CORRELATION OF STABILITY/RHEOLOGY RELATIONSHIP WITH COAL
PROPERTIES AND CHEMICAL ADDITIVES.

Quarterly Progress Report
September 15, 1989- December 15, 1989

DOE/PC/88925--T9

FRANK OHENE
Department of Chemistry
Grambling State University
Grambling, LA 71245

DE92 007927

Technical Project Officer
U. S. Department of Energy
Pittsburgh Technology Energy Center
P. O. Box 10940
Pittsburgh, PA 15236

Work Performed for the Department of Energy Under
Contract #DE-FG22-88PC025 ~~88~~ 925

DISCLAIMER

"This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference therein to any specific commercial product, process or service by tradename, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of the author expressed herein do not necessarily state or reflect those of the United States or Government or any agency thereof."

MASTER

JAN 16 1990

OVERALL OBJECTIVE:

The overall objective of this project is to perform experiments to evaluate the necessary boundary conditions in the preparation and utilization of Coal Water Slurries (CWS) and also develop a data base for the conceptual analysis of a prescription to predict slurry quality for a given coal candidate.

PROJECT STATUS:

Experiments were performed to study the static stability of the coal slurry compositions whose viscosity were measured and reported in the third quarterly report.

Two different methods were used in this study. In the first approach, the coal slurry was introduced into a 100 mL graduated cylinder and the boundary between the sediment and supernatant liquid was measured periodically and the ratio of supernatant to the coal sediment determined.

It was observed that there was a gradual settling of the coal particles. The maximum height of clear supernatant observed above the slurry was 8 cm. after a 10 day period.

In the second approach, the coal slurry was introduced into a column of two concentric glass cylinders of 6 ft in height and 3 inches in diameter (Fig. 4). This had three ports from which coal samples could be drawn and the weight content of the coal at each level determined.

The slurry samples were maintained in the cylinders for an initial period of 14 days. Samples were withdrawn every three days from

each of the ports and the coal content in the samples were determined after drying to a constant weight. In this approach, water was circulated in the jacket in order to maintain a constant temperature during the duration of the experiment.

The results obtained are as shown in table 2 and fig 2.

The plot shows that there is a gradual settling of the coal particles from the onset.

Adsorption Studies:

During the past two quarters, adsorption studies of the various surfactants currently in use, namely; Igepal 990, Coal master A-23, Coal Master-A-23-S, Aerosol OT, Cetyltrimethylammonium Bromide (CTAB) on Elkhorn # 3 has been initiated. Only the adsorption studies of Igepal 990 has been completed in detail due to initial experimental difficulties.

The amount of the surfactant adsorbed from an aqueous solution on the coal particles were obtained by measuring the concentration of the surfactant in aqueous solution before and after equilibration. Surface Tension measurements were used in this study. The concentration of surfactants in aqueous solution changes the surface tension of the solution in an orderly and reproducible manner (2,4). This is large enough to monitor the surfactant concentration changes in this study.

The surface tension was measured by the du Nouy method, using Fisher Scientific's Surface Tensiomat Model 21.

It was initially very difficult to obtain reproducible results from this measurements. This was found to be due to the fact that the differences may be due to the degree to which humic acid materials

and other impurities get released into the aqueous solution, when the surfactant solution is contacted with the coal. In order to minimize this effect, the coal samples were contacted with distilled water for three days, centrifuged and the supernatant was used to prepare the surfactant solutions for the adsorption studies.

A 35% (w/w) slurry of the coal sample was prepared using surfactant concentrations ranging from 10^{-6}M to 10^{-4}M . This concentration range was used because the surface tension was found to be a linear function of the $\log[\text{concentration}]$ below the concentration of 10^{-4}M . A calibration curve was therefore established prior to the adsorption measurements.

The samples were agitated for a period of three days. This was then centrifuged and the surface tension of the supernatant measured. The equilibrium concentration of the surfactant was estimated from the calibration curve.

