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GRAND FORKS ENERGY RESEARCH CENTER  
GORDON H. GRONHOVD, DIRECTOR

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Grand Forks Energy Research Center  
Energy Research and Development Administration  
Box 8213, University Station  
Grand Forks, North Dakota 58202

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Summary of Research Progress  
Grand Forks Energy Research Center  
January 1 to March 31, 1977

Coal Liquefaction - CO-Steam Process

A reaction temperature approaching 460° C was shown to be critical in reducing the concentration of high molecular weight material in the soluble oil produced in the CO-Steam process.

A column chromatographic method for determination of 1) hydrocarbons plus ethers and 2) polar and polymeric materials is under development for rapid evaluation of product quality. This will augment indices relating to molecular weight, which are the current mainstay.

Installation and checkout of ventillating facilities for the continuous processing unit (CPU) were completed. The final assembly of the CPU is nearing completion and pressure testing has been started.

Slagging, Fixed-Bed Gasification

Four tests were conducted at 400 psig for comparison with previous operation at 200 psig. The first three tests were terminated due to operational problems; the fourth was successfully completed to a scheduled shutdown. The higher pressure resulted in reduced concentrations of H<sub>2</sub> and CO and increased levels of CO<sub>2</sub> and CH<sub>4</sub>. Gas offtake temperature was increased at the higher pressure.

Computer modeling of hearth plate temperatures for the heat-up stage of gasifier operation has resulted in reasonable agreement between observed and calculated temperatures. This work along with testing of new refractories and calculation of slag characteristics has the purpose of improving hearth plate design and thereby improving operating reliability of the gasifier.

Tar analyses for 400 psig operation and 200 psig operation were found to be closely comparable. MS analyses were performed on water soluble organics.

SO<sub>2</sub> Removal Using Ash-Alkali Wet Scrubbing'

Tests on the 5000-acfm pilot scrubber conducted under a cooperative agreement with area utilities and a scrubber vendor were completed March 1. Variables studied this quarter were ionic strength and pH. Addition of 3 pct sodium (as Na<sub>2</sub>SO<sub>4</sub>) to the scrubber solution increased removals by about 15 pct (nominally 50 to 65 pct) at low L/G (10 to 50 gal/1000 scfm). Addition of magnesium (MgSO<sub>4</sub>) produced only a slight effect. Utilization of the alkali in the flyash was more than doubled as pH was reduced from 5 to the range of 2 to 3; removal efficiency was somewhat reduced.

Six one-week tests were run on the 130 scfm scrubber at GFERC. Sodium and magnesium were added in two test series paralleling work on the 5000 acfm unit. In these tests addition of magnesium resulted in very high removals, and addition of sodium lower removals. This is a reversal of the relative effects observed in the larger unit; the apparent discrepancy will be investigated in further tests.

#### Fluidized-Bed Combustion of Lignite and Western Subbituminous Coals

Following completion of modifications to the FBC, studies were conducted to determine the effects of bed temperature, air-fuel ratio, superficial gas velocity, and coal particle size on the retention of coal sulfur on ash during combustion. Retentions from 38 to 58 pct were observed for a typical North Dakota lignite. In the next quarter, tests will be conducted on 10 different Western coals to study sulfur retention in relation to ash composition; thereafter the FBC will be modified by adding ash reinjection to extend ash-SO<sub>2</sub> contact time.

#### Control of Ash Fouling in Power Boilers

Fouling tests were run on Mt. Pleasant, Texas lignite and Naughton, Wyoming subbituminous coal. Five additional tests were run to determine effects due to addition of calcium nitrate or silica. Calcium was observed to reduce deposit strength but not the rate of deposition.

A 30-day field test program performed in cooperation with the United Power Association was completed March 7. Power plant personnel collected data both by observation of the fouling condition in the boiler and by probe testing. GFERC is contributing ash analysis and data interpretation.

The JEOL scanning electron microscope was received and installed. Calibration of the heated stage microscope was completed and work on the melting behavior of the inner sinter layer of probe deposits was started.

#### Electrostatic Precipitation of Fly Ash

Construction of the 75-lb/hr furnace and pilot ESP was essentially completed, with shakedown tests to begin the second week of April.

Equipment for measuring the dielectric constant of flyash was calibrated and preliminary tests were performed on selected ashes.

## Project 1. CO-STEAM PROCESS

Submitted by: Everett A. Sondreal, Research Supervisor

Begun: FY 1975                    Expected Completion: Continuing

Personnel:

Everett A. Sondreal, Research Supervisor  
Curtis L. Knudson, Research Chemist  
Joseph E. Schiller, Research Chemist  
Richard Bunn, Chemical Engineer  
Thomas H. May, Chemical Engineer  
Willis Beckering, Research Chemist  
Samuel H. Givand, Chemist  
Bruce W. Farnum, Chemist  
David J. Miller, Chemist  
Randall J. Molmen, Chemist  
Richard M. Payfer, Chemist  
LuAnn Sidney, Chemist  
James L. Larsen, Engineering Technician  
John D. Hilley, Research Equipment Operator  
Dean N. Evenstad, Machinist Helper  
Arthur L. Ruud, Graduate Fellow in Chemistry

## SUMMARY

The temperature-dependent depolymerization that occurs during coal liquefaction was observed at 440, 450, 460, and 470° C; the greatest change was observed upon reaching 460° C. A dramatic drop was seen in the concentration of high molecular weight material when a slurry was heated between 450 and 460° C; temperatures in this range appear to be a minimum for rapid production of oil by the CO-Steam process. Additional non-aqueous titration data have indicated that oil, asphaltene, pre-asphaltene, and THF insoluble residue of a 470° C product made at GFERC contains only half the weak acid groups of a comparable product made at lower temperatures. Four autoclave runs were performed in order to obtain accurate material balance and yield data, and results are being tabulated.

Work on the continuous process unit has been slowed by problems in the interlock system, but some pressure testing has been done.

Methods have been investigated for rapid evaluation of CO-Steam product quality. A column chromatographic method for determination of hydrocarbons plus ethers and polar/polymeric materials is under development. The HPLC procedure for molecular weight distribution will also yield data on the extent of coal depolymerization by taking a ratio of absorbances for 950 MW and 250 MW in the chromatograms.

The unexpected appearance of dimers and methylated homologs has been observed in several reaction mixtures where pure compounds were reacted under COSteam conditions. Cracking of naphthenic rings appears to give rise to the radicals needed to promote these reactions.

Nitrogen compounds in CO-Steam product and other coal liquids have been identified and measured. A number of acidic nitrogen species (carbazole and benzocarbazoles) were found in significant concentrations.

#### Temperature-Dependent Depolymerization of Coal Liquids

As previously reported (GFERC/QTR-76/5), we have obtained evidence that the molecular weight distribution of the non-distillable, THF soluble fraction of products decreased dramatically with increased reactor temperature and was influenced to a lesser extent by reactor residence time. During this quarter the temperature where the concentration of 950 MW material dropped to essentially zero has been determined. In this experiment, slurry samples were obtained over half-hour intervals at 440, 450, 460, and 470° C. Figure 1 depicts the molecular weight profile changes that occurred with temperature. As previously indicated, residence time effects are observed at 440° C. A reasonable decrease is seen in the 950 MW region for samples 1 and 4 that were taken upon reaching 440° C and after 26 minutes at 440° C, respectively.

The profiles for samples 6, 9, and 11 are each averages of four profiles obtained at 450, 460, and 470° C, respectively, since little change occurred during the half hour residence time at each temperature. The data indicate that during the ten minutes of heating from 450° to 460° C, the 950 MW material essentially disappeared. This means that a continuous unit operating between 460 to 470° C should produce a coal liquid which could be pumped at room temperature. It is advantageous that the depolymerization occurs rapidly at 460° C since less methane, ethane, and propane will be produced.

Studies to determine the kinetics of the production of compounds from coal that are volatile under MS inlet conditions (350°) have been attempted. The use of pyrene as a solvent indicated that not enough volatiles are produced to give accurately measurable concentrations of product if a 30 pct as-received coal slurry is used. We have measured the viscosities of slurries of higher percents of coal in anthracene oil at different temperatures to determine the greatest percent coal slurry that can be charged to the batch reactor. A slurry of 48 pct as-received lignite in anthracene oil was charged successfully. The reaction of slurries with higher coal percents or with pyrene plus hydroxyphenes as solvent may enable the production of volatile products in high enough concentration to measure reaction rates accurately. The economics of the CO-Steam process would be improved by using more concentrated slurries.

#### Acidities of CO-Steam Products

CO-Steam products were separated into four fractions based on solubility in hexane, toluene, and tetrahydrofuran (Table 1). Since viscosity of model coal-derived solutions was previously found to be dependent on acid content (hydrogen bonding), the acidity of the total products and the four fractions was measured by non-aqueous titration

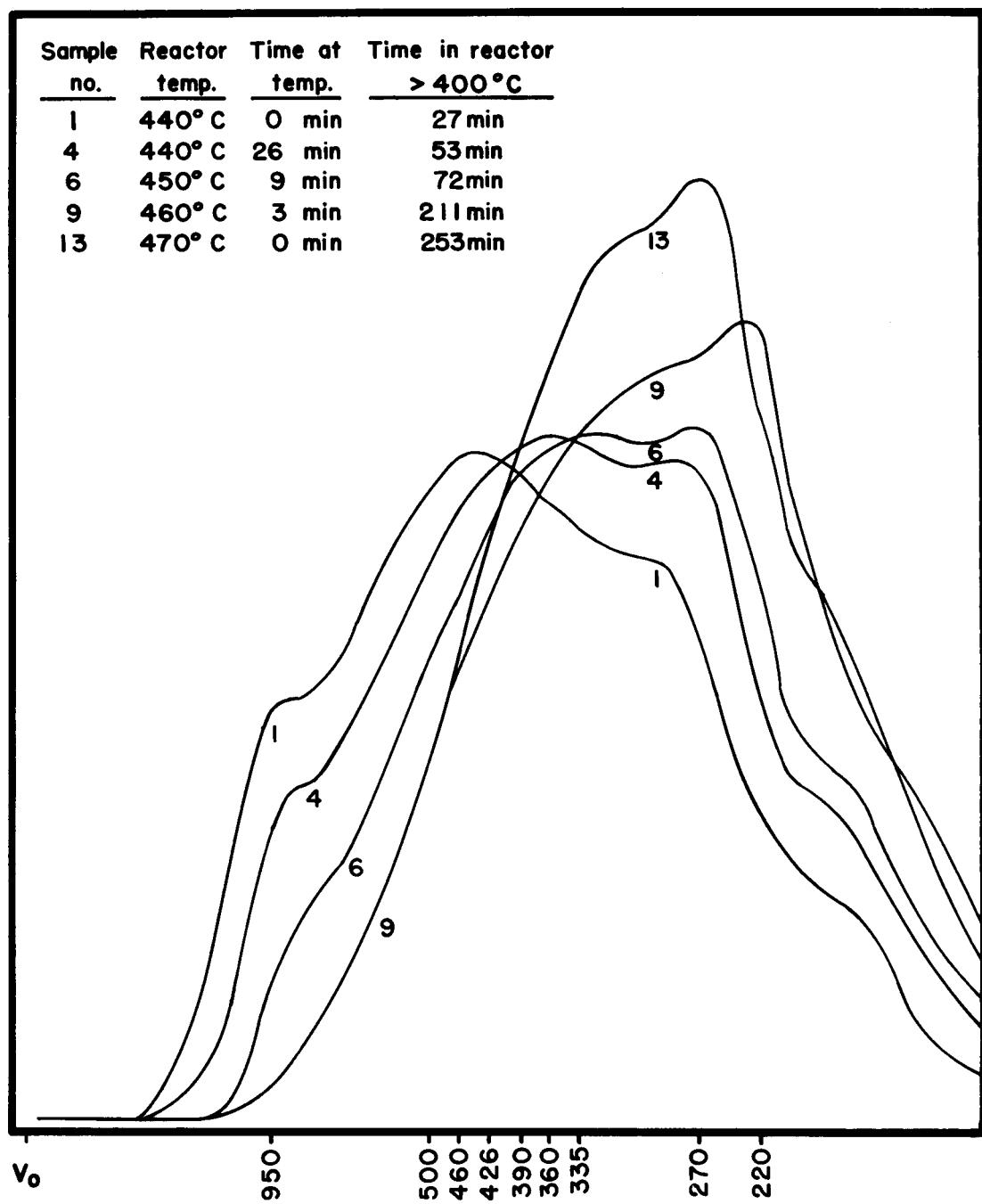


FIGURE 1. The effects of temperature on the molecular weight distribution of the THF soluble, non-distillable fraction of coal liquefaction product. Data from Run # 53.

TABLE 1

CO-Steam Product	A	B	C
<b>Solubility fractions (wt. %):</b>			
Oil (hexane soluble)	55.9	48.7	52.3
Asphaltene (toluene soluble hexane insoluble)	22.6	18.4	22.8
Preasphaltene (THF soluble toluene insoluble)	20.9	17.9	4.7
Tetrahydrofuran insoluble	0.6	15.0	20.2
 <b>Acidity (Meg H<sup>+</sup>/g):</b>			
Oil	1.587	1.361	0.513
Asphaltene	1.945	2.449	0.873
Preasphaltene	1.974	2.052	1.058
THF Insoluble	1.518	1.027	0.266
Total Product	1.729	1.725	0.544
Calculated Acidity <sup>a</sup>	1.748	1.635	0.571

<sup>a</sup> Acidity calculated as the weighted sum of the acidities of the individual fractions.

with tetra butyl ammonium hydroxide. This reagent measures the total nitrogen acids such as carbazole and indole as well as phenolic type acids. Product A was deashed, resulting in removal of nearly all of the THF insoluble fraction. Figure 2 illustrates the contribution of each solvent separation fraction to total acidity of each CO-Steam product.

#### Dimerization and Methylation in the CO-Steam Process

Mass spectral examination of several CO-Steam reaction mixtures has revealed the formation of dimers and methylated compounds from major components present at the beginning of the reaction. In autoclave Run 54, pyrene was used as solvent for lignite in the reaction. Only small quantities of individual compounds were formed from the lignite, but about 2 pct of the pyrene was converted to methylpyrene, and about 0.1 pct of the pyrene dimerized. In early autoclave runs where tetralin was used as the vehicle oil, a substantial yield (2-3 pct) of dimer was also observed. Samples from the University of North Dakota Chemistry Department of the model compounds quinoline and anthracene which had been reacted under CO-Steam conditions also showed substantial quantities of methylated and dimeric products. The formation of larger molecules during coal liquefaction reactions is both unexpected and undesirable, and processing conditions must be adjusted, if possible, to minimize their production. Distillation and solubility data indicates that with a hydrogen donor solvent and synthesis gas reactants, product quality is not reduced due to re-polymerization in reactions at 470° C.

