	120	100-850

---

[a] For this program, concentrations were measured using inductively coupled argon plasma emission spectrometry. Solids were brought into solution using a perchloric acid digestion.

[b] Radian Corporation, Coal-Fired Power Plant Trace Element Study, Volume IV, Station III, Environmental Protection Agency, Region VIII, Denver, Colorado, EPA Contract 68-01-2663, Sept. 1975, p. 30. Power Station III burned North Dakota lignite.

[c] Hollard, W.F., K.A. Wilde, J.L. Parr, P.S. Lowell, R.F. Pohler, The Environmental Effects of Trace Elements in the Pond Disposal of Ash and Flue Gas Desulfurization Sludge. Research Project 202, Final Report, Electric Power Research Institute, Palo Alto, California, September 1975.

[d] Not reported because boron could not be determined using the perchloric acid.

[e] Concentrations in blind duplicate digestion and analysis.

TABLE 8-4

CONCENTRATIONS OF EIGHT RCRA TRACE ELEMENTS IN EP EXTRACTS OF AFBC FLY ASHES (Concentrations are given in mg/ℓ)

Sample Type:	North Dakota Lignite	North Dakota Lignite, Limestone Added	Texas Lignite	Illinois Bituminous Coal, Limestone Added	RCRA Limits
DOE Run Number	0380	3080	3280	1680	--
Sample Number	7	9	12	8	--
Element					
Arsenic	0.006	0.007 0.005[a]	0.30	0.004	5
Barium	0.083	0.22 0.23	0.26	0.11	100
Cadmium	0.03	0.03 0.03	0.0030	0.03	1
Chromium	0.1	0.01 0.01[a]	0.11	0.1	5
Lead	0.4	0.4 0.4[a]	0.005	0.4	5
Mercury	0.0005	0.0005 0.0005	0.0009	0.0005	0.2
Selenium	0.004	0.25 0.24	0.14	0.008	1
Silver	0.06	0.06 0.06[a]	<0.002	0.06	5
Final pH	5.7	8.9 8.9	4.5	7.6	

[a] Concentration in Duplicate Extraction

Concentrations of major elements in EP extracts and additional elements in EP extracts are listed in Tables 8-5 and 8-6. The primary value of measuring concentrations of elements other than the RCRA elements in EP extracts is to screen for leachable species which may be important in evaluation of impacts on groundwater quality. Few measurements of concentrations of elements other than RCRA trace elements in EP extracts have been reported.

All samples of AFBC fly ashes tested were alkaline, and pH values were above 5 after addition of the maximum amount of acetic acid called for in the EP procedure. Values of pH at the end of the EP extraction are given in Tables 8-4 through 8-6.

8.2.2 Hydrological and Geotechnical Procedures Manual for Western Strip Mine FGD Sludge Disposal

Work on this project is being conducted under contract by the University of North Dakota. This project will delineate hydrogeologic and geotechnical considerations required to establish an FGD sludge disposal site using a western coal strip mine. Activities include: 1) description of state-of-the-art groundwater monitors; 2) groundwater flow monitoring requirements; 3) description of disposal techniques in the overburden spoils and the strip mine pit bottoms; and 4) the size of the geographic area which must be considered in selecting the strip mine disposal site. The product of this project will be a manual detailing strip mine disposal site survey requirements and techniques, description and recommendations on sludge placement and burial, and instructions on how to establish a groundwater sludge leachate monitoring station network.

A computer literature search was completed to collect information on: 1) waste disposal practices; 2) groundwater quality monitoring; and 3) fly ash/FGD waste chemistry. The search yielded over 1,000 titles, of which 83 proved useful. A working bibliography of 140 papers has been compiled. These documents have been reviewed and will form part of an annotated bibliography that will eventually be placed in a computer file. The structure and leachate chemistry of fly ash is the subject of 50 papers; scrubber waste chemistry is discussed in four papers, while only seven papers deal with groundwater quality monitoring at disposal sites. The literature survey provided general background on coal-fired power plants in the study region which are equipped with FGD systems.

