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A PROGRAM OF BASIC RESEARCH ON THE PREPARATION AND
STABILITY OF COAL/WATER SLURRIES

Quarterly Report for the Period Ending June 30, 1984

By
H. Atlas
E. Z. Casassa
G. D. Parfitt
E. W. Toor

Work Performed Under Contract No. FG22-84PC70765

Carnegie-Mellon University
Pittsburgh, Pennsylvania

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A PROGRAM OF BASIC RESEARCH ON THE
PREPARATION AND STABILITY OF
COAL/WATER SLURRIES:
QUARTERLY REPORT
FOR THE PERIOD ENDING
JUNE 30, 1984

to the
U.S. Department of Energy
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from

H. Atlas
E. Z. Casassa
G. D. Parfitt
E. W. Toor

Department of Chemical Engineering
Carnegie-Mellon University
Pittsburgh, PA 15213

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1. INTRODUCTION

This is the first quaterly report of Grant No. DE-FG 22-84 PC70765 from the U.S. Department of Energy, Pittsburgh Energy Technology Center (DOE/PETC) entitled "A Program of Basic Research on the Preparation and Stability of Coal/Water Slurries". The objective of the research proposed here is to relate the surface chemistry (surface charge, wettability and additive adsorption) of a coal to its previous history of oxidation and beneficiation, and to surface analysis of each coal sample. These studies will be used to further develop the model for coal/water slurry behavior which was proposed as a result of previous studies of coal/water slurry surface chemistry carried out between September 1981 and September 1983 under Grant No. DE-FG281PC40285 from DOE/PETC. These studies are expected to lead to a better understanding of the balance among and effects of the different types of materials on the heterogeneous coal surface which will allow more effective utilization of coal/water slurries, regardless of coal source.

The current two-year research program was initiated June 1, 1984, and the present report for the calendar quarter ending June 30, 1984, covers progress during the month of June, as well as some preliminary work carried out earlier in the quarter before initiation of the program. The report is organized according to specific tasks listed in the proposal. For each task, research accomplishments and plans for the next report period are discussed.

2. PREPARATION AND STABILITY OF COAL/WATER SLURRIES

2.1 Scope of Tasks for the Report Period

The original plan was to carry out Task 1, the standardizing of grinding conditions to produce 100% <100 mesh pulverized coal, and Task 2, characterization of the pulverized coal by several methods at Carnegie-Mellon University, for the first coal selected. Because the proposed grinding equipment could not be obtained immediately, work was begun on Task 2 and Task 5, characterization of coal/water slurries for stored coals, for a sample of Illinois #6 (one of the six coals proposed for this study) that was the remainder of the material used in our previous study of coal/water slurry surface chemistry. This coal had been ground to nominally 100% <100 mesh approximately two years ago and had been stored under air in a closed container. Preliminary tests indicated that considerable oxidation had occurred during that time. Therefore it is expected that information on the effects of oxidation can be obtained by using this sample, though the degree of oxidation cannot be specified precisely.

2.2 Task 1: Standardizing of Grinding Conditions for Coal #1

2.2.1 Research Accomplishments

The Bantam Mikro-Pulverizer has been ordered and is expected to arrive in mid-August, 1984. We have observed the grinding of a sample of Splash Dam coal for our use in similar equipment at Gulf Research and Development Corporation laboratories, so will have some familiarity with the equipment when it arrives.

2.2.2 Plans for the Next Report Period

When the grinding equipment arrives, we plan to carry out Task 1 for all the remaining selected coals so that samples will be available as soon as possible for the surface analyses to be undertaken by Gulf Research and Development Corporation.

2.3 Task 2: Characterization of Pulverised Coal at C.M.U.

2.3.1 Research Accomplishments

The original analysis of Illinois #6 coal is shown in Table 2-1, the proximate analysis as obtained from Conti Laboratories, Pittsburgh, PA for this sample, and proximate and ultimate analyses as obtained from DOE/PETC for a sample from the same mine. The aged coal was used both as stored and after washing five times

to remove soluble minerals from the surface. To wash the coal a 20% (wt) slurry was mixed in water and allowed to stand for 24 hours with intermittent stirring. The liquid was then filtered off under suction. This process was repeated the desired number of times, and then the solids were allowed to air dry for several days.