#### Nitrogen Compounds in Coal Liquids

Work is almost complete on characterization of the nitrogen compounds contained in the first polar fraction eluted during column chromatography of CO-Steam products and other coal liquids or solids. Unambiguous identification of many individual compounds was accomplished using GC/MS. A chromatogram of one SRC process solvent is shown in Figure 3. The GC column was 3 pct OV 17 on Chromasorb W, and the temperature was programmed from 100-275° C at 8°/min. The compound names that are abbreviated in Figure 3 are listed in Table 2 together with the means of identification. No attempt was made to distinguish among the many possible isomeric methylated heterocyclics encountered, but quinoline and isoquinoline are resolved, and acridine and three other benzoquinolines are separated from each other. In this coal-derived liquid, as in several others studied, quinoline is much more abundant than isoquinoline, and acridine accounts for only a small part of the total benzoquinoline type compounds. Carbazole is generally the most concentrated single compound present.

Table 3 summarizes the LVMS data for several SRC process solvents and for one CO-Steam product. Since the CO-Steam product is not a distillate, high boiling constituents such as benzocarbazoles, azachrysenes, and dibenzocarbazoles are present in significant quantities. The

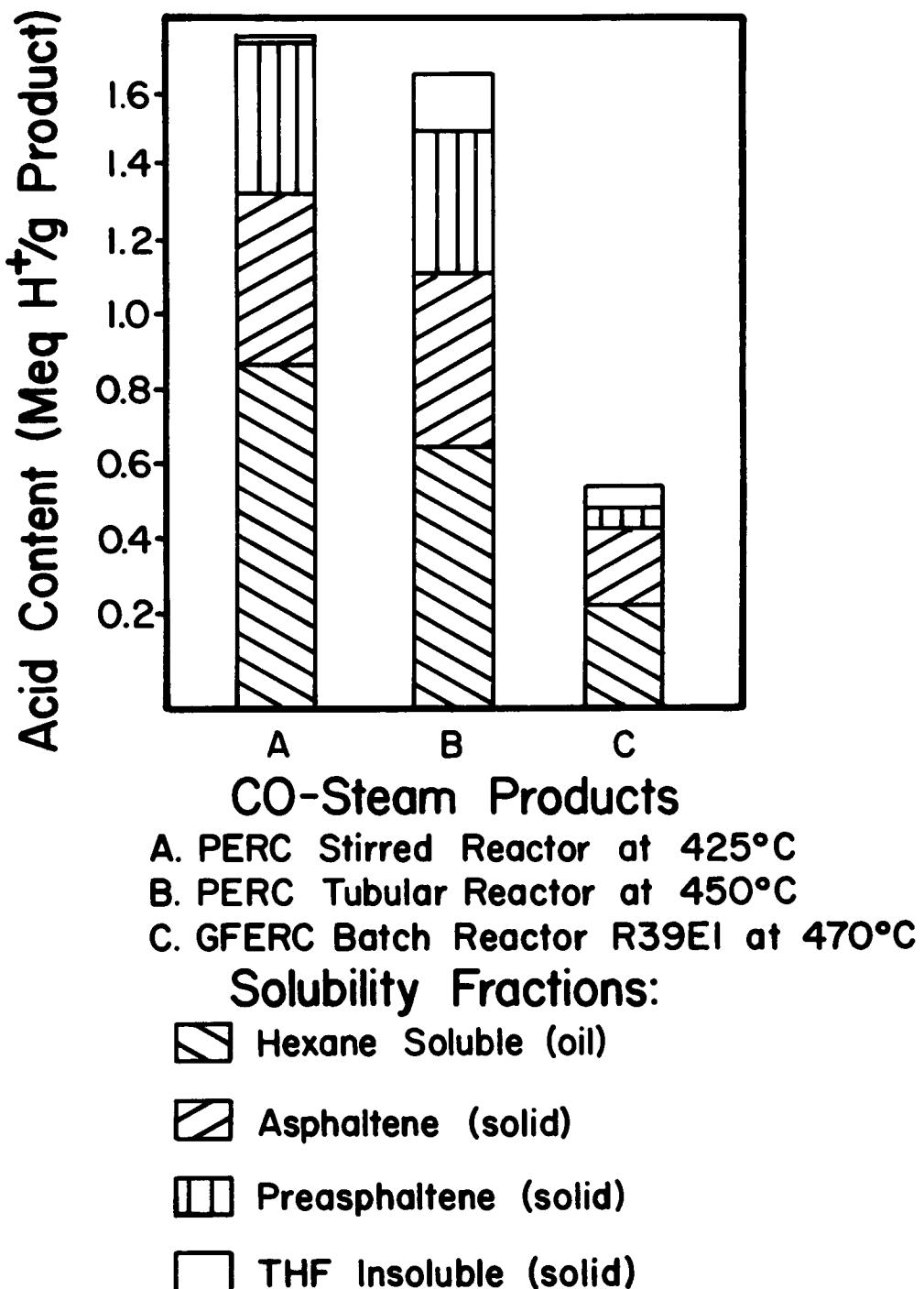


FIGURE 2. Acidity distribution in CO-Steam products.

# SRC SOLVENT – FIRST POLAR FRACTION

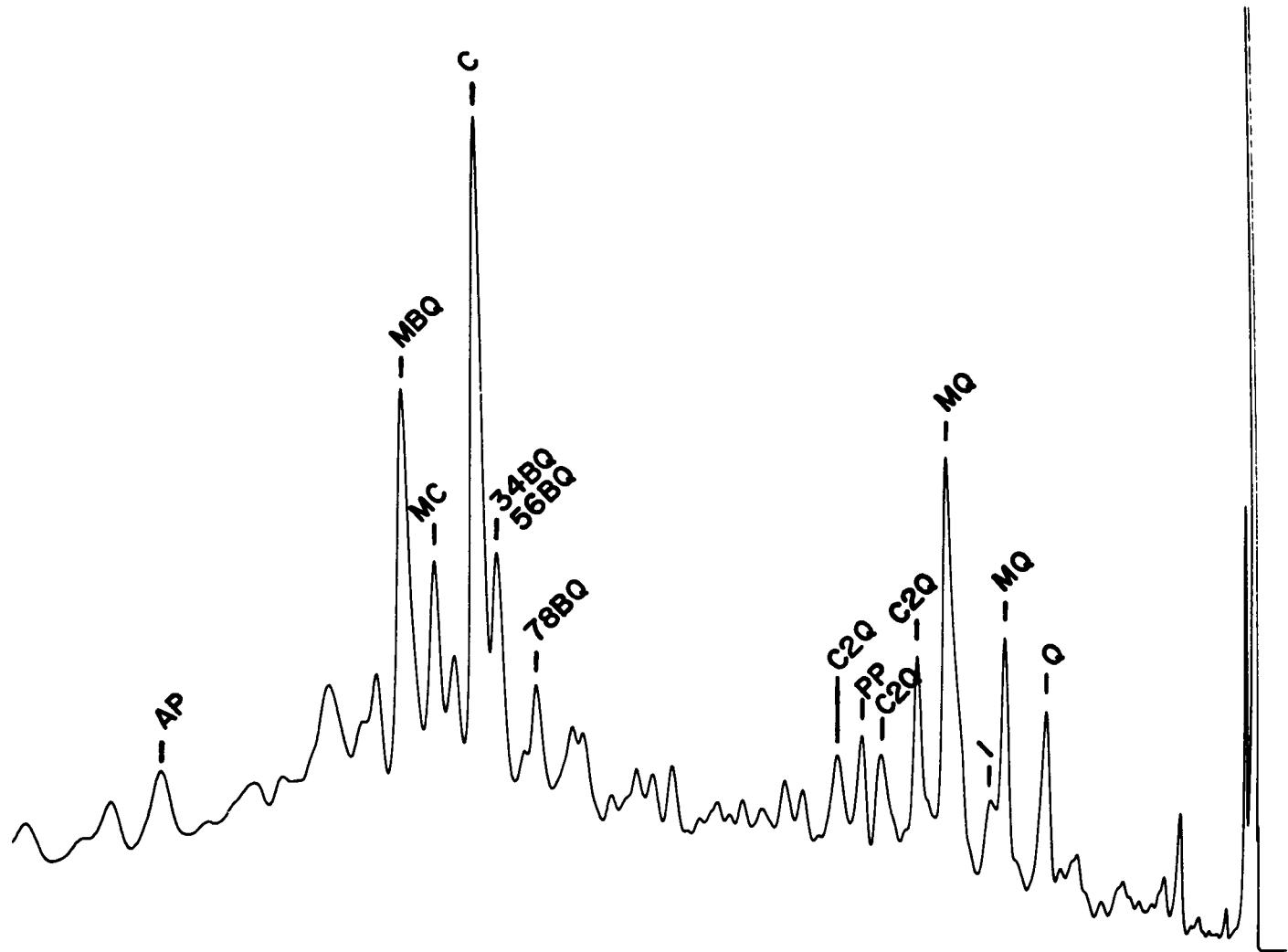


FIGURE 3. Chromatogram of the nitrogen compounds in an SRC process solvent. Compound names are listed in Table 2.

TABLE 2. - Compound names that correspond to abbreviations in figure 3

<u>Abbreviation</u> <sup>1/</sup>	<u>Identification</u>	<u>Compound</u>
Q	a	Quinoline
iQ	a	Iso-Quinoline
I	a	Indole
MQ	b	Methylquinoline
C <sub>2</sub> Q	b	Dimethylquinoline or Ethylquinoline
PP	a	2-Phenylpyridine
34BQ	a	3,4- Benzoquinoline
56BQ	a	5,6- Benzoquinoline
78BQ	a	7,8- Benzoquinoline
A	a	Acridine
C	a	Carbazole
MC	b	Methylcarbazole
MBQ	b	Methylbenzoquinoline
AP	a	1-Azapyrene

1/ Abbreviation of compounds from figure 3.

a Identified by GC retention time and MS.

b Identified by MS only, since standards were not available.

TABLE 3. - Quantitative data from LVMS analysis of the N-rich fractions.  
Numbers in the table are weight percent of this fraction.

Probable compound type	Mass Z Series	SRC Solvent (307)	SRC Solvent (122)	SRC II Solvent (115R)	SRC Solvent Wilsonville	CO-Steam Product
Pyridines, Anilines	5N	0.0	2.2	3.9	7.9	1.0
Tetrahydroquinolines	7N	1.8	5.2	8.3	5.0	1.9
Indoles	-9N	0.0	0.5	1.3	0.6	0.5
Quinolines	-11N	20.0	16.9	8.2	22.5	5.2
Phenylpyridines, Diphenylamines	13N	10.3	14.5	18.1	8.9	5.8
Amino biphenyls						
Carbazoles	-15N	19.7	10.5	10.5	6.9	7.0
Benzoquinolines	-17N	15.5	12.0	8.2	8.2	8.1
Naphtheno benzo-quinolines	-19N	1.2	2.3	2.8	0.8	2.8
Azapyrene, Azafluor-anthenes	-21N	1.1	2.0	3.5	1.3	1.8
Benzocarbazoles	-21N	3.5	2.0	1.4	0.7	3.8
Azachrysenes	23N	0.6	0.6	0.3	0.5	2.4
Naphthemoazachrysenes	25N	0.0	0.0	0.0	0.0	1.2
Dibenzocarbazoles	-27N	0.0	0.0	0.0	0.0	2.2
Non Volatile		8.3	4.1	5.1	7.6	35.1
Non-Nitrogen Compounds		18.0	27.2	28.4	31.7	21.2

presence of these suspected carcinogens should be noted so adequate safety precautions may be taken. For the CO-Steam product as well as the other liquids studied, the bulk of the volatile compounds fall in the range of quinolines to benzoquinolines. A publication is in preparation where these results are reported.

#### Accuracy Of Mass Spectral Analysis

In order to determine the accuracy of low voltage mass spectral (LVMS) analysis of coal-derived oils at GFERC, several samples have been examined both by LVMS and gas chromatography (GC). Results for two oils are given in Table 4. Values from LVMS are generally about 10-20 pct (relative) lower than concentrations of the same compounds measured by GC. This difference resulted from the fact that the GC resolved these mixtures into 28 and 33 components, respectively, while the mass spectrometer saw, respectively, 66 and 99 individual masses. Some components which were unresolved in the GC separation therefore "inflated" those peaks that did appear and caused them to be larger. The values from LVMS are thus probably more accurate than those by GC analysis, and the more complicated the mixture, the more unreliable the GC becomes.

#### Rapid Methods for CO-Steam Product Quality

A method is under development for rapid measurement of hydrocarbons plus ethers and polar/polymeric compounds in CO-Steam product by a modification of the column chromatography procedure used at GFERC. The sample is dissolved in methylene chloride and eluted from activity I neutral alumina with methylene chloride and then with 9:1 tetrahydrofuran-methanol. The resulting fractions are quantitatively diluted, and the integrated absorbance of each solution is used as a measure of concentration. The ultraviolet spectra of the hydrocarbon plus ether fractions from several CO-Steam products were essentially identical, and studies are underway to determine if the absorptivities are also the same. The polar/polymeric fractions absorbed in the visible region, and the range 750 nm to 400 nm were used for quantification.

The ratio of the absorbance at 950 MW and 250 MW in the gel permeation chromatographic separation of solutions of the non-distillable fraction of CO-Steam product has indicated use as a product quality value. These ratios correlate with reaction conditions, since more material of 250 MW is made at higher temperature and longer residence time while the 950 MW materials are consumed. The ratios of A<sub>950</sub>/A<sub>250</sub> are concentration independent and are therefore a characteristic value for a given coal liquid.

#### CO-Steam Continuous Process Unit

Installation of heating and ventilating facilities by a contractor was completed this quarter. Small problems with air balance and temperature control are still being ironed out.

TABLE 4. - Comparison of gas chromatographic and mass spectral analysis of two coal-derived oils

<u>Compound</u>	Crowley Coal Tar Oil		Allied Creosote Oil	
	MS (66 masses) pct	GC (28 peaks) pct	MS (99 masses) pct	GC (33 peaks) pct
Naphthalene	5.6	8.5	5.3	6.6
Methylnaphthalene	15.5	20.3	14.1	16.4
Fluorene	6.2	7.0	6.0	6.7
Phenanthrene	16.1	18.8	14.3	17.2
Pyrene and Fluoranthrene	11.0	12.7	9.2	12.8

Work has progressed well this quarter, as can be seen by the pct completion indicated on Table 5. The only major holdup has been an interlock system designed and supplied by an outside contractor. Numerous errors had to be corrected by in-house personnel.

Deionized water was pumped through a portion of the system, demonstrating the operability of two pumps at approximately 2000 psig.