A mail and telephone survey of state regulatory agencies and utilities in the study region (Nevada, Arizona, Utah, New Mexico, Texas, Colorado, Wyoming, Montana, South Dakota, and North Dakota) produced a comprehensive summary of: 1) state regulations concerning disposal of power plant wastes and water quality monitoring; and 2) utility practices concerning waste disposal and groundwater quality monitoring. A summary of the waste disposal sites are presented in Table 8-7. All states, with the exception of Nevada and Utah, require some monitoring at the disposal site. Of the 42 operational units found at 21 sites throughout the study area, 26 have monitoring programs. Water quality data from half of these units will be incorporated into the final report.

TABLE 8-5.

CONCENTRATIONS OF MAJOR ELEMENTS IN EP EXTRACTS OF AFBC FLY ASHES

(Concentrations are given in mg/ℓ)

Sample Type:	North Dakota Lignite	North Dakota Lignite, Limestone Added	Texas Lignite	Illinois Bituminous Coal, Limestone Added
DOE Run Number	0380	3080	3280	1680
Sample Number	7	9	12	8
Element				
Aluminum	0.25	0.61 0.59	78.	0.59
Calcium	1500.	1100.[a] 1100.	890.	2500.
Iron	0.019	0.02[b] 0.07	3.7	0.013
Magnesium	400.	300. 350.	140.	31.
Sodium	500.	2400. 2400.	1100.	44.
Final pH	5.7	8.8 8.9	4.5	7.6

[a] Duplicate extraction and analysis

[b] Less than five times analytical detection limit

TABLE 8-6.

CONCENTRATIONS OF ADDITIONAL ELEMENTS IN EP EXTRACTS OF AFBC FLY ASHES

(Concentrations are given in mg/ℓ)

Sample Type:	North Dakota Lignite	North Dakota Lignite, Limestone Added	Texas Lignite	Illinois Bituminous Coal, Limestone Added
DOE Run Number	0380	3080	3280	1680
Sample Number	7	9	12	8
Element				
Boron	18.	27. 27.	77.	8.4
Copper	0.001	0.001 0.001	0.033	0.005
Manganese	3.3	0.11 0.096	28.	1.4
Molybdenum	0.050	1.0 0.99	0.14	0.17
Nickel	0.007	0.003 0.003	0.48	0.009
Strontium	35.	19.	27.	2.0
Vanadium	0.024	0.077 0.063	0.097	0.024
Zinc	0.003	0.003 0.003	1.2	0.14
Final pH	5.7	8.8 8.9	4.5	7.6

[a] Duplicate extraction and analysis

[b] Less than five times analytical detection limit

TABLE 8-7

SUMMARY OF COAL WASTE DISPOSAL SITES

	Total (Operational & Planned)		Operational		Groundwater Quality Monitoring		
State	Units	Sites	Units	Sites	Required	Units	Sites
North Dakota	7	5	4	3	Yes	4	3
Montana	4	1	2	1	Site Specific	2	1
Wyoming	8	3	4	3	Yes	4	3
Colorado	4	2	3	1	Yes	3	1
New Mexico	10	3	9	2	Yes	4	1
Arizona	11	4	7	3	Site Specific	2	1
Texas	19	13	7	5	Yes	7	5
Utah	9	4	3	2	No		
Nevada	9	3	3	1		—	—
Totals	81	38	42	21		26	15

9.0 - EXPLORATORY RESEARCH

PTPA No.: 622

Submitted by: H.H. Schobert, Manager, Analytical Research Div.

Prepared by: H.H. Schobert, Manager, Analytical Research Div.

Assigned GFETC Personnel: John W. Diehl
James F. Grohs
George G. Montgomery
Edwin S. Olson

9.1 GOALS AND OBJECTIVES

The goal of the Exploratory Research Project at the Grand Forks Energy Technology Center (GFETC) is to perform long-term research related to the GFETC mission as lead laboratory for low-rank coal technology and to the needs of the various conversion and utilization projects. The research conducted as part of the Exploratory Research Project does not necessarily interface with the immediate, day-to-day concerns or problems of the other projects.

The current objectives of the Exploratory Research Project are to: 1) extend the knowledge of the chemical and geological characteristics of low-rank coals by appropriate laboratory-scale experiments; 2) upgrade the analytical capabilities at GFETC by developing, testing, or evaluating new analytical methods and instrumentation; and 3) synthesize key organic compounds needed for reference or calibration standards but which are not available commercially.