Table 2-1. Analysis of Illinois #6

<u>Proximate Analysis</u>	<u>From Conti Testing</u>	<u>From DOE/PETC</u>	
Moisture	5.3%	17.6%	
Ash	9.7%	8.3%	
Fixed Carbon	---	40.3%	
Sulfur	3.8%	4.3%	
Volatiles	42.3%	33.8%	
Heating value, btu/lb	11,822	10,500	
<u>Ultimate Analysis</u>		<u>(As Received)</u>	<u>(DAF)</u>
C		58.0%	78.3%
H		4.1%	5.6%
N		0.8%	1.1%
O		7.5%	9.1%
S		3.5%	4.8%
Pyrite		1.3%	
Organic Sulfur		3.0%	
Sulfite		0.06%	

a. Particle Size Distribution

Particle size distributions have been obtained by sieving and with the Coulter Counter for the aged Illinois #6. The results are shown in Table 2-2, with the size originally found for this coal sample before aging. As expected there is little difference in particle size distribution for the samples before and after aging.

Table 2-2. Particle Size Distribution for Illinois #6

Sample Size (μm)	Original		Aged	
	wt. % (a)	vol. % (b)	wt. % (a)	vol. % (b)
2.0	---	100.0	---	100.0
2.5	---	99.7	---	99.8
3.2	---	99.2	---	99.6
4.0	---	98.5	---	99.2
5.0	---	97.4	---	98.8
6.4	---	96.1	---	97.9
7.2	100.0	---	99.7	---
8.0	---	94.6	---	95.7
10.1	---	92.4	---	94.3
12.7	97.8	89.5	97.9	92.0
16	---	86.0	---	88.0
20	92.6	81.3	92.4	83.0
25	---	75.7	---	76.5
32	---	69.2	---	70.5
38	67.2	---	63.2	---
40	---	64.0	---	64.0
44	61.9	---	58.2	---
51	---	55.0	---	55.0
53	54.0	---	50.4	---
64	47.2	46.3	44.7	46.0
75	39.4	---	36.6	---
81	---	35.0	---	38.0
88	28.8	---	27.4	---
101	---	24.6	---	26.0
105	23.1	---	20.8	---
125	14.0	---	12.0	---
128	---	7.4	---	11.0
149	6.6	---	5.9	---
161	---	5.0	---	5.5
Median Size	57 μm	57 μm	54 μm	57 μm
Geometric Standard Deviation	----	3.4	----	3.2
(a) Obtained by sieve analysis				
(b) Obtained by Coulter Counter analysis				

b. Surface Area

A B.E.T. surface area using nitrogen as adsorbate was determined for the aged Illinois #6 as stored and after washing five times. Nitrogen surface areas were also measured for a number of other coals, both those which we had used in

the earlier study of slurry surface chemistry for DOE/PETC and some which had been obtained from Gulf Research and Development Corporation for other work. The results are shown in Table 2-3. The surface areas found for the aged Illinois #6 as well as for San Juan are very much larger than those found for all the other coal samples. These two coals are much more porous than the others. Illinois #6 and San Juan were found to adsorb surfactants to a greater extent than either Pittsburgh Seam #8 or Hiawatha, the adsorption being most marked with Illinois #6. The high porosity found for these coals accounts for this effect. In addition, we found Illinois #6 and to a lesser extent San Juan to be less hydrophobic than other coals. Other investigators have also found Illinois #6 to be more hydrophilic than other Eastern bituminous coals. This effect may be related to porosity.

Although the surface area of only Pittsburgh #8-3 was measured earlier, it is unlikely that the surface area of a coal would change very much with aging. The large surface area of Illinois #6 may cause this coal to be especially vulnerable to oxidation. The washed Illinois #6 was found to have a lower surface area possibly because moisture was retained in pores.

The agreement between the surface areas measured for the Lower Kittanning coals in our laboratory and at Gulf Research and Development Corporation is good in one case, less so for the other two. All three samples had approximately the same median size and might be expected to have similar surface areas.

Table 2-3. B.E.T. Surface Areas of Coals

Coal	Surface area (m^2/gm)	
	Measured at CMU	Measured at Gulf R&D Corp
Pittsburgh #8-3 (median size = $41\mu\text{m}$)		
As received	2.1	
5 - $10\mu\text{m}$	4.4	
44 - $53\mu\text{m}$	1.5	
88 - $105\mu\text{m}$	0.8	
Pittsburgh #8-4 (median size = $75\mu\text{m}$)	1.4	
Illinois #6, Aged	44.0	
Illinois #6, Aged/Washed	11.1	
San Juan	27.4	
Hiawatha	1.4	
Splash Dam	2.0	
Lower Kittanning, 1/83	2.8	1.2
Lower Kittanning, 6/83	2.5	2.5
Lower Kittanning, 6/83 beneficiated	2.3	1.1