TABLE 5. - Completion of CO-Steam continuous processing unit at GFERC

Area	% complete			Estimated completion date	
	Mech.	Elec.	Util.	Latest Estimate	Original
<b>Gas Supply:</b>					
Design	95	100	100	E-4/18/77	M-4/29/77
Purchase	95	100	100	M-4/29/77	E-4/15/77
Construct	95	99	100		
<b>Gas Metering:</b>					
Design	100	100	--	E-4/18/77	M-4/21/77
Purchase	100	100	--	M-4/21/77	E-4/15/77
Construct	90	99	--		
<b>Slurry Metering:</b>					
Design	70	100	--	E-4/21/77	M-4/29/77
Purchase	100	100	--	M-4/29/77	E-4/14/77
Construct	70	80	--		
<b>Reaction:</b>					
Design	50	100	40	E-4/21/77	M-5/6/77
Purchase	60	100	90	M-4/6/77	E-4/21/77
Construct	70	95	70		
<b>Gas-Liquid Separation:</b>					
Design	90	100	80	E-4/18/77	M-4/21/77
Purchase	100	100	100	M-4/21/77	E-4/14/77
Construct	90	80	50		
<b>Let-Down:</b>					
Design	90	100	90	E-4/18/77	M-4/29/77
Purchase	100	100	100	M-4/29/77	E-4/14/77
Construct	60	90	0		
<b>Panel Board:</b>					
Design	95	100	100	E-4/21/77	U-4/29/77
Purchase	95	99	100	M-4/21/77	M-4/29/77
Construct	95	95	90	U-4/29/77	E-4/21/77

## Project 2. SLAGGING, FIXED-BED GASIFICATION

Submitted by: Robert C. Ellman, Research Supervisor

Begun: FY 1975      Expected Completion: FY 1980

Personnel:

Robert C. Ellman, Research Supervisor  
M. Merle Fegley, Chemical Engineer  
Jerome J. Hoepfner, Chemist  
Philip G. Freeman, Research Chemist  
Leland E. Paulson, Chemical Engineer  
Bruce C. Johnson, Chemical Engineer  
Robert B. Porter, Chemical Engineer  
Harold H. Schobert, Research Chemist  
David Mioduszewski, Chemical Engineer  
Edward F. Bitzan, Chemist  
S. Alex Cooley, Mechanical Engineer  
Wayne A. Kinney, Physical Science Aid  
Jacquelyn K. Olson, Lab. Technician (Chemistry)  
Gale G. Mayer, Laboratory Technician  
Paul L. Mattern, Foreman  
Ronald R. Brown, Instrumentation Mechanic  
Alan V. Lilke, Laboratory General Mechanic  
Robert C. Johnson, Sheet Metal Worker  
Owen B. Varnson, Machinist Helper  
James E. Tibbetts, Laboratory General Mechanic  
Wayne J. Hansel, Graduate Fellow in Mechanical Engineering

## SUMMARY

A pilot-scale pressure fixed-bed slagging gasifier, constructed and operated at GFERC in the period 1958 to 1965, has been reconditioned for further studies. The pilot plant was designed originally to establish operability of the slagging method of ash discharge and to evaluate process parameters.

A major objective of the reactivated program is to utilize the pilot plant to produce liquid, solid, and gaseous effluents for study. It is planned to determine the properties and characteristics of effluents produced as a function of coal source and operating variables. These studies will aid in developing methods for maximizing the recovery of usable products, facilitating design of control technology for treatment of environmentally undesirable wastes, and aiding in achieving maximum reuse of water.

The objectives of operation to date have included accumulating personnel operational experience, upgrading control and operating techniques, establishing the variability of operational parameters, assessing the reliability and reproducibility of sample collection techniques for

the condensable effluents and the effect of operating parameters on their characteristics. When these objectives have been achieved, a control test condition for the comparative evaluation of various coals will be selected.

During the past quarter the effect of operating pressure on gasifier results was investigated. Test conditions were identical with tests of the previous quarter, except for operating pressure. In respect to gasifier operation, gas composition was somewhat affected by increased pressure; methane and carbon dioxide contents increased at the expense of carbon monoxide and hydrogen concentrations. Other phases of operation were not appreciably affected.

#### DISCUSSION

##### Operating Observations and Results

Four tests were attempted during the quarter as indicated in Table 1. Three of the tests were terminated by operational problems at the hearth area while the fourth Test (RA-16) continued to a scheduled shutdown after 7.6 hours of slagging operation. Operating conditions for the four tests were 400 psig operating pressure, 4000 scf/hr oxygen rate, and 1.0 molar oxygen/steam ratio. The objective of these tests was to obtain results from the 400 psig operation for comparison with 200 psig operation at the same oxygen and steam rates.

TABLE 1. - Summary data for runs RA-13 through RA-16

Run Number.....	RA-13	RA-14	RA-15	RA-16
Date.....	1/26/77	2/23/77	3/17/77	3/29/77
Operating pressure....psig..	400	400	400	400
Fuel gasified.....	lignite <sup>a/</sup>	lignite <sup>a/</sup>	lignite <sup>a/</sup>	lignite <sup>a/</sup>
Oxygen rate.....scfh..	4000	4000	4000	4000
Steam rate.....lb/hr..	190	190	190	190
Oxygen/steam molar ratio....	1.0	1.0	1.0	1.0
Hrs of slagging operation...	1.4	3.6	0.0	7.6
Cause of shutdown.....	plugged taphole	high fuel bed loss	plugged taphole	end of test
Fuel rate (as chg'd)..lb/hr.	1119	1095	--	1122
Product gas rate (inert gas free).....scfh..	--	20,006	--	20,079

<sup>a/</sup> Indian Head.

Test RA-13 proceeded for only 1.4 hours of slagging before a stoppage of slag flow led to shutdown. The cause of the taphole plugging which terminated the test was established when the slagging section was removed for cleanout. Four "pockets" were observed -- one in front of each tuyere -- but they did not extend to the taphole, indicating that the entering oxygen-steam mixture did not have sufficient velocity to penetrate to the taphole. In order to increase the entering velocity, inserts were fabricated and installed in each tuyere reducing the cross-sectional area of the opening by approximately half. Thus at 400 psig operation with the inserts, the entrance velocity is very similar to that used for the 200 psig tests (approx. 51.0 ft/sec). The inserts were used for the remaining tests this quarter.

In test RA-14 slag flowed satisfactorily for almost 2-1/2 hours and then stopped. In an attempt to resume slag flow the taphole burner was ignited and cooling water to the taphole coil was reduced. After a 17-minute interval without slag flow, the high (100,000 Btu/hr) heat output from the burner cleared the taphole and slag flow resumed. The reduced cooling water and excessive use of the taphole burner resulted in failure of the taphole cooling coil. The taphole soon eroded and excessive fuel bed loss terminated the test.

Slag appeared briefly at the taphole at a time corresponding with the scheduled start of slag flow in RA-15, but none actually discharged. After a variety of attempts to initiate slag flow failed and 20 minutes without any slag, the test was terminated.

Test RA-16 continued satisfactorily for a total of almost 7-1/2 hours of slagging operation to a scheduled termination. Some minor problems were encountered during the test, such as poor visibility in the bath section during each coal charging interval, but slag flow was unaffected.

Two of the four tests (RA-14 and RA-16) were long enough to obtain meaningful test results. Table 2 lists average gas analyses calculated to a purge gas free basis for these two tests along with analyses from two tests at 200 psig operating pressure carried out during the previous quarter. All of these tests used a 4000 scf/hr oxygen rate, 1.0 molar oxygen/steam ratio and a common test coal. As pressure increased, the CO<sub>2</sub> and CH<sub>4</sub> contents of the product gas increased while CO + H<sub>2</sub> decreased. Heating value of the higher pressure gas was also slightly higher.

TABLE 2. - Average gas analyses for 200 and 400 psig operation<sup>a/</sup>

Run Number.....	RA-11	RA-12	RA-14	RA-16
Pressure.....psig..	200	200	400	400
Component:				
CO <sub>2</sub> .....	7.8	7.4	10.9	8.9
H <sub>2</sub> .....	.5	.6	.5	.5
C <sub>2</sub> .....	.2	.1	.1	.2
H <sub>2</sub> .....	28.6	29.1	26.6	27.4
CO.....	57.6	57.7	54.3	55.7
C <sub>2</sub> H <sub>6</sub> .....	.2	.2	.3	.4
CH <sub>4</sub> .....	5.1	4.9	7.3	6.9
TOTAL.....	100.0	100.0	100.0	100.0
Heating value...Btu/ft <sup>3</sup> ..	339.1	340.0	345.9	349.3

a/ Corrected for purge gas.

Table 3 shows a comparison of results from the two 400 psig tests from this quarter and the two 200 psig tests from the previous quarter. Most of the results compare closely but, because of the lower CO + H<sub>2</sub> content of the 400 psig product gas, oxygen and steam consumption values based on the CO + H<sub>2</sub> were higher for 400 psig operation and CO + H<sub>2</sub> production per pound of fuel was lower. Average gas offtake temperatures also increased with increasing pressure.

#### SLAG CHARACTERIZATION

Since the gasifier slag is a mixture of silicates and oxides, characterization of the slag was found to be facilitated by applying the conceptual and experimental techniques of geochemistry and igneous petrology. Expressing the slag composition in terms of a set of standard or normative minerals provides a method for readily predicting or describing slag behavior in terms of known phase diagrams or melting relations. A computer program, PETCAL, originally developed by the Nevada Bureau of Mines and Geology, has been adapted for performing the petrographic normative calculations on gasifier slag. The slag differs from naturally occurring magmas in two important respects: slag is extremely deficient in silica and it occasionally contains large amounts of sulfur. As a result the original PETCAL program had to be modified to take these considerations into account. The modified program has been debugged and is now in regular use.

TABLE 3. - Comparison of operating results at 200 and 400 psig

Run Number.....	RA-11	RA-12	RA-14	RA-16
Operating pressure..psig..	200	200	400	400
Total slagging.....hr..	4.68	6.88	3.35	7.43
Calculating period....hr..	4.60	6.73	2.28	6.68
Oxygen/steam ratio				
.....mole/mole..	1.0	1.0	1.0	1.0
Oxygen rate.....scf/hr..	4,000	4,000	4,000	4,000
Steam rate.....lb/hr..	190	190	190	190
Fuel rate.....lb/hr..	1,087	1,114	1,095	1,122
Fuel rate (maf)....lb/hr..	708	731	729	763
Fixed carbon rate..lb/hr..	372	384	391	414
Trial gas rate (inert gas free).....scf/hr..	20,125	20,458	20,006	20,079
Slag rate.....lb/hr..	71	74	55	72
Oxygen consumption (inert gas free):				
cu ft/M cu ft gas.....	198.8	195.5	199.9	199.2
cu ft/M cu ft CO+H <sub>2</sub> .....	230.7	225.4	247.3	239.6
cu ft/lb fuel.....	3.68	3.59	3.65	3.56
cu ft/lb maf fuel.....	5.65	5.48	5.49	5.24
Steam consumption (inert gas free):				
1b/M cu ft gas.....	9.44	9.29	9.50	9.46
1b/M cu ft (CO+H <sub>2</sub> ).....	10.96	10.70	11.75	11.38
1b/lb fuel.....	.17	.17	.17	.17
1b/lb maf fuel.....	.27	.26	.26	.25
Gas production:				
cu ft/lb fuel.....	18.52	18.37	18.27	17.89
cu ft/lb maf fuel.....	28.43	28.01	27.45	26.32
CO+H <sub>2</sub> production:				
cu ft/lb maf fuel.....	24.50	24.30	22.19	21.89
Cold gas efficiency..pct..	85.4	84.2	84.6	82.8
Average steady state off- take temperature....°F..	284	284	332	338

One of the most important aspects of the slag characterization studies concerns the development of methods for producing a frozen, protective layer of slag on the hearth refractory. As a part of that development, values for many of the important fluid mechanical constants were calculated or estimated in order to develop a qualitative understanding of the likely heat and momentum transfer behavior of the slag. The results of the calculations are summarized in Table 4.

TABLE 4. - Selected fluid mechanical constants for Indian Head slag

<u>Quantity</u>	<u>Symbol</u>	<u>Value</u>
Fourier number	Fo	$1.6 \times 10^{-2}$
Reynolds number	Re	$2.2 \times 10^{-1}$
Grashof number	Gr	$1.5 \times 10^2$
Prandtl number	Pr	$3.2 \times 10^3$
Nusselt number	Nu	$3.1 \times 10^{-1}$

For this calculation, the slag discharge temperature was assumed to be 2400° F, at which temperature the viscosity is 22 poises.

Since the Fourier number is fairly small, large temperature gradients should exist in the slag, and any temperature disturbance will penetrate only a short distance into the slag. The very low value of Re, and a corresponding large value for  $Gr/Re^2$  indicates that flow is laminar and free convective. The large value of Pr also suggests that a thermal disturbance would penetrate much less into the slag than a momentum disturbance. Although the results summarized here are rough estimates, the trends are such that it should certainly be possible to produce a frozen or extremely viscous layer of slag without freezing the entire slag stream.

Comprehensive analyses of the contents of the hearth section, as sampled during clean-out after a run, have been initiated. Samples of the material found in the hearth are taken at 0-.5, 1, 2, and 3 feet over the hearth plate. This purpose of this work is to acquire a data base for developing understanding of the mechanism of slag formation, and the extent and shape of the gasification reaction zone.

#### REFRACTORY TESTING

An isothermal cup test was completed using a chrome-alumina refractory (Harbison-Walker "Ruby") and Indian Head slag. The test was run for 168 hours at 1180° C. At the end of the test the specimen showed a +0.04 pct weight change and a +1.64 pct enlargement of the cavity. Other than some slight discoloration in the vicinity of the test cavity, there were no noticeable effects. A supply of Ruby hearth plates has been ordered, with delivery expected in May.

## HEAT TRANSFER

A model was developed for calculating the temperature behavior of the hearth plate during the heat-up stage of the gasifier operation. This model assumes that the hearth plate is heated primarily by thermal radiation from the "fireball". A computer program is used to perform a Runge-Kutta integration scheme to calculate temperatures and the time derivatives of temperature.

The predicted temperatures are then corrected for changes caused by changing the purge gas or drawdown gas flows derived from empirical data. Corrections have the following values:  $-0.32^{\circ}$  F/scfh for an increase in purge gas flow rate, and  $10.8^{\circ}$  F/scf for drawdown gas flow. The technique has shown reasonable agreement between observed and calculated hearth plate temperatures.

An analysis of the likely magnitude of error for thermocouples mounted on or embedded in the hearth plate is in progress. This is being combined with calculations of the temperature distribution in the hearth plate to provide a design for locating and mounting thermocouples to achieve the most meaningful and accurate information regarding hearth plate temperature distribution.

Effluent Characterization and Analysis

Samples of liquid effluents for characterizing condensibles in the raw product stream have been collected in a staged condenser through which a side-stream of gas is passed, grab samples of the recycled spray washer liquor, and from the accumulated condensibles from each run. An objective of present operation is to improve and evaluate sampling techniques and develop analytical procedures.