9.2 ACCOMPLISHMENTS

9.2.1 Improved Analytical Methods

An advantage often claimed for inductively coupled argon plasma spectroscopy (ICAP) is its linearity of response over sample concentrations varying by many orders of magnitude. In practice it should be possible to calibrate the instrument at only a few points over a wide range but nevertheless obtain accurate results both within and beyond the calibration points. The general practice in the past has been to use a 10 ppm standard as the lowest concentration calibration. Although results on actual samples may indicate concentrations lower than 10 ppm, good accuracy was nevertheless assumed because of the alleged linearity of the instrument. A check was made on barium analysis, comparing results obtained using three different standards. The results from analysis of some laboratory samples are summarized in Table 9-1. The results with the 10 ppm standard are consistently low. If a similar trend is observed with other metals occurring in low concentration, a reprogramming of the ICAP computer to accept 100 ppb rather than 10 ppm standards could improve results significantly. This will be investigated in the near future.

TABLE 9-1

COMPARISON OF ICAP ANALYTICAL RESULTS FOR CALIBRATION WITH THREE DIFFERENT STANDARDS. DATA SHOWN ARE BARIUM ANALYSES EXPRESSED AS ppb.

Sample	100 ppb	1 ppm	10 ppm
1	298	301	
2	131	122	53
3	96.5	94.6	81
4	55.9	53.5	45
5	117	117	98
6	109	110	93
7	114	117	91
8	181	190	135
9	137	144	117
10	94.3	96.1	78
11	288	308	234

A project has been started to collect electron spectroscopy data (ESCA) on a number of mineral standards in order to establish a baseline data file to use for future identification of mineral species in coal and fly ash samples. There seems to be enough shift (due to chemical bonding or structural differences) in the spectral peaks to provide a means of identification even for minerals which have the same chemical formula. A case in point is the minerals calcite and aragonite which have the same formula, $CaCO_3$. The shift in the calcium peak between the two spectra can be used for identification. Table 9-2 lists the minerals on which data useful for identification have been obtained.

TABLE 9-2

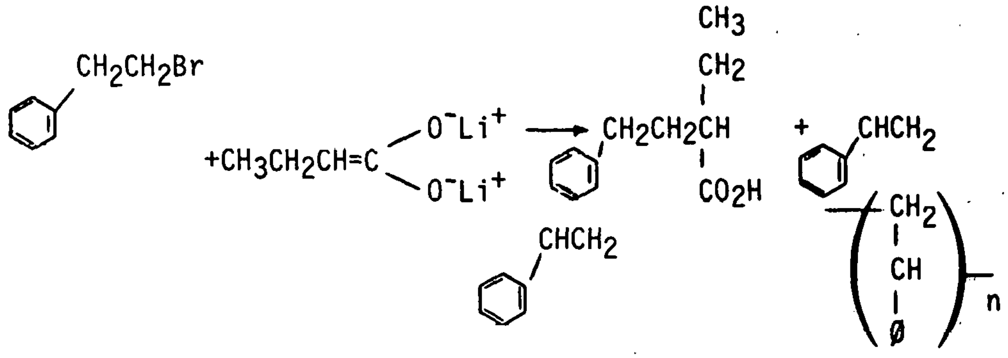
STANDARD MINERALS FOR ELECTRON SPECTROSCOPIC IDENTIFICATION OF SPECIES IN COAL AND ASH SAMPLES

Mineral	Formula	Peaks used for Identification
Albite	$Na_2Al_2Si_6O_{16}$	Na,O
Anhydrite	$Ca\ SO_4$	Ca,O
Apatite	$Ca_{10}P_6O_{24}F_2$	Ca,O
Aragonite	$Ca\ CO_3$	Ca,O
Biotite	$K_2\ (Mg,Fe)_2\ (Al,Fe)_2\ (SiO_4)_3$	O
Calcite	$Ca\ CO_3$	Ca,O
Epiclote	$Ca_4\ (Al,Fe)_6Si_6O_{25}\cdot H_2O$	Ca,O
Grossularite	$Ca_3Al_2Si_3O_{12}$	Ca,O