c. Wettability in Triton X-100 and in CTAB Solutions

Measurements of the wettability of Illinois #6 in surfactant solutions were made using the same technique as we used in our earlier work. The results are given in Table 2-4 and Figure 2-1, and the data for the sample before aging we included for comparison. With Triton X-100 aging has clearly improved the wetting, dramatically so for the washed sample. Only a small increase is seen with CTAB, suggesting that the adsorption sites are different for the two surfactants. For further analysis, wetting experiments with methanol/water mixtures are required.

Table 2-4. Wettability of Illinois #6 in Triton X-100 and CTAB Solutions

Surfactant	Surfactant Concentration % (Wt)	Sink Rate, mgs ⁻¹	
		Aged Coal	Aged/Washed Coal
CTAB	0.010	0.0	0.0
	0.020	0.0	0.0
	0.025	0.0	
	0.028	0.0	
	0.030	2.6	3.2
	0.050	6.0	5.4
	0.100	9.2	5.2
	0.150	8.8	7.0
	0.170		8.9
	0.180		10.1
	0.200	12.1	14.8
	0.250	16.8	16.5
Triton X-100	0.0011	0.0	0.0
	0.0033		0.0
	0.0056	0.5	1.8
	0.0078		9.8
	0.0111	3.7	45.9
	0.0333	18.7	
	0.0444		60.2
	0.0556	22.7	67.6
	0.0778	25.9	
	0.1110	31.6	66.7
	0.1667	41.2	70.4
	0.2220	42.0	
	0.2780	51.5

Figure 2-1. Wettability of Illinois #6 in Surfactant Solutions:

- As received
- Aged
- ◇ Aged and washed five times

2.3.2 Plans for the Next Report Period

The particle size distribution for washed aged Illinois #6 will be obtained, also the dry packing volumes and the wettability in methanol/water mixtures of both samples. Task 2 analysis for Splash Dam coal (Coal 2) will be started

2.4 Task 5: Characterization of Coal/Water Slurries Prepared from Aged Coals

2.4.1 Research Accomplishments

a. Microelectrophoresis

Microelectrophoretic mobilities were determined as a function of pH for both Illinois #6 samples, in 10^{-3} mol dm $^{-3}$ KNO $_3$ and in slurry supernatant diluted to the same conductance, using the Pen Kem Lazer-Zee equipment. The results are given in Table 2-5 and Figure 2-2.

Table 2-5. Microelectrophoretic Mobility of Illinois #6 as a Function of pH

Aged Illinois #6		Washed Aged Illinois #6	
pH	Electrophoretic Mobility ($\mu\text{ms}^{-1}/\text{volt cm}^{-1}$)	pH	Electrophoretic Mobility ($\mu\text{ms}^{-1}/\text{volt cm}^{-1}$)
(a) In 10^{-3} M/dm 3 KNO $_3$			
2.7	-0.86	2.6	-0.95
3.4	-1.04	3.0	-0.91
3.9	-1.67	4.1	-2.20
4.2	-1.08	5.5	-1.88
4.4	-0.75	5.9	-1.62
6.8	-1.73	6.6	-1.80
7.1	-1.92	8.1	-2.28
8.6	-1.91	9.3	-1.49
9.2	-0.97	10.4	-1.88
10.1	-1.83	11.1	-2.28
10.2	-0.94		
(b) In Diluted Slurry Supernatant			
2.8	+0.49	2.2	-0.52
3.1	+0.48	2.8	0.00
3.9	+0.36	3.8	-0.92
5.0	+0.73	5.1	-0.65
5.6	+0.13	6.2	-1.01
6.0	+0.61	7.6	-0.52
8.7	-0.03	8.4	-0.32
9.8	-0.01	9.9	-0.23
10.5	-0.18	10.5	-0.57
		11.0	-0.04

Figure 2-2. Electrophoretic Mobility as a Function of pH for Aged Illinois #6, as stored and after washing:

- in dilute KNO_3
- in diluted slurry supernatant

b. Sedimentation

Tables 2-6 and 2-7 show the sedimentation rates and final settled volumes as a function of coal concentration, for an initial suspension and resuspension after two weeks, for both samples of Illinois #6.