A second sidestream sampler was tested in RA-16. In this sampler, tar, water and dust aerosols in the gas stream greater than 5 microns in size are removed and collected in a cyclone separator prior to staged condensation. Sampling consists of passing a gas stream through insulated lines to a pressure letdown, through the cyclone, into two stages of heat exchange, through a gas meter, and then vented to the stack. Water and tar vapor are condensed and collected in catch pots at the cyclone and heat exchangers. Gas temperature is measured before and after pressure letdown, after the cyclone, and after each stage of cooling. It was found that tar with little water is collected in the cyclone with the majority of the water and some light oil collected in the first stage of cooling.

In addition to the second sidestream sampler, mass rates of water and tar were measured using a Gas Chromatograph system consisting of two Gow-Mac Series 150 Gas Chromatographs attached to Spectra Physics System I computing integrators. The mass quantity of water is determined in the first GC and organics are detected as a single peak with the second unit. With the existing parallel GC systems, water determinations can be made at 5-minute intervals and organics every 15 minutes. The procedure has not been sufficiently refined to provide absolute values to tar and water production, and the variability is appreciable. Encouraging results have been obtained however and refinement of procedures and methods are in progress.

The gas liquor effluent data obtained during RA-14 and RA-16 are presented in Table 5. Table 5 compares results from three separate collection methods: 1) sidestream gas sampler; 2) spray cooler recycle liquor samples collected at the start of each data period; and 3) a composite sample from the total accumulated effluent produced during the test and collected in the spray cooler. The sidestream samplers collect samples during specific controlled periods. In contrast, the composite sample represents the final accumulation collected during the entire run. The recycle water sample, collected at the beginning of each data period, is used to determine the progressive change in composition of the accumulating recycle liquor during operation. From liquid levels in the receiver, mass production rates are computed.

The data in Table 5 shows that results from the recycle liquor samples for RA-14 and RA-16 were consistent in production of water, ammonia, and TOC but higher than those reported for the composite sample. Water production as determined by the accumulation of recycle liquor ranged from 939 to 1113 lb/ton MAF coal, while the rate as determined by the composite samples ranged from 624 to 849 lb/ton MAF. Ammonia production ranged from 8.3 to 12.1 lb/ton MAF coal using the recycle liquor samples and from 6.0 to 7.2 lb/ton MAF coal using the composite method. Total organic carbon production ranged from 8.8 to 15.4 lb/ton MAF coal in the recycle sampling method and from 6.3 to 10.4 using the composite method. Tar products as determined by composite sample methods were 50.6 lb/ton (dry basis) MAF coal for RA-14 and 60.4 lb/ton (dry basis) MAF coal for RA-16. Effluent production rates of Tests RA-14 and -16 performed at 400 lbs pressure are of the same magnitude as the effluent production rates reported in RA-11 and 12 which were run at 200 lbs pressure.

Results from the second sidestream sampler appear consistent with those from the sidestream sampler #1. The second sampler has been designed to handle a larger volume of gas, be easier to clean, and have a shorter turnaround time.

TABLE 5. - Comparative gas liquor results using three sample collection methods

DATA PERIOD: <sup>a/</sup>	RA-14				RA-16						
	Recycle water			Composite sample	Recycle water			Composite sample			
	2	3	4		2	3	4	5	6	7	
1b H <sub>2</sub> O/ton coal (MAF)	1082	1034	1066	624	1113	939	1022	963	1030	968	849
1b NH <sub>3</sub> /ton coal (MAF)	12.1	8.3	9.9	6.0	8.3	10.3	8.7	8.2	10.9	8.8	7.2
1b TOC/ton coal (MAF)	10.1	8.8	15.4	6.3	9.6	11.5	10.2	10.1	9.2	9.4	10.4
1b Tar (dry basis)/ ton coal (MAF)	--	--	--	50.6	--	--	--	--	--	--	60.4

DATA PERIOD: <sup>a/</sup>	Sidestream sampler		
	<u>3 &amp; 4<sup>b/</sup></u>	<u>5<sup>c/</sup></u>	<u>6 &amp; 7<sup>b/</sup></u>
1b H <sub>2</sub> O/ton coal (MAF)	781	831	888
1b NH <sub>3</sub> /ton coal (MAF)	7.2	9.8	8.1
1b TOC/ton coal (MAF)	6.9	8.2	8.4
1b Tar (dry basis)/ ton coal (MAF)	60.0	58.1	51.2

a/ Data period is the time interval between coal charges.

b/ Collected with sidestream sampler I.

c/ Collected with sidestream sampler II.

Tar analyses for 400 psig operation (run RA-14 and RA-16) and 200 psig operation (RA-11 and RA-12) were found to be closely comparable. Data indicate that there is little or no significant difference between the composition of tars produced at 200 psig compared to 400 psig operation when normal characterization tests are used as the basis for comparing the tars. Mass spectrometer analyses, of the composite tar sample collected in tests RA-14 and RA-16 also compared closely to analyses of RA-11 and RA-12 produced at operating pressure of 200 psig.

The aqueous fraction of gas liquor contains a variety of water soluble organics. In Table 6 is given an MS analysis of the soluble organic material in the liquor fraction of the composite sample of RA-14. The phenolic grouping (phenol, cresol, and xyleneol) accounted for approximately 80 pct of the material, while the remaining fraction consisted of heavier organic components. Usually these components are not appreciably water soluble, but their solubility may be increased by interaction with other components.

TABLE 6. - Mass spectrometer analysis of organics in liquor fraction from composite sample RA-14

<u>Component</u>	<u>ppm</u>	<u>Percent</u>
Phenol.....	5,647	56.382
Cresol.....	1,965	19.616
Xyleneol.....	453	4.523
Methylnaphthalene.....	34	0.341
Biphenyl.....	19	0.188
Dimethylnaphthalene.....	26	0.264
Fluorene.....	17	0.174
Carbazole.....	9	0.091
Dibenzofuran.....	74	0.740
Phenanthrene.....	318	3.175
Methyloibenzofuran.....	101	1.009
Methylphenanthrene.....	76	0.764
Pyrene/Fluoranthene.....	100	1.004
Methylpyrene.....	178	1.776
Benzonaphthofuran.....	68	0.684
Chrysene.....	12	0.119
Benzopyrene.....	71	0.711
 TOTAL	 9,168	 91.561

Project 3. SULFUR OXIDE EMISSION CONTROL FOR COMBUSTION  
OF WESTERN U.S. COALSProject 3A. SO<sub>2</sub> REMOVAL FROM STACK GAS BY  
WET SCRUBBINGProject 3B. FLUIDIZED-BED COMBUSTION OF LIGNITE AND  
WESTERN SUBBITUMINOUS COALSSubmitted by: Everett A. Sondreal, Research SupervisorBegun: FY 1971                           Expected Completion: ContinuingPersonnel:  
Everett A. Sondreal, Research Supervisor  
Harvey M. Ness, Research Chemist  
Willis Beckering, Research Chemist  
Samuel H. Givand, Chemist  
Gerald M. Goblirsch, Mechanical Engineer  
Franklin I. Honea, Chemical Engineer  
Arthur L. Severson, Chemical Engineer  
Dean L. Habberstad, Laboratory Technician  
Tim Gerdes, Chemist  
Bruce D. Keifenheim, Chemist  
Frederick R. Stern, Chemical Engineer  
Al Volesky, ChemistProject 3A. SO<sub>2</sub> REMOVAL FROM STACK GAS BY  
WET SCRUBBING

## SUMMARY

The fly ash derived from many Western coals contains sufficient calcium to react with all of the relatively low sulfur content of the coals to form the basis for sulfur emission control. Other alkaline oxides in the fly ash, such as magnesium and sodium, can also contribute to sulfur removal. Studies investigating the utilization of Western coal fly ash alkali in wet scrubbers to remove sulfur dioxide are being performed on a 130-scfm pilot scrubber located at GFERC, and on a 5000-acfm pilot scrubber located at the Milton R. Young Generating Station, Center, North Dakota. Tests on the 5000-acfm pilot scrubber conducted under a cooperative agreement between GFERC, Square Butte Electric Cooperative, Minnesota Power and Light Company, and Combustion Equipment Associates, were completed in March 1977.

Tests on the 130-scfm pilot scrubber were continued using a scrubber solution high in sodium and magnesium. A low sodium fly ash in lieu of high sodium was used to compare sulfur dioxide removal efficiencies and scaling rates.

Tests on the 5000-acfm scrubber using low pH to increase the utilization of fly ash alkali were performed using 1000 ppm inlet sulfur dioxide, 80 to 154 gal/ 1000 acf L/G ratios, and 0.35 to 0.63 CaO/SO<sub>2</sub> stoichiometric ratios. Calculated utilization of calcium varied from 94.2 pct at 0.76 CaO/SO<sub>2</sub> to 214.8 pct at 0.27 CaO/SO<sub>2</sub>. Utilization over 100 pct is accounted for by the reaction of cations other than Ca.

Tests on the 5000-acfm scrubber using high concentrations of sodium and magnesium were performed using 1000 ppm inlet sulfur dioxide, 10 to 40 gal/1000 acf L/G ratios, and a 0.63 CaO/SO<sub>2</sub> stoichiometric ratio. The sulfur dioxide removal was increased by 10 to 15 pct when sodium levels were increased from 1.3 to about 4 pct; the removal was marginally increased by about 5 pct when magnesium levels were increased from 0.9 pct to about 3 pct.

#### RESULTS AND DISCUSSION

##### Research Conducted with the 130-scfm Pilot Scrubber at Grand Forks

Six tests were conducted on the 130-scfm pilot scrubber during the last quarter using a low sodium fly ash from a pc-fired boiler burning lignite from Beulah, North Dakota. The tests were designed to determine sulfur dioxide removal efficiencies as a function of various liquid-to-gas ratios, and at various concentrations of sodium and magnesium in the scrubber liquor. A typical analyses of the low sodium fly ash is shown in Table 1.

TABLE 1. - Beulah, North Dakota fly ash

	High sodium ash	Low sodium ash
Loss on ignition at 800° C.....	0.2	0.1
SiO <sub>2</sub> .....	21.7	36.8
Al <sub>2</sub> O <sub>3</sub> .....	14.6	19.8
Fe <sub>2</sub> O <sub>3</sub> .....	7.9	7.9
TiO <sub>2</sub> .....	0.5	0.8
P <sub>2</sub> O <sub>5</sub> .....	0.8	0.4
CaO.....	24.3	20.4
MgO.....	7.3	6.4
Na <sub>2</sub> O.....	10.3	4.0
K <sub>2</sub> O.....	0.3	0.8
SO <sub>3</sub> .....	<u>12.0</u>	<u>2.7</u>
TOTAL	99.0	100.1

One set of tests (three tests) were conducted using a scrubber solution containing about 4 pct magnesium and a sodium concentration of about 1.5 pct. The second set of tests (three tests) were conducted using a sodium concentration of about 3.7 pct and a magnesium concentration of about 1.5 pct. The sulfur dioxide removal efficiency was determined at various liquid-to-gas ratios; the level of suspended solids was maintained below 0.2 pct. The results are illustrated in Figure 1.

The solid line represents the sulfur dioxide removal efficiency obtained using a scrubber solution containing 4 pct magnesium and 1.5 pct magnesium. The removal efficiency increased from 91 pct to 96.1 pct as L/G was increased from 10 to 31 gal/1000 scf.

The dashed line represents the sulfur dioxide removal obtained using a scrubber solution containing about 3.7 pct sodium and a magnesium concentration of 1.5 pct. The removal efficiency varies from 45.4 pct at L/G 5.5, to about 71.3 pct at L/G 31. The increase in sulfur dioxide due to sodium was not as great as that due to magnesium, especially at the low L/G values. Future experiments will investigate sulfur dioxide removal using scrubber solutions low in magnesium and sodium to establish baseline data.

#### Research Conducted with the 5000-acfm Pilot Scrubber at Center, ND

The cooperative test program being conducted during this quarter on the 5000-acfm pilot scrubber was continued from the previous quarter. The testing program was designed to investigate increasing the utilization of fly ash alkali by using low pH scrubber liquor, and also, increasing sulfur dioxide removal at low L/G by using a scrubber liquor containing high levels of magnesium and sodium. The tests were completed on March 1, 1977, concluding the cooperative test program.

#### Sodium and Magnesium Studies

The test series using high concentrations of sodium and magnesium were conducted at nominal L/G values of 10, 20, and 40, using sodium concentrations of 4 pct while maintaining magnesium at normal levels, or magnesium concentrations of 3 pct while maintaining sodium at its normal levels. The stoichiometric ratio was maintained at a constant value of about 0.6 CaO/SO<sub>2</sub>; suspended solids were about 2.5 pct. The results are tabulated in Table 2.

Figure 2 illustrates the sulfur dioxide removal efficiency as a function of L/G. The solid line denoted by squares represents the baseline data in which sulfur dioxide removal efficiencies were collected at soluble sodium and magnesium concentrations normally present in the scrubber. The removal efficiencies ranged from 39.4 pct at L/G 12.3 to 57.4 pct at L/G 41.5. The effect of increasing the soluble sodium concentration on sulfur dioxide removal is represented by the dashed line denoted by triangles. In