A variety of methods were investigated to develop a means for obtaining ESCA data on coals. A major problem in this type of analysis is the formation of an electric charge on the surface of the samples. A consequence of this surface charging is that it becomes nearly impossible to separate the peaks arising from the different types of carbon atoms. A number of coatings, ranging from soap to gold, were tried to eliminate the problem. An important criterion of a coating is that it must provide complete coverage of the surface while being only a few angstroms thick. Gold proved to be the most chemically inert and easiest to apply. Gold was also chosen because it is used in the calibration of the ESCA instrument. However, the gold coating proved to be inadequate because oil vapors from the vacuum pump of the gold coater were also deposited on the surface of the samples. Another approach involved finely grinding the samples and pressing the resulting powders into indium foil. The samples were then analyzed with and without neutralization. The neutralizer essentially floods the sample with electrons to neutralize the positive charge that was built up on the surface. This proved to be the method that gave the best results and did not require altering the sample surface.

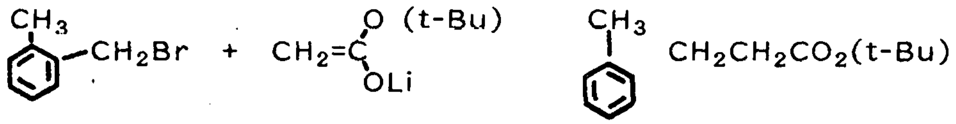
9.2.2 Organic Syntheses

The failure of dilithium acetate to undergo the substitution reaction with naphthylethyl bromide (as discussed in DOE/FC/QTR-82/1) necessitated finding an alternative reaction that would not proceed with a preponderance of the elimination reaction. Thus the reaction of dilithium butanoate with phenethyl bromide was studied to see if the problem concerns the solubility of the dilithium acetate. A very poor recovery of acids was obtained.



It was concluded that the conditions favor elimination over substitution for any nucleophilic enolate dianion. An attempt was made to overcome the elimination reaction problem by reacting α-bromoacetonaphthone with dilithium propanoate. The reaction did not proceed as well as expected, since a poor yield of acids was obtained. The major product of the reaction has not yet been identified.

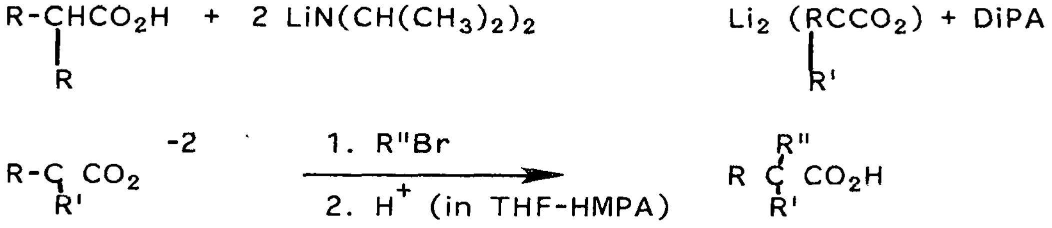
The substitution of acetate on alkyl halides to give arylalkanoic acids useful for synthesizing hydroaromatics was studied in another manner. The monolithium anion of t-butyl acetate was prepared by reaction with lithium diisopropylamide. The anion gave a high yield of the substitution product with o-methylbenzyl bromide:



This ester will be used to synthesize 4-methylindane, 7-methylindene, 3,7-dimethylindene, and 1,4-dimethylindane. The use of this ester as the ^{13}C-labelled lithium enolate is being considered for the synthesis of ^{13}C, D-labelled dihydropyrene and other hydroaromatics.

Experience over the past months with Friedel-Craft acylation reactions has shown their limitations in both reactivity and selectivity. Consequently, the reactions of the dilithium salts of fatty acids and the lithium enolates of fatty acid esters with aryl halides are being studied. The respective reaction schemes are:

Scheme 1.