Table 2-6. Sedimentation of Aged Illinois #6 as a Function of Coal Concentration

Coal Concentration		Initial Suspension			Resuspension After Two Weeks		
% (Wt)	% (Vol)	pH	Rate (cm hr ⁻¹)	Settled Volume (%)	pH	Rate (cm hr ⁻¹)	Settled Volume (%)
15	11.2	2.8	23.2	33.3	2.5	25.1	25.3
20	15.2	2.7	14.3	38.0	2.4	13.8	36.0
25	19.2	2.6	8.0	43.8	2.4	8.6	39.7
30	23.4	2.6	5.3	52.9	2.3	6.8	45.2
35	27.8	2.8	3.7	67.5	2.6	3.5	63.3
40	32.3	2.8	2.1	76.2	2.6	2.6	72.3
45	36.9	2.8	0.3	81.6	2.4	0.7	78.4
50	41.7	2.7	0.2	88.9	2.5	0.3	85.1
55	46.6	2.6	0.2	95.7	2.5	0.1	93.8
15	11.2	7.4	18.7	32.6	3.8	25.7	29.9
20	15.2	6.7	12.0	37.4	3.4	12.7	35.0
25	19.2	6.5	7.6	44.3	3.4	7.8	41.7
30	23.4	7.0	5.2	52.5	3.6	5.3	49.4
35	27.8	6.7	3.6	64.4	3.5	3.5	60.7
40	32.3	5.4	1.8	71.6	3.4	2.0	68.3
45	36.9	6.8	1.4	77.6	3.7	0.3	77.2
50	41.7	6.3	0.3	84.3	3.6	0.3	81.8
55	46.6	6.4	0.2	91.1	3.7	0.2	89.9

The pH changes are of interest. Originally the natural pH of Illinois #6 was 4.0; now it is ~ 2.5. Furthermore slurries made up at pH 7 shifted to pH 3-4 after two weeks. There are some interesting effects of aging to be studied.

2.4.2 Plans for the Next Report Period

Measurements of rheology and electrophoretic mobility of concentrated slurries already started, will be completed, hence to finish Task 5 for Illinois #6.

Table 2-7. Sedimentation of Washed Aged Illinois #6 as a Function of Coal Concentration

Coal Concentration		Initial Suspension			Resuspension After Two Weeks		
% (Wt)	% (Vol)	pH	Rate (cm hr ⁻¹)	Settled Volume (%)	pH	Rate (cm hr ⁻¹)	Settled Volume (%)
15	11.2	2.6	20.2	33.2	2.3	28.6	32.2
20	15.2	2.4	15.3	33.9	2.2	17.5	34.8
25	19.2	2.4	8.8	46.2	2.1	9.5	45.1
30	23.4	2.4	5.8	55.0	2.1	6.3	54.6
35	27.8	2.7	4.0	67.9	2.2	4.9	63.5
40	32.3	2.4	2.7	75.3	2.2	2.8	71.8
45	36.9	2.2	0.4	82.6	2.2	0.3	80.0
50	41.7	2.3	0.2	90.3	2.2	0.3	88.2
55	46.6	2.1	0.2	96.8	2.2	0.2	93.5
15	11.2	9.3	---	27.3	3.3	10.3	29.1
20	15.2	8.2	15.9	42.3	2.8	9.1	38.3
25	19.2	8.0	9.5	50.1	3.1	7.0	45.1
30	23.4	7.0	5.2	58.7	2.9	5.0	53.8
35	27.8	7.1	1.2	67.0	3.0	3.6	64.6
40	32.3	8.2	0.2	75.5	3.4	1.4	72.6
45	36.9	7.9	0.2	83.5	3.6	0.3	---
50	41.7	7.3	0.2	88.1	3.6	0.2	82.3
55	46.6	7.6	0.1	93.5	4.1	0.2	88.6

3. OTHER RELATED ACTIVITIES

During June we gave two presentations of our previous work on Stability of Coal/Water Slurries, supported by DOE/PETC.

1. Contractors Meeting, Pittsburgh, June 6-7
2. Paper entitled "The Effects of Surface Active Agents on Coal/Water Slurry Stability" at the Sixth International Symposium on Coal Slurry Combustion and Technology, Orlando, Florida, June 25-27.

We have also sent some recommendations to the EPRI on the establishment of standards for coal/water slurry preparation.

We are discussing with Professor Norman Chigier (Dept. of Mechanical Engineering, CMU) ways of extending our model for slurry behavior to take account of atomization and combustion characteristics, and have been contacted by Brookhaven National Laboratory who wish to apply our results to slurry atomization.