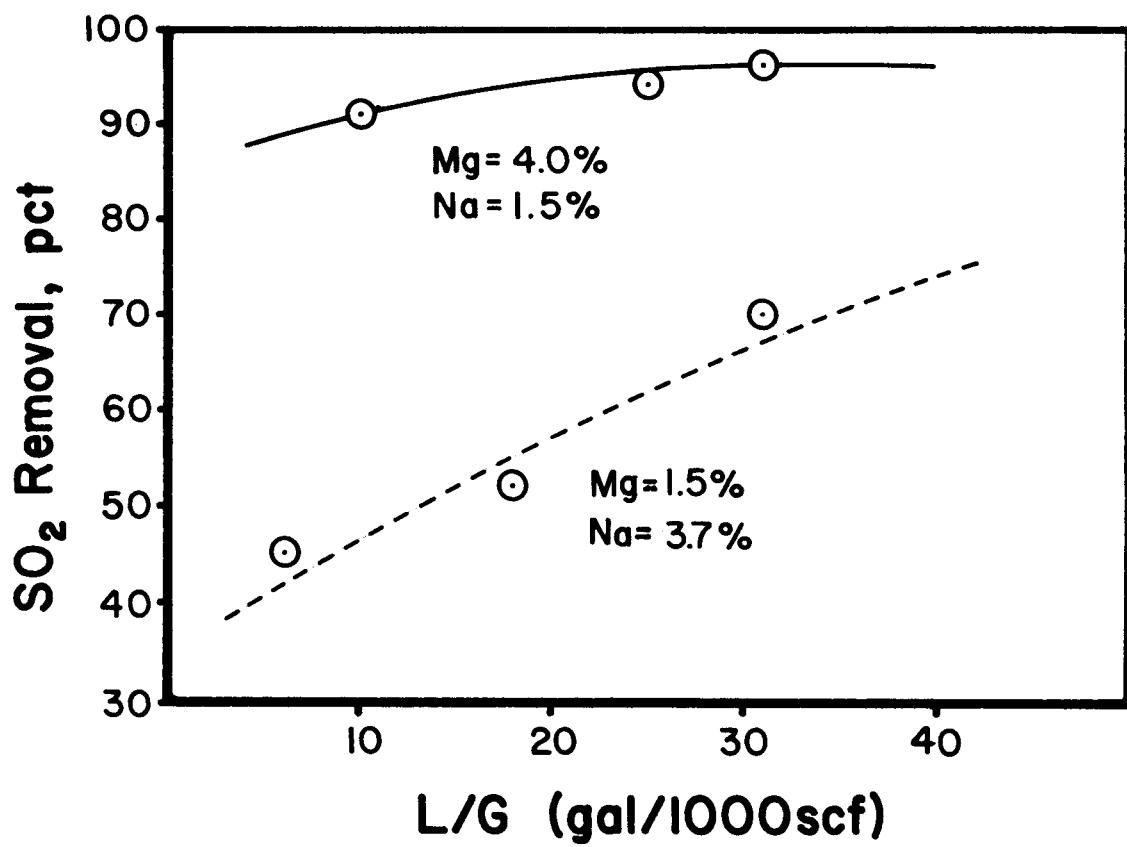


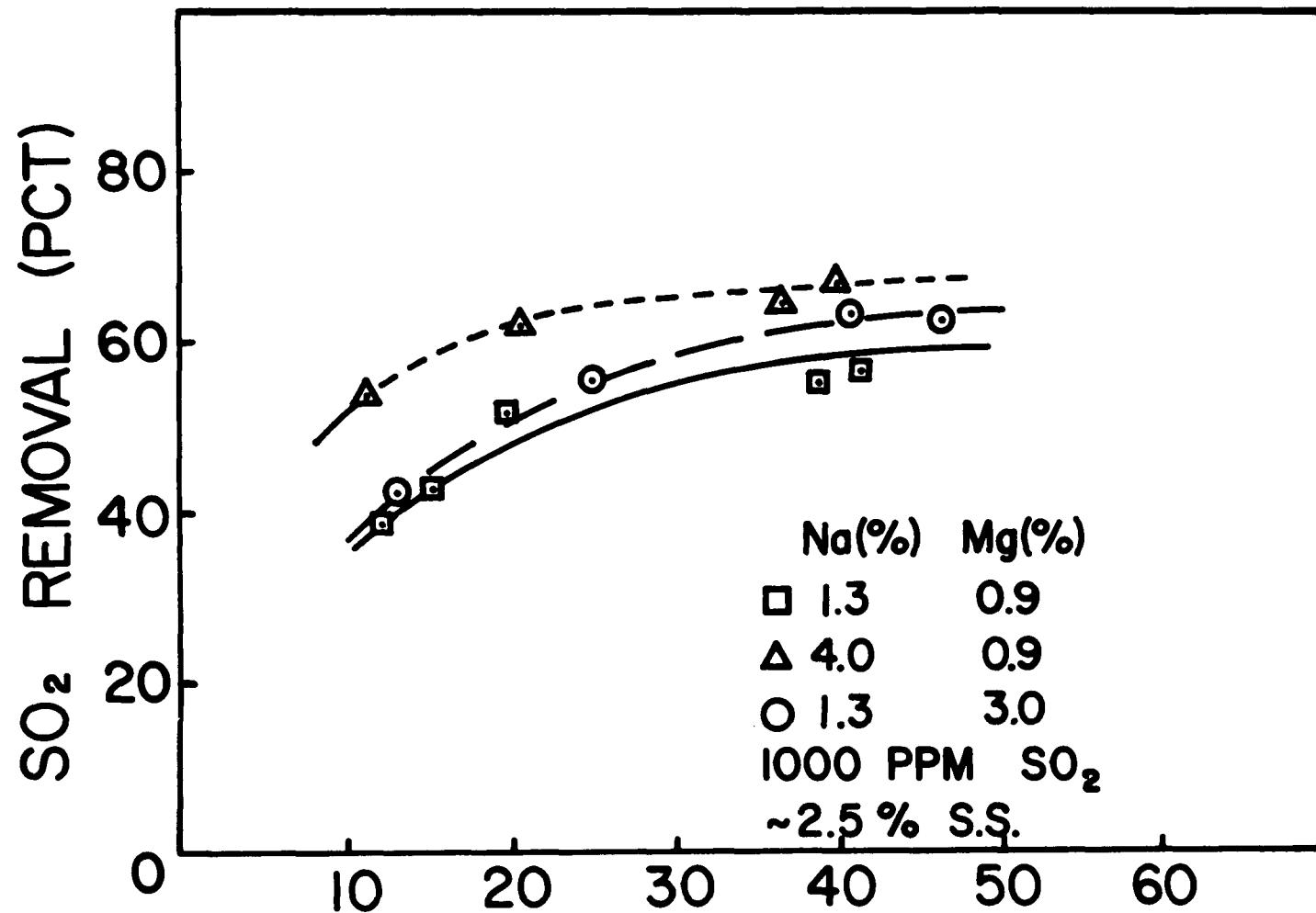
FIGURE 1. Sulfur dioxide removal as a function of L/G. Solid line was obtained using 4.0 pct magnesium and 1.5 pct sodium in the scrubber liquor. Dashed line was obtained using 3.7 pct sodium and 1.5 pct magnesium in the scrubber liquor.

TABLE 2. - Results of sodium and magnesium study using  
Center, North Dakota fly ash in the 5000 acfm scrubber

Test	scfm-dry	L/G <sup>†</sup>	CaO/SO <sub>2</sub> * Fly ash	Lime	SO <sub>2</sub> , ppm-dry		Pct SO <sub>2</sub> removal	Fly ash CaO util- ization	Suspended solids, pct	pH	Pct CaSO <sub>4</sub> satu- ration	Pct sodium	Pct magne- sium
5-0	3686	15.1	0.63	--	1002	566	43.5	69.0	6.05	3.6	113.3	1.3	0.63
-0A	3686	12.3	0.63	--	1002	566	39.4	62.4	6.95	3.6	127.6	1.3	0.63
-1	3340	19.7	0.63	--	993	475	52.2	83.4	5.09	4.0	135.6	1.3	1.01
-2	3424	41.5	0.64	--	963	410	57.4	88.9	3.54	3.4	126.1	1.4	1.03
-2B	3380	38.6	0.62	--	838	368	56.4	91.0	2.39	4.0	116.4	1.4	1.05
-3	3750	11.4	0.66	--	937	428	54.3	82.3	2.78	4.2	126.6	3.4	0.92
-4	3554	20.5	0.62	--	958	360	62.4	100.0	2.58	4.0	118.1	4.5	0.88
-5	3385	36.8	0.64	--	984	340	65.4	102.0	2.03	3.4	106.8	4.0	0.83
-12	3883	13.3	0.72	--	993	571	42.5	59.0	1.97	4.5	131.3	1.3	2.80
-13	3442	25.2	0.66	--	983	431	56.2	85.2	0.64	3.8	137.6	1.3	2.80
-14	3442	40.9	0.66	--	937	334	64.4	97.6	3.20	3.8	122.6	1.3	3.00
-15X	3442	46.4	0.66	--	1008	371	63.1	95.6	6.33	3.2	130.0	1.3	2.40

<sup>†</sup> Gallons of recirculated slurry per 1000 acf (saturated) flue gas.

\* Stoichiometric ratio based on inlet SO<sub>2</sub> concentration.



## L/G (GAL/1000 ACF-SATURATED)

FIGURE 2. Sulfur dioxide removal as a function of liquid-to-gas (L/G) ratio using high concentrations of sodium and magnesium. Solid line was obtained at sodium and magnesium levels normally present in scrubber liquor. Dashed line denoted by triangles was obtained by increasing the sodium concentration to 4 pct. Dashed line denoted by circles was obtained by increasing only the magnesium concentration to 3 pct.

general, increasing the soluble sodium concentration from a normal concentration of about 1.3 pct to about 4 pct increased the sulfur dioxide removal by about 15 pct. The effect of increased sodium on the rate of scale formation could not be quantified; however, scale deposits in the fly ash preparation tank and feed lines to the retention tank disappeared completely during the high sodium tests. The only scale-free operation of the fly ash preparation tank and feed line in the entire eight-month test program was during the high sodium tests. Scale deposits in the fly ash preparation tank were an operational problem when thickener overflow liquor was used to slurry the fly ash; when retention tank liquor was used, growth of the scale deposits was stopped; therefore, retention tank liquor was used to slurry the fly ash throughout most of the eight-month test program. It should be noted that scale formation under normal conditions in the rest of the scrubber system was not a problem during the entire testing program.

The effect of increased soluble magnesium concentrations on sulfur dioxide removal efficiencies are also represented in Figure 2 by the dashed line denoted by circles. At low L/G the increased magnesium concentration appears to have a negligible effect on removal; however, the sulfur dioxide removal appears to increase by about 5 to 10 pct at higher L/G values. In general, increasing the soluble magnesium concentration had a marginal effect on sulfur dioxide removal. These results differ significantly from the sodium and magnesium studies conducted on the 130-scfm pilot scrubber at GFERC, in which a pc-fired Beulah, ND, lignite fly ash was used. The reasons for the contrasting results will be further investigated in the future.

#### Low pH Scrubbing

The test series at low pH were designed to increase the utilization of fly ash alkali. The results are tabulated in Table 3. Figure 3 is a summary of the fly ash utilization as a function of pH. This figure includes data from all of the tests conducted by GFERC on the 5000-acfm scrubber. These pilot plant results confirm that more alkali is available from fly ash at lower pH.

The customary way of expressing stoichiometric ratios has been to consider only the CaO present in the fly ash. However, with utilization numbers in excess of 100 pct, it is obvious that additional fly ash alkalies are being solubilized and reacting with the sulfurous acid. The other species present in the fly ash available to react are magnesium oxide, sodium oxide, aluminum oxide, ferric oxide, titanium oxide, and potassium oxide. Considering these species, the amount of fly ash alkali is doubled compared to only CaO.

TABLE 3. - Results of low pH study using  
Center, North Dakota fly ash in the 5000 acfm scrubber

Test	scfm-dry	L/G <sup>†</sup>	CaO/SO <sub>2</sub> <sup>*</sup>		SO <sub>2</sub> , ppm-dry		Pct SO <sub>2</sub> removal	Fly ash CaO utilization	Suspended solids, pct	pH	Pct CaSO <sub>4</sub> saturation
6-1	3295	79.7	0.76	--	1017	287	71.8	94.2	1.89	3.3	104.5
-2	3423	77.4	0.43	--	982	442	55.0	128.0	1.53	2.6	113.2
-3	2247	115.0	0.47	--	1008	351	65.2	139.0	1.84	2.6	112.9
-3B	2275	117.6	0.27	--	1288	540	58.0	214.8	1.38	2.6	119.5
-4B	2275	115.3	0.63	--	960	268	72.1	114.0	1.16	2.7	126.1
-5	1764	154.0	0.59	--	1014	151	85.1	144.2	1.05	2.8	128.7
-6	1767	153.0	0.34	--	1002	350	65.1	186.0	0.81	2.2	126.5

<sup>†</sup> Gallons of recirculated slurry per 1000 acf (saturated) flue gas.

\* Stoichiometric ratio based on inlet SO<sub>2</sub> concentration.

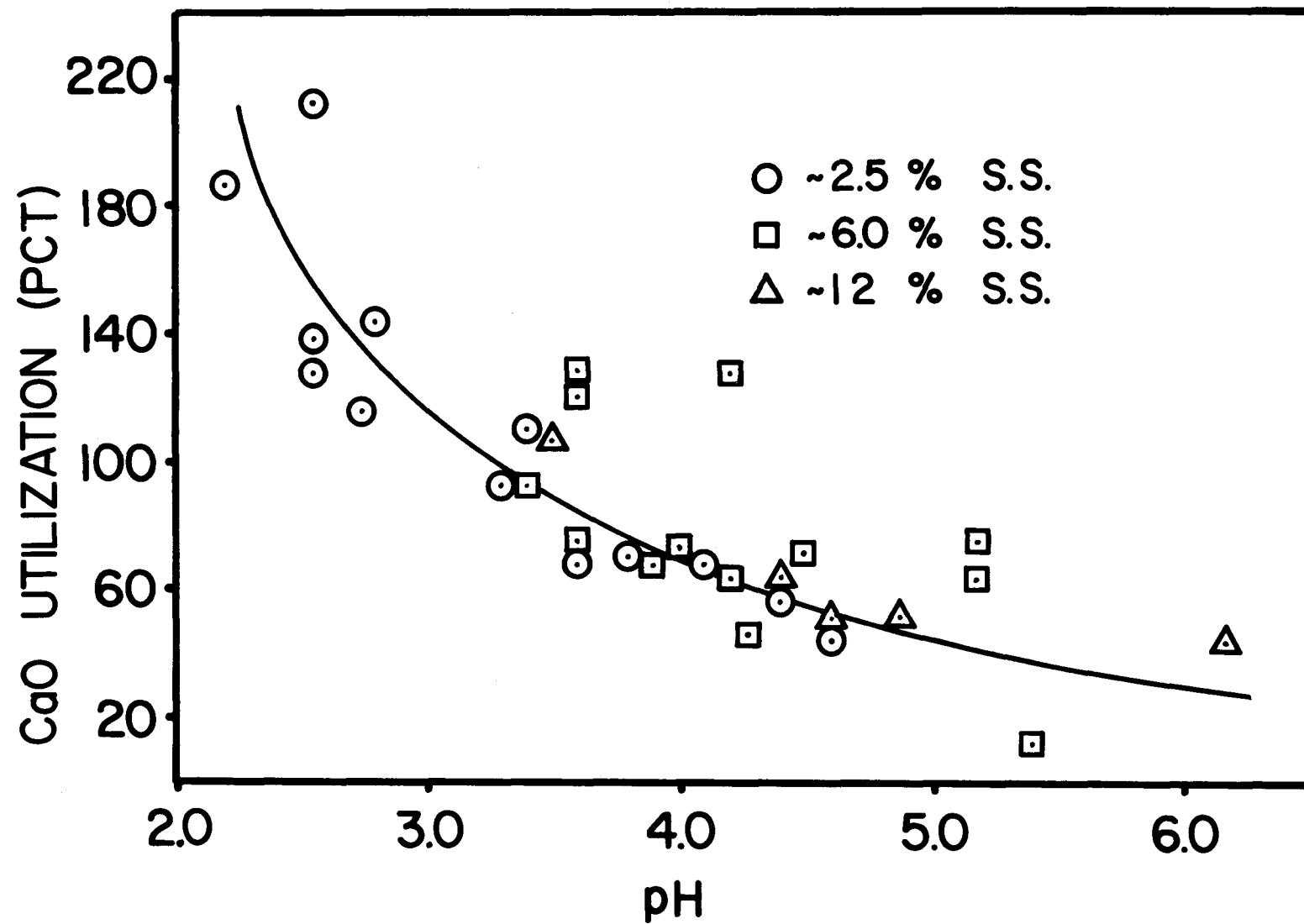


FIGURE 3. Summary of fly ash CaO utilization as a function of pH for all test conditions.