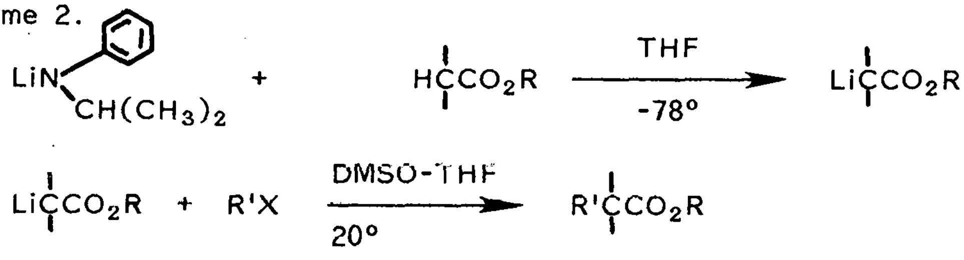


$$R\text{-}\underset{R}{CH}CO_2H + 2\ LiN(CH(CH_3)_2)_2 \qquad Li_2\ (\underset{R'}{R C}CO_2) + DiPA$$

$$\overset{-2}{R\text{-}\underset{R'}{C}\ CO_2} \xrightarrow[\text{2. } H^+ \text{ (in THF-HMPA)}]{\text{1. } R''Br} R\ \underset{R'}{\overset{R''}{C}}\ CO_2H$$

where R,R' = H, CH_3, or C_2H_5

Scheme 2.



Several attempts have been made with Scheme 1 using 1-bromo-2-naphthylethane, 1-bromo-2-phenylethane, and α-bromo-2'-acetonaphthone. All three reactions gave low yields (<10 pct) but the great potential of the reaction sequence makes more development work desirable. Scheme 2 has not yet been investigated.

∂-1-Naphthylbutyric acid was converted to the acid chloride via thionyl chloride. The acid chloride was then refluxed in carbon disulfide with aluminum chloride to produce 1-keto-1,2,3,4-tetrahydrophenanthrene in 90 pct yield. Cyclization with methanesulfonic acid gave only 80 pct yield, indicating the aluminum chloride method to be better for working with small amounts of isotopically labelled compounds.

β-2-Naphthoylpropionic acid was reduced to γ-2-naphthylbutyric acid by a modification of the Wolff-Kishner reduction using diethylene glycol as solvent. The yield was only 60 pct. Gas chromatography of the methyl ester of the product (formed with $BF_3:CH_3OH$) showed some impurities. Further investigation of this method is desirable.

6-Methoxy-1-tetralone was converted to 4-methyl-7-methoxy-1,2-dihydronaphthalene by running the Grignard reaction and then dehydrating the product with P_2O_5. Part of the dihydronaphthalene was dehydrogenated by heating in the presence of 5 pct Pd on carbon. The methoxy group was then cleaved to a hydroxyl group with 30 pct HBr in acetic acid, giving the final product 5-methyl-2-naphthol. The remainder of the dihydronaphthalene was hydrogenated to form the tetralin, which was also treated with 30 pct HBr to form 2-hydroxy-5-methyltetralin. A portion of the 5-methyl-2-naphthol was hydrogenated to form 2-hydroxy-5-methyltetralin as confirmation of the synthesis. In a similar fashion, 6-methyl-2-naphthol, 2-methyl-6-hydroxytetralin, 5-methyl-1-naphthol and 1-methyl-5-hydroxytetralin were all prepared.

A new reaction procedure using lithium aluminum hydride and aluminum chloride appears to be superior to the Clemmenson reduction in terms of time, yield, and convenience. This was demonstrated by the conversions of 2-hydroxy-4-methoxybenzaldehyde to 2-hydroxy-4-methoxytoluene and of 4-methyl-1-indanone to 4-methylindane.

3-Methyl-2a,3,4,5-tetrahydroacenaphthene was prepared using the following synthetic scheme: 2-methyl-1-tetralone was reacted with lithium t-butyl acetate to produce 2-methyl-1-hydroxy-1-(t-butylacetyl) tetralin. This was hydrogenated and saponified, using routine procedures, to produce α-1-(2-methyl-1,2,3,4-tetrahydronaphtyl)acetic acid. The acid was cyclized to the ketone using thionyl chloride and aluminum chloride. The ketone was reduced to the final product with lithium aluminum hydride and aluminum chloride.

1,2,3,4-Tetrahydrophenanthrene-1,4-$^{13}C_2$-4,4-D_2 was synthesized use in labelled compound studies in the liquefaction project.

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