Project 3B. FLUIDIZED-BED COMBUSTION OF LIGNITE AND  
WESTERN SUBBITUMINOUS COALS

SUMMARY

Studies investigating coal sulfur retention on the alkaline ash of Western coals and lignites using a fluidized-bed combustor are being performed at GFERC. Studies conducted during the second quarter used a Beulah, North Dakota lignite to determine the effects of various fluidized-bed operating parameters on sulfur retention. The parameters studied were: average bed temperature, air-fuel ratio, superficial gas velocity, and to a lesser extent, average coal particle size. Preliminary results indicate that the retention of coal sulfur varied from 38 to 58 pct. Variables that significantly affect sulfur retention are average bed temperature and air-fuel ratio.

DISCUSSION

Figure 4 shows a revised schematic of the atmospheric fluidized-bed combustor in which the particulate collection system was changed from one large sintered stainless steel filter to two high efficiency cyclones and a fiber filter.

Studies on the operating conditions of the fluidized-bed using a base coal were completed this quarter. The base coal was a Beulah, North Dakota lignite, and coal sulfur retentions varied from 38 to 58 pct. These retentions are considerably lower than values reported earlier in a Master's thesis project, which included values up to 95 pct retention. The values obtained during the Master's project were determined to be in error because of a sampling problem.

Figure 5 illustrates the results of a temperature parameter study using 30 pct excess air and about 7 ft/sec superficial gas velocity. The data indicate that the sulfur retention has a maximum at about 1400° F, at which 51 pct of the sulfur was retained. This is equivalent to an emission level of just slightly greater than the 1.2 lb SO<sub>2</sub>/10<sup>6</sup> Btu Federal New Source Performance Standard. The tests were conducted without ash reinjection using Beulah lignite, which has a 1.27 calcium-to-sulfur stoichiometric ratio. Using ash reinjection, the sulfur retention is expected to be greater due to a higher because of the increased contact time of the calcium and sulfur dioxide.

Figure 6 illustrates the sulfur retention as a function of the air-fuel ratio. The data indicate that the retention of the coal sulfur on the alkaline ash increases as the percentage of excess air increases. The range of sulfur retentions as a function of excess air varied from a low of about 39 pct at 10 pct excess air, to a high of about 58 pct at 60 pct excess air. The 58 pct sulfur retention value is equivalent to an emission level of about 1.1 lb SO<sub>2</sub>/10<sup>6</sup> Btu, which meets the requirements of the Federal New Source Performance Standard.

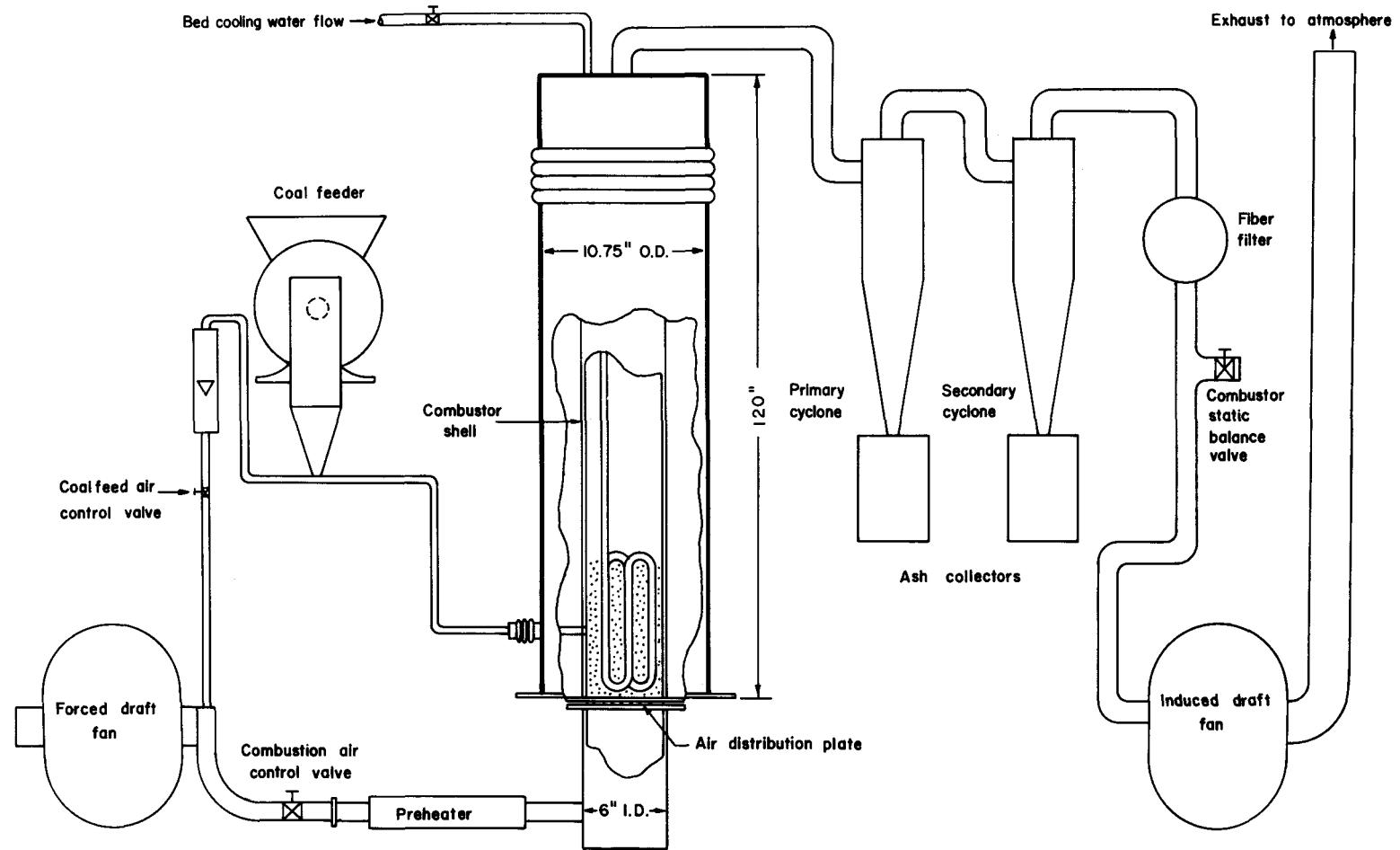


FIGURE 4. Schematic of GFERC's 6-inch FBC.

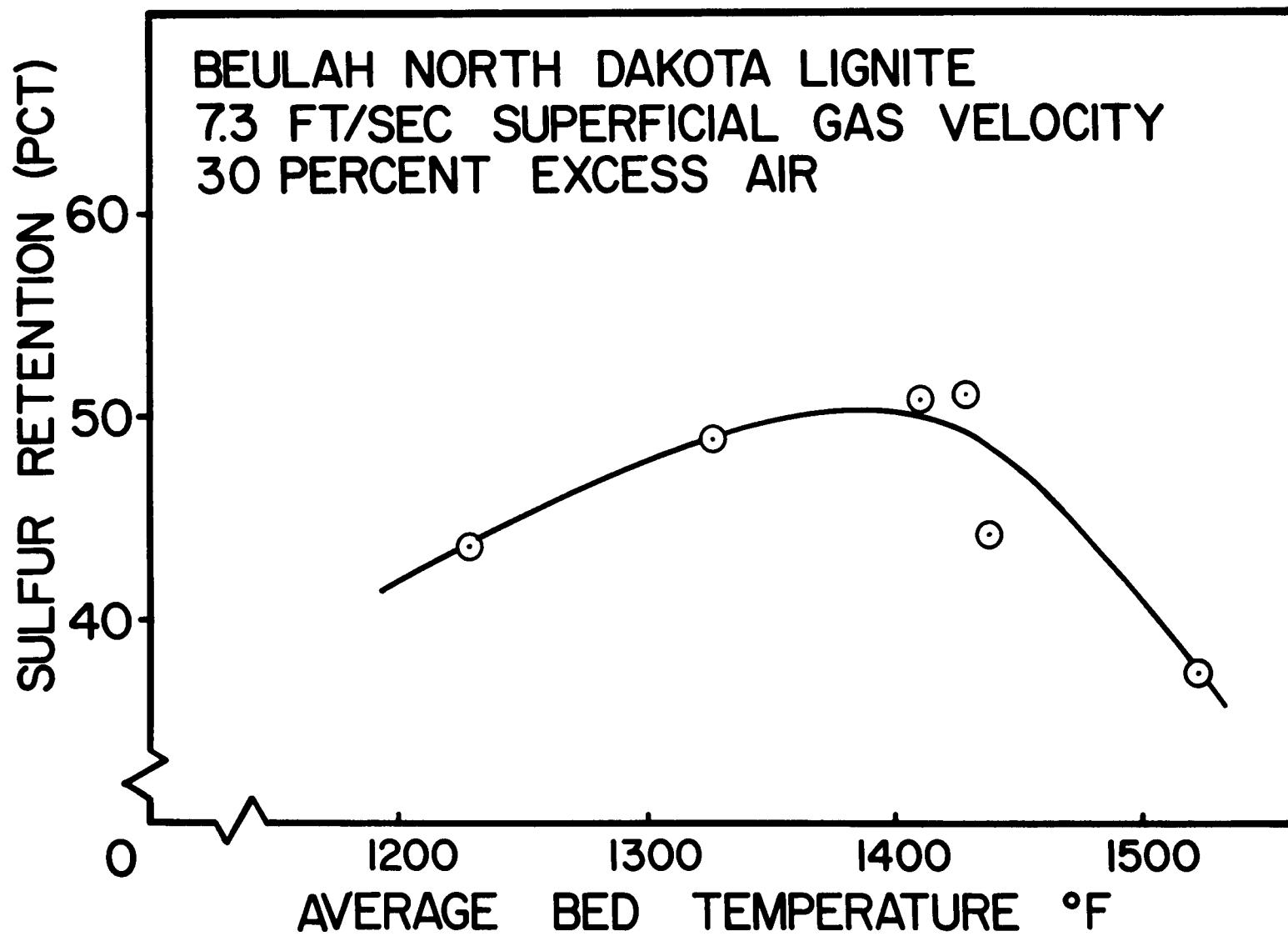


FIGURE 5. Sulfur retention versus average bed temperature.

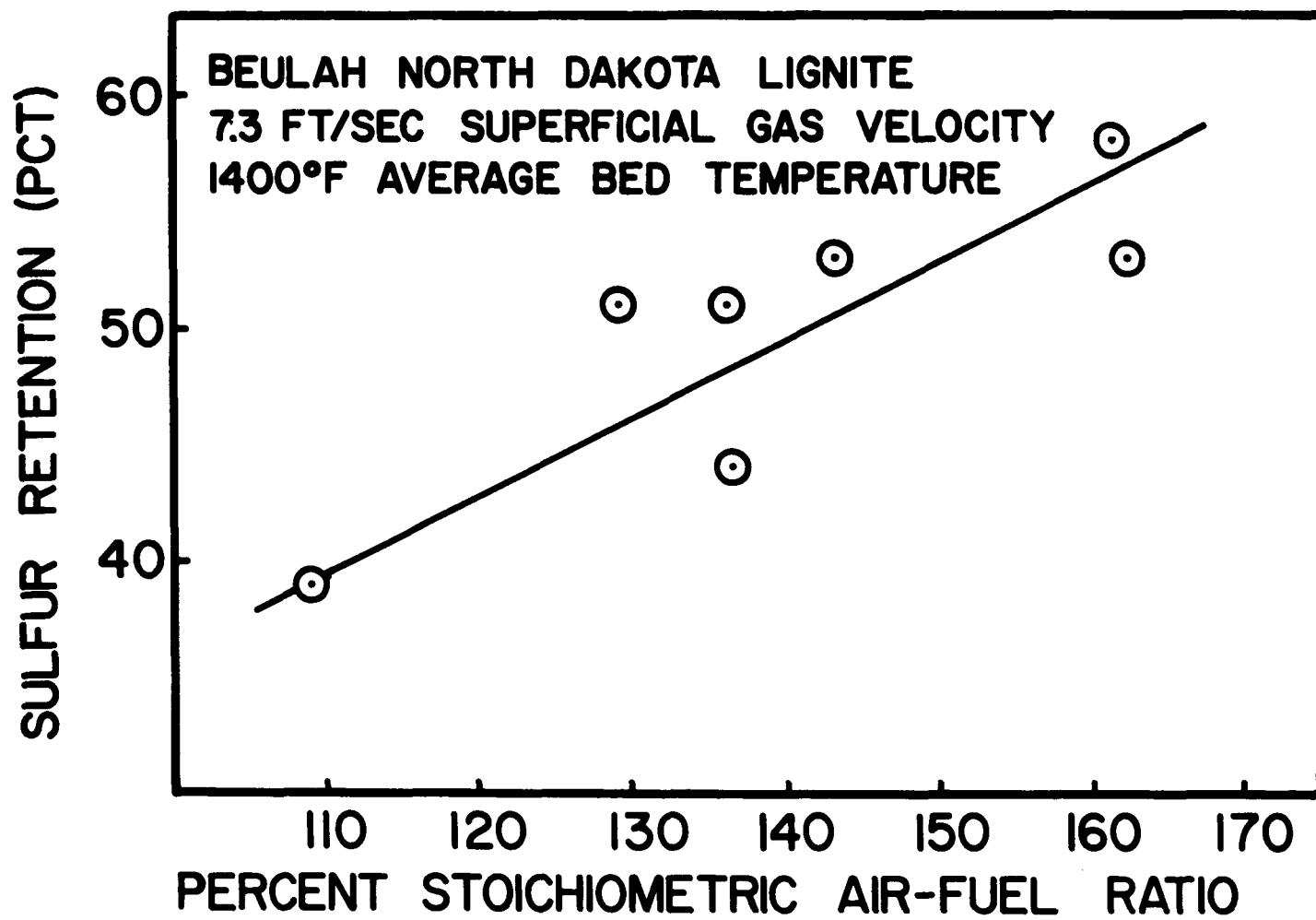


FIGURE 6. Sulfur retention versus air-fuel ratio.

The effects of superficial gas velocity and coal feed particle size distribution on coal sulfur retention were very small. The results indicate a slight decrease in sulfur retention with increased gas velocity, which is believed to be caused by the increased elutriation of ash fines at high gas velocities.

Tests during the next quarter will include a survey of 10 Western coals which represent the variability in ash composition and quantity found in low-rank Western coals. The ash reinjection system is expected to be operational by the first of June, at which time a test series on fluidized-bed operating conditions using ash reinjection will be initiated.

Two papers will be prepared and presented next quarter. One paper entitled, "Effects of Operating Parameters on Sulfur Retention on Alkaline Ash During Fluidized-Bed Combustion of a North Dakota Lignite" will be presented at the Fluidized Bed Combustion Technology Exchange Workshop in Reston, Virginia. The second paper, entitled "Fluidized Combustion of North Dakota Lignite," will be presented at the Ninth Biennial Lignite Symposium in Grand Forks, North Dakota.

## Project 4. CONTROL OF ASH FOULING

Submitted by: Everett A. Sondreal, Research Supervisor

Begun: FY 1966                           Expected Completion: Continuing

Personnel:

Everett A. Sondreal, Research Supervisor  
Philip H. Tufte, Chemical Engineer  
Franklin I. Honea, Chemical Engineer  
Willis Beckering, Research Chemist  
Arthur L. Severson, Chemical Engineer  
Samuel H. Givand, Chemist  
Diane K. Rindt, Chemist  
Sara E. Gruenhagen, Chemist  
Francis J. Schanilec, Engineering Technician  
Scott N. Strand, Research Equipment Operator Worker

## SUMMARY

Fouling of boiler heat transfer surfaces by ash from low-rank coals is a continuing problem resulting in significant reductions in boiler peak load capacity, efficiency, and availability. The problem has been found to be closely related to the concentration of sodium in the coals, with the ash content of coal also being a factor. No effective means has yet been found for preventing formation of fire-side ash deposits in the combustion of coal with high sodium levels. Progress has been made in studies on the mechanism of ash fouling, but additional work is necessary to resolve the problem.

A pilot pulverized-coal combustor of 75-lb/hr capacity, designed and constructed at GFERC, is used to measure fouling under controlled conditions. In this way, relatively small samples of candidate coals can be tested prior to plant design, and utilization criteria can be established on the basis of the characteristics of the coal to be used.

Ash fouling rates and effects are also measured on-site at power-plants using two methods. The first method involves operator observation and rating of the condition of the boiler on a daily basis. The second method utilizes two air cooled probes--one to measure the fouling rate and to obtain fouling ash samples, and the other to measure the furnace temperature at the test point. For all field tests, plant operating data and coal samples are also collected on a daily basis. The coal samples and fouling ash samples are analyzed chemically at GFERC. Reduced data are correlated using regression analysis to determine possible unidentified causes of the fouling problem.

During this quarter, eight tests were conducted in the 75-lb/hr pc-fired ash fouling combustor. Two of these tests were of Mt. Pleasant, Texas, lignite and of Naughton subbituminous coal. Five other tests were conducted with silica and calcium nitrate added to Beulah Standard lignite as part of the continuing effort to decrease ash fouling. The calcium nitrate added at 4.7 lb/100 lb of lignite resulted in about the same amount of ash deposit, but the deposit was weak and could be easily removed.

Although the study of the new 440-MW, cyclone-fired lignite plant at Otter Tail Power Company was completed in June, the statistical analysis results indicate that some additional test data are desirable to fill in the sample distribution. Additional selected coal samples from June until December of 1976 will be analyzed at GFERC during the next quarter.

The United Power Association (UPA), North American Coal Company, and GFERC are cooperating on a study of aggravated fouling and consequent derating of the 175-MW UPA plant at Stanton, ND. Testing was begun in late January for over 30 days. The results are being analyzed and will be discussed at a meeting scheduled at GFERC in mid-May.

The JEOL scanning electron microscope was installed during this quarter; the elemental analyzing system has been received and is scheduled for installation.

Analytical work has progressed in mineral separation and identification by float-sink separation and analysis. Sample stubs have been prepared for SEM analysis of a Decker subbituminous coal, Kentucky bituminous coal and lignite, and three Texas lignites. Stubs of probe ash samples have also been prepared.

## DISCUSSION AND RESULTS

### Ash Fouling Tests in the Pilot Plant Combustor

In this quarter, eight ash fouling tests were completed in the 75-lb/hr pc pilot plant combustor. These tests included a Texas lignite coal from Mt. Pleasant and a subbituminous coal from Naughton in Wyoming. Also, five tests were run to evaluate the effect of calcium nitrate and silica additives on a high fouling lignite (Beulah Standard II) from Beulah, ND. One additional test was run with the Beulah Standard II lignite in order to standardize the test furnace.

Results from the Mt. Pleasant, Texas, lignite showed a high fouling rate due to high ash content. However; the probe ash deposit was weak and fell off the probe. The Naughton subbituminous coal was low fouling with insignificant buildup of deposits on the probe.

The tests of Beulah Standard II lignite with additives included two tests with silica particles and three with calcium nitrate particles. The silica added at the ratio of 1.66 lb/100 lb of lignite and at 3.33 lb/100 lb gave no appreciable change in the deposit formation amount or strength. The calcium nitrate added at 2.35 lb/100 lb of lignite also showed very little improvement in deposit weight and strength. When the calcium nitrate addition ratio was doubled to 4.7 lb/100 lb, the deposit weight remained in the high fouling regions at 328.5 g and 506.9 g for two tests, but the deposit strength in both tests was significantly weakened and could be brushed off the probe.

Additional tests with lignite from other areas in Texas and with a dried and oil-treated subbituminous coal are scheduled for next quarter. Additional tests are also planned for additives, including the tests with magnesium injection.

#### Field Tests on Ash Fouling

##### UPA Stanton Plant

GFERC, United Power Associates (UPA), and the North American Coal Company (NA) have been cooperating in a study of ash fouling problems at the UPA power generating plant in Stanton, ND, which burns lignite from NA's Zap mine.

The UPA plant at Stanton came online in 1966. Although the plant was design-rated at 175 MW, the boiler had to be derated to about 150 MW. The derating was necessitated because of a periodic slagging problem in the secondary superheat and reheat sections of the boiler. Shutdowns have been caused when slag which was soot blown from these front areas of the boiler caused plugging in the more constricted downstream flue gas passes. During 1975, these operating problems have become more severe, and the peak operating load has been decreased to 140 MW. Even at 140 MW load, the operating period is only 30 days before shutdown is required for cleanout of the plugged passages.

A 30-day test program was initiated at the Stanton plant in January, and ran through March 7. The plant was run for seven days each, using lignite from several locations in the Zap mine, with different known levels of sodium. The plant was then run with a blend of low and high sodium lignite from the mine. The plant was operated at 150 MW during the day shift to assure that the slagging problem would show up during the test period. The slagging did occur, and the plant was ready to shut down about one week after the test ended.

The UPA operators took samples of coal during each shift during the test program. In addition, they recorded all plant operation parameters and made observations of the boiler condition. Plant personnel also used the GFERC 10-foot temperature and ash fouling probes to measure furnace temperature and ash fouling rates and to collect samples of fouling ash. These samples were collected on a 3-times-per-day basis.

During this quarter, North American Coal also took bore samples and mapped the sodium levels for the lignite at the Zap mine.

A meeting was held at Stanton on March 17, to review the test program. UPA and NA agreed to have the daily coal samples analyzed by an independent laboratory to keep from overloading the GFERC laboratory. In the meantime, GFERC will perform X-ray fluorescence analysis of the probe ash inner and outer layers for the 56 samples collected during the test. All coal and ash analyses are scheduled for completion before a meeting to be held at GFERC in mid-May. At this meeting all of the test results will be reviewed and future test efforts and possible solutions to the problem will be discussed.

#### Big Stone Plant

GFERC has been involved in an extensive study and test program of ash fouling at the Otter Tail Power Company's Big Stone Plant at Big Stone City, SD. Shutdowns due to blockages in the convective passes have been experienced in the new 440-MW cyclone unit at sodium levels which could be handled in older pc-fired units. Concern was expressed on the possibility of some other key factor besides the sodium level of the lignite acting to cause the fouling problem.

The main test program, as reported in previous quarterly reports, ended in June 1976. The regression analyses reported last quarter indicated that the sodium level was still the main prediction of ash fouling.

In a meeting held at GFERC on March 22, Otter Tail Power outlined further plans for modifications to decrease ash fouling at Big Stone. GFERC will be provided with a schedule of modifications and will be able to obtain performance and ash fouling data to evaluate each modification.

#### Scanning Electron Microscope (SEM)

The JEOL JSM-35 scanning electron microscope, less the elemental analyzing system, was installed during the quarter. Preliminary examination of an inner sinter layer probe deposit from Beulah lignite revealed a number of interesting features. A number of fragments were observed where two or three particles were just beginning to attach to each other. The surface of the particles had a fluid-like appearance. In order to look at the inside structure of the particles, another sample was prepared and the particles were crushed by lightly rolling a glass stirring rod over the sample. Three types of inside structures were observed. These are: a) solid spheres, b) cenospheres or hollow spheres, and c) porous particles where the inside material contained many small spherical voids.

### Heated Stage Microscope

Calibration of the heated stage microscope in the temperature range of 1000-1500° C has been completed using direct heating methods. Previously used indirect heating methods proved unsuccessful in reaching temperatures in the higher temperature range. Particles are now placed directly on a tantalum heating strip for melting point determinations, as opposed to being heated indirectly in a crucible.

Standards used in this calibration were copper wire (m.p. 1083° C), diopside (m.p. 1391° C), and nickel wire (m.p. 1455° C). The following results were obtained:

<u>Standard</u>	<u>True M.P.</u>	<u>Average Observed M.P.</u>	<u>Standard Deviation</u>
Copper	1083° C	1084.2° C	1.3° C
Diopside	1391° C	1388.0° C	2.1° C
Nickel*	1455° C	1443.3° C	1.5° C

\* Due to nickel alloying with tantalum, producing low melting points, it was necessary to place the nickel standard on a platinum chip substratum.

Work on inner sinter layer probe deposits has begun. Nine different categories of particles have been separated and mounted on tantalum heating strips for melting point determinations. Colored slides of the particles have been taken for future talks, presentations, and papers.

### Inductively Coupled Argon Plasma (ICAP)

A new crossed flow nebulizer was installed. This has resulted in considerable improvement in the plasma stability. The software for the automatic background corrector (ABC) was also received. In order to use the automatic background corrector, it is necessary to determine which side of the peak gives the best background reading for each element. This was determined by plotting intensities versus wavelength for each of the forty elements in the vicinity of the characteristic emission wavelength. Such plots are necessary for each major change in the matrix of the solutions for analysis. Five different matrices are currently planned in the ICAP analysis program and therefore a total of 200 plots were made. These plots are completed and are now being examined to determine optimum background location. The results will be incorporated in the computer program.

Pure standards were prepared for all 38 elements at the 1000 ppm level. These standards were prepared from pure metals or compounds having a purity of 99.999 pct or better. This high purity is necessary to minimize spectral inter-element interference in trace analysis.

Attempts to improve the sample digestion procedure described in the last quarterly report are being made. The Parr digestion bomb has been replaced by a smaller, more inexpensive Uniseal Decomposition Vessel. Shorter decomposition times (currently 18 hours for 1 gram) are being tried, and the volume of acid is being decreased to minimize acid attack on the sample container.

#### Mineral Separation and Identification

Sink particles from a float-sink separation of Decker subbituminous coal, Kentucky bituminous coal, and lignites from Philips, Bryan, and Fairfield, Texas, were mounted on stubs for SEM examination and analysis. Two stubs were prepared for each coal; one stub was made up of a random collection of sink particles to determine mineral distribution and the second stub consisted of selected particles representing the different minerals observed under the optical microscope.

Similar stubs were prepared for SEM examination of the inner and outer sinter layer probe deposit from a high sodium Beulah lignite and a high sodium Zap lignite. Some of the ash particles were partially crushed by carefully rolling a glass stirring rod over the particles.

A sample of ash from Otter Tail Power Company was analyzed for arsenic by X-ray fluorescence. Comparison of the unknown sample with prepared standards indicated a concentration of  $150 \pm 30$  ppm of arsenic in the unknown sample.

Project 5. REMOVAL OF FLY ASH FROM STACK GASES BY ELECTROSTATIC  
PRECIPITATION

Submitted by: Everett A. Sondreal, Research Supervisor

Begun: FY 1968                           Expected Completion: Continuing

Personnel: Everett A. Sondreal, Research Supervisor  
Stanley J. Selle, Mechanical Engineer  
Ronald G. Landman, Engineering Technician  
Clyde L. Ziegelmann, Laboratory General Mechanic Helper  
Gary R. Dubuque, Research Equipment Operator  
Bert M. Gumeringer, Research Equipment Operator Helper  
Russell N. Evans, Graduate Fellow in Physics

#### SUMMARY

Problems are being encountered in the application of electrostatic precipitation (ESP) to the removal of fly ash from powerplant flue gas while burning Western coals. Pilot-scale and laboratory techniques are under development within this project which can reduce the uncertainties involved in sizing ESPs for new installations. These techniques can assist in solving problems in existing units, as well, and answer basic questions concerning ESP operation.

Construction was nearly completed this quarter on a new 75-lb/hr pc-fired furnace/pilot-scale ESP combination. Shakedown of this equipment should extend through next quarter, with the test program to begin during the final quarter of FY 77. The purpose of this equipment is to provide a means of burning relatively small quantities of coal and generating fly ash and flue gas representative of that produced when the same coal is burned in a full-scale powerplant. The pilot ESP will allow for comparison of removal difficulty for fly ash from a proposed application with those from installations where ESPs are in operation. The study and comparison of various ESP conditioning agents, as well as some dry SO<sub>2</sub> absorbent schemes, will also be possible. The study and optimization of the use of Nahcolite (naturally occurring NaHCO<sub>3</sub>) for both ESP conditioning and SO<sub>2</sub> removal is the first test series planned for this equipment.

Laboratory capabilities for the study of fly ash properties related to ESP performance are being expanded. The installation of a scanning and analyzing electron microscope has been partially completed and, beginning next quarter, should allow for the study and characterization of single particles down to micron size or smaller. Apparatus and techniques for determining particle size, specific gravity, fly ash resistivity, dielectric properties, and coal and fly ash analysis will act to support pilot plant and field work.

## DISCUSSION

Construction of the 75-lb/hr pc-fired furnace was nearly completed this quarter. Shakedown will begin the second week in April, with up to three months allowed for any modifications required. During this quarter the air and flue gas piping and insulation were completed, as were the installation of remotely controlled valves, instrumentation lines and sensors, natural gas and house air service, and fabrication and installation of sight ports.

Installation of electrical service to the furnace/ESP equipment by an outside contractor was completed this quarter. Bids were received and a contractor selected to fabricate and install stairways on the attendant multilevel structure. This work is expected to be completed early in May. The consulting engineering firm has also been employed to develop complete engineering drawings of the 75-lb/hr furnace/pilot ESP equipment and services, with completion expected early next quarter.

Fabrication and installation of the pilot ESP was completed during this quarter. The only component remaining is the power supply, of which delivery has been delayed until April due to problems at the manufacturer. It is still projected that the entire ESP unit can be operational around the end of May, coincident with the first serious attempt to burn coal in the furnace. This will be followed by a series of shakedown tests to characterize the fly ash and flue gas generated by the furnace and establish ESP operability.

Significant progress was made in the development of the ESP computer model during the quarter. The model has been advanced in its applicability to the new pilot ESP to the point where data generated on the operating unit are required for any further effort to be meaningful. The model has already demonstrated its usefulness by aiding in the dimensioning of some key components in design of the new unit.

Equipment calibration for the study of fly ash dielectric properties was completed this quarter. Preliminary measurements on selected ashes are now being made, with the major test program to be underway by June 1. A tentative model of the dielectric behavior of a fly ash layer has been developed which at least qualitatively agrees with the data obtained to date. This model indicates a relationship between dielectric behavior and resistivities measured on the same fly ash.

All components of the simulated flue gas injection system for laboratory resistivity measurement have been received. Installation has been delayed until early next quarter due to the press of other work, but the apparatus should be fully operational in time to support the pilot plant work. No laboratory resistivity determinations were made during the quarter.

Laboratory equipment for the determination of fly ash specific gravity was ordered this quarter, with delivery expected early in April. Selection and ordering of laboratory particulate size measurement has been delayed until April. Installation of the scanning and analyzing electron microscope was partially completed this quarter. The computer and analyzing components of the system are scheduled for installation in April.

The float-sink test series was continued during the quarter. A computer program using multiple regression was developed for study of the data generated. Results to date on a wide variety of coals indicate, in general, an increase in the percent of the total ash in the sink portion with increased  $SiO_2$  and  $Al_2O_3$  content and a decrease with increasing alkali content in the coal ash. This effort has been temporarily reduced because of the need to select and obtain additional coal samples.

Work was initiated during the quarter to develop a technique for analyzing reacted Nahcolite and fly ash mixtures resulting from the dry  $SO_2$  absorption work. A suitable procedure is required to allow for determining the degree of conversion of bicarbonate to carbonate and carbonate to sulfate at various conditions in order to evaluate optimization tests on this process. The analytical techniques are considerably complicated by the presence of fly ash; however, the techniques presently under study appear to adequately overcome the problem. Work on this problem will continue through next quarter.

Analyses performed on the 50-ton sample of Kemmerer, Wyoming, subbituminous coal (the first standard coal for the pilot plant ESP work) indicated that the ash content was about one half of that observed during the tests at UP&L's Naughton plant in November. In spite of this result, all parties involved have agreed that the proposed testing in the GFERC pilot furnace/ESP facility can be performed on the coal received without jeopardizing the results. UP&L feels that the coal delivered to GFERC is more representative of the coal normally delivered to the Naughton plant. In addition, full-scale ESP test results are available from earlier work at the plant and on coals similar to the 50-ton sample at GFERC.

## MANUSCRIPTS

<u>Title</u>	<u>Author</u>	<u>Form</u>	<u>Status</u>
Reduction of Sodium in Lignite by Ion Exchange	L.E. Paulson R.C. Ellman	R.I.	Revisions in progress.
Variability of Ash Composition of Lignite and Subbituminous Coals from the Northern Great Plains Province	R.C. Ellman S.A. Cooley E.A. Sondreal	R.I.	In review.
Experiments in Shipment, Handling, and Stockpiling Dried Low-Rank Coal	R.C. Ellman L.E. Paulson S.A. Cooley	R.I.	In preparation.
Experiences in Transportation of Dried Low-Rank Western Coal	L.E. Paulson S.A. Cooley D.J. Wegert R.C. Ellman	Outside publication	Published in Dec. 1976 issue of SME/AIME Transactions.
Petrochemistry of Coal Ash Slags. 1. Formation of Melilite and a High Temperature Glass from a Calcium-Rich, Silica-Deficient Slag	H.H. Schobert D.L. Barbie O.D. Christensen F.R. Karner	Presentation and outside publication	In preparation for presentation at the ACS National Meeting, Montreal, Que., May 1977.
Petrochemistry of Coal Ash Slags. 2. Correlation of Viscosity with Composition and Petrographic Class	H.H. Schobert	Presentation	In preparation for presentation at the ACS National Meeting, Montreal, Que., May 1977.
Ash Fouling Characteristics of Western Subbituminous Coals	P.H. Tufte E.A. Sondreal	Presentation and outside publication	Presented at the American Power Conference Annual Meeting, April 1976. Awaiting publication in APC Proceedings.
Factors Affecting ESP Performance on Western Coals and Experience with North Dakota Lignites	S.J. Selle L.L. Hess	Presentation and outside publication	Presented at the EPA/EPRI Symposium on Particulate Control, May 1976. Published in <u>Symposium on Particulate Control in Energy Processes</u> , Blake, David E., editor, EPA-600/7-76-010 September 1976.

<u>Title</u>	<u>Author</u>	<u>Form</u>	<u>Status</u>
Effect of Solvent on Molecular Composition in Coal Liquefaction	J.E. Schiller C.L. Knudson	Outside publication	Submitted for publication in FUEL.
Composition of Solvent Refined Coal, Recycle Solvents, and Coal Liquefaction Products	J.E. Schiller	Outside publication	Published in HYDRO-CARBON PROCESSING, Jan. 1977, Vol. 56, No. 1, pp. 147-152.
Research and Development Relating to Lignite Use in Power Production	E.A. Sondreal G.H. Gronhovd W.R. Kube	Presentation and outside publication	Presented at the Gulf Lignite Symposium, Austin, Texas, June 1976. Awaiting publication in Proceedings.
Analysis of Solvent Refined Coal, Recycle Solvents, and Coal Liquefaction Products	J.E. Schiller	Presentation	Presented at Symposium on Comparison of Tar Sands, Shale Oil, Coal and Petroleum at New Orleans ACS Meeting, March 1977.
A Simple Separation Method for Coal Derived Solids and Heavy Liquids	J.E. Schiller D.N. Mathiason	Outside publication	In press in ANALYTICAL CHEMISTRY
Flue Gas Desulfurization Using Fly Ash Alkali Derived from Western U.S. Coals	H.M. Ness E.A. Sondreal	Report to the EPA, to be published in the EPA Technology series.	In review at EPA.
Temperature Effects on Coal Liquefaction; Rates of Depolymerization and Product Quality as Determined by Gel Permeation Chromatography	C.L. Knudson A.L. Ruud J.E. Schiller	Presentation and outside publication	In preparation.
Coal Minerals and Mechanisms Affecting Ash Fouling in Combustion of Low Rank Western U.S. Coals	E.A. Sondreal P.H. Tufte W. Beckering	Outside publication	Submitted to A. Macek, AFE, for transmittal and publication in Journal of Combustion Science and Technology.
Pilot Plant Operation of a Fixed-Bed Slagging Gasifier	R.C. Ellman H.H. Schobert	Presentation	Presented at the ACS National Meeting, New Orleans, LA, March 1977.

<u>Title</u>	<u>Author</u>	<u>Form</u>	<u>Status</u>
Correlation of Fireside Boiler Fouling with North Dakota Lignite Ash Characteristics and Power Plant Operating Conditions	E.A. Sondreal S.J. Selle P.H. Tufte V.H. Menze V.R. Laning	Presentation	In preparation for presentation and distribution at the 1977 American Power Conference.
Ash Fouling Studies of Low Rank Western U.S. Coals	E.A. Sondreal P.H. Tufte W. Beckering	Presentation	In preparation for presentation at the ASME 1977 International Symposium on Corrosion and Deposits.
Viscosity of Coal Liquids - The Effect of Character and Content of the Non-distillable Portion	J.E. Schiller B.W. Farnum E.A. Sondreal	Presentation and outside publication	In preparation.
CO-Steam Process: Coal-Catalyzed and -Uncatalyzed Rates of CO, H <sub>2</sub> , and H <sub>2</sub> O Reactions in the Reactor Gas Phase	C.L. Knudson E.A. Sondreal	Outside publication	In preparation.
Using Fly Ash Alkali Flue-Gas Desulfurization	H.M. Ness	Presentation	In preparation for presentation at the AIChE Annual Conference, 3/24/77.
Flue Gas Desulfurization Using Western Fly Ash Alkali	H.M. Ness	Presentation	Presented at Fly Ash Utilization Symposium, Univ. of No. Dak., March 19, 1977.
Effects of Operating Parameters on the Sulfur Retention on Alkaline Ash During Fluidized-Bed Combustion of a North Dakota Lignite	G.M. Goblirsch E.A. Sondreal	Presentation	In preparation for presentation at Fluidized-Bed Combustion Technology Exchange Workshop, April 14, 1977, Reston, Virginia.
Nitrogen Compounds in Coal-Derived Liquids	J.E. Schiller	Outside publication	In preparation.
Preparation and Low-Voltage Mass Spectrometry Sensitivities of Methylated Polynuclear Aromatic Hydrocarbons	J.E. Schiller	Presentation and outside publication	In press in ANALYTICAL CHEMISTRY and presented at the Pittsburgh Conference on Analytical Chemistry of Applied Spectroscopy.

<u>Title</u>	<u>Author</u>	<u>Form</u>	<u>Status</u>
Analysis of Coal-Derived Liquids	J.E. Schiller	Outside publication	Invited paper to be presented at the Great Lakes Regional ACS Meeting.
Analysis of the Phases Present in a Batch Reactor During Coal Liquefaction at 400, 440, and 470° C and Over 4000 psig.	C.L. Knudson J.E. Schiller E.A. Sondreal	Presentation and outside publication	In preparation.
Current Status of Studies in Slagging Fixed-Bed Gasification at GFERC	R.C. Ellman B.C. Johnson H.H. Schobert L.E. Paulson M.M. Fegley	Presentation and publication in ERDA IC	In preparation for presentation at the 9th Biennial Lignite Symposium, Grand Forks, ND, May 18-19, 1977.
Pilot Plant Scrubbing of SO <sub>2</sub> with Fly Ash Alkali from North Dakota Lignite	H.M. Ness F.I. Honea E.A. Sondreal P. Richmond	Presentation and publication in ERDA IC	In preparation for presentation at the 9th Biennial Lignite Symposium, Grand Forks, ND, May 18-19, 1977.
Fluidized Combustion of North Dakota Lignite	G.M. Goblirsch E.A. Sondreal	Presentation and publication in ERDA IC	In preparation for presentation at the 9th Biennial Lignite Symposium, Grand Forks, ND, May 18-19, 1977.
Development of the CO-Steam Process for Liquefaction of Lignite and Western Subbituminous Coals	E.A. Sondreal C.L. Knudson J.E. Schiller T.H. May	Presentation and publication in ERDA IC	In preparation for presentation at the 9th Biennial Lignite, Symposium, Grand Forks, ND, May 18-19, 1977.

## VISITORS

<u>Date</u>	<u>Name</u>	<u>Affiliation</u>	<u>Purpose of Visit</u>
1/1/77	Milt Russen Fred R. Wetzel G.C.Y. Lee J.J. Smortchevsky	Utah Power & Light Salt Lake City, UT	To discuss Nahcolite/SO <sub>2</sub> removal test program.
1/12/77	Stuart E. Schoppele	Oklahoma State Univ.	To evaluate status of mass spec capabilities at GFERC.
1/15/77	Frank Karner	Univ. of N. Dak. Grand Forks, ND	To discuss slag composition for preparation of paper.
1/18/77	Virgil I. Stenberg	Univ. of N. Dak. Grand Forks, ND	To discuss Lignite Seminar.
1/24/77	R.R. Dillon	Univ. of N. Dak. Grand Forks, ND	To discuss analysis of samples of Project Lignite solvent.
1/27/77	G.E. Smith J. Falconer	Manalta Coal Co. Calgary, Alberta	To discuss coal preparation.
2/2/77	Paul Foot T.M. Phillips	Pacific Power & Light Portland, OR	To discuss Nahcolite tests.
2/14/77	Richard Baltisberger Neil Woolsey Ken Klabunde Virgil Stenberg Max Soubey	Univ. of N. Dak. Grand Forks, ND	To attend bi-weekly seminar on lignite research conducted in Grand Forks.
2/16/77	Rolf Maurer Wayne Krill	Acurex Mt. View, CA	To discuss sampling problems in gasifier.
	Carlton Johnson	Peabody Engrg. Co. Stanford, NJ	To discuss Minnesota Power and Light pilot plant.
2/27/77	K.C. Malick Y.T. Hung	Univ. of N. Dak. Grand Forks, ND	To discuss X-ray analysis of Na.
3/2/77	Oscar Manz	Univ. of N. Dak. Grand Forks, ND	To obtain samples of FA scrubber sludge.
3/3/77	Tom Owens Y.T. Hung	Univ. of N. Dak. Grand Forks, ND	To discuss gas liquid analysis and processing.
3/3/77	Karen Shewbart	Dow Chemical	To discuss lignite analysis using XRFA.

<u>Date</u>	<u>Name</u>	<u>Affiliation</u>	<u>Purpose of Visit</u>
3/7/77	Clark Markell David Binkel	Minot State College Minot, ND	To discuss energy research relating to a planned workshop for high school teachers.
3/10/77	D.L. Glaser	Stearns-Roger, Inc.	Contract negotiations for
3/11/77	T.G. Towers K.P. Worthan	Denver, CO	slagging gasifier.
3/11/77	Dean Bursheim Curt Kolbo	Engineering Associates	To discuss preparation of plans and specs for instrument panel on gasifier.
3/14/77	Oscar Manz	Univ. of N. Dak. Grand Forks, ND	To discuss sludge field test program.
3/15/77	F.W. Camp R.D. Gordon	Sunedco Dallas, TX	To observe tests in 75-lb/hr PC combustor of Sunedco, Texas, lignite.
3/16/77	L. Stelland David Schaat	Natural Gas Pipeline Chicago, IL	To discuss status of gasification research project.
3/21/77	D.L. Reid	Battelle Northwest Richland, WA	To discuss research programs and fine particulate removal.
3/22/77	Robert Jimeson N.F. Barr	ERDA Washington, DC	To discuss biomedical program for coal conversion processes.
	R.F. Middleton V.H. Menze R.G. Johnson	Otter Tail Power Co.	To discuss ash fouling tests at the Big Stone Station.
3/28/77	Marion Vardaman	Stearns-Roger, Inc. Rapid City, SD	To observe gasification test run and gasifier operation.
3/29/77	Donald I. Walker	Associated Western Universities, Salt Lake City, UT	To discuss fellowship program.
	Donald W. Gellman	ERDA Morgantown, WV	To discuss gas treatment at MERC and compare status of programs.
3/30/77	Don Evenstad	Univ. of N. Dak. Grand Forks, ND	To discuss common interests in industrial hygiene and work place monitoring of CO.
3/31/77	Jack Wang	Univ. of N. Dak. Grand Forks, ND	To discuss MS analysis of Chem. Dept. samples.

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