Adsorption Isotherm of the Surfactant:

The amount of surfactant adsorbed on the coal surface from the surfactant solution can be determined as follows:

$$N_0 \frac{\Delta X_2}{m} = N_2^s X_2 - N_1^s X_2$$

Where N_0 = Total number of moles of solute before adsorption

X_2 = Change in mole fraction of solute after adsorption

X_1, X_2 = mole fraction of solvent and surfactant at adsorption equilibrium.

N_1^s, N_2^s = number of moles of solvent and surfactant
adsorbed per unit weight of adsorbent at
adsorption equilibrium, gmole/gm.

m = mass of adsorbent in gm.

For very dilute solutions, the surfactant (N_2) is much more strongly adsorbed onto the solid surface than the solvent.

$$\text{Thus, } N_0 \Delta X_2 = N_2$$

where N_2 = change in number of moles of component 2 in solution.

Also, $N_1^s = 0$ and $X_1 = 1$

$$\text{and } N_2^s = \frac{N_2}{m} = \frac{N_0 \Delta X_2}{m}$$

A plot of N_2^s against X_2 (Equilibrium surfactant concentration) gives the adsorption isotherm.

Fig. 3 shows the adsorption isotherm obtained using Igepal 990 as a surfactant on PSOC-1475.

Rosen has reported that the amount of surfactant adsorption at solid-liquid interface may depend on the equilibrium concentration of the surfactant in the liquid phase, the concentration of the surfactant on the adsorbent at the point of surface saturation and the orientation of the adsorbed

surfactant(4).

The plot in figure 3, shows three distinct regions. This suggests that three different mechanisms of adsorption may be involved. In region I, the equilibrium concentration is very low, and thus the amount available from the bulk solution for adsorption is very low. This region, therefore, shows a low surfactant density on the coal surface. In this region, the surfactant molecules are likely to lie parallel to the surface of the coal (1,2,4,5,6).

As the bulk concentration of the surfactant increases, the adsorption density of the surfactant on the coal will also increase and the surfactant molecules may come closer to each other. Van der Waals attractive forces between the hydrocarbon chains may be very significant in this situation and thus adsorption increases. The phenomenon associated with hydrocarbon association has been observed previously and has been termed as hemimicelle formation (1,2). The bulk concentration necessary to initiate the hemimicelle formation is the hemimicelle concentration. At the onset of hemimicelle formation, the orientation of the adsorbed molecule changes from parallel to perpendicular. This probably explains the steep rise in slope in region 2.

Further increase in the surfactant concentration shows a slower rise in slope (region 3.). This slow rise may be due to steric interaction which results in decrease in adsorption.

PLANS FOR THE NEXT QUARTER.

Procedure for measuring the adsorption of surfactants on the coal particles has been established. Thus, work will continue on the adsorption of the various surfactants on the coal particles and the effect on the surfactants and dispersing agents on the stability of the slurry. Also, Zeta Potential Measurements of the coal samples in various surfactants as well as, atomic absorption measurements will continue.

Table 1

Stability Measurement of 65% Coal Slurry
(Elkhorn # 3, pH=10, 0.25% by weight of Igepal 990)

Height of Slurry	Height of Clear liquid above Slurry	Time (days)
100 cm	0 cm	0
98 cm	2 cm	1
95 cm	5 cm	3
94 cm	6 cm	5
92 cm	8 cm	8
90 cm	10 cm	10

Table 3
 Adsorption Isotherm of Igepal 990 on -100/+140 mesh
 on Elkhorn #3 at 25°C

Initial Surfactant Concentration $\times 10^{-6}$ M	Surface Tension (dynes/cm)	Equilibrium Surfactant Concentration $\times 10^{-7}$ M	Surface Tension (dynes/cm)	Amount* Adsorbed /gm coal $\times 10^{-6}$ (gmole/g)
1.0	61.2	98.4	62.2	2.12
5.0	60.2	48.5	59.5	20.0
10.0	58.8	96.2	58.4	50.0
50.0	56.2	447	55.8	700
100	54.6	924	54.6	1000
200	53.0	1092	54.3	1200
250	52.2	1441	53.8	1400
300	51.3	1638	53.6	1800
400	50.8	2486	52.9	2000
600	49.6	4335	52.0	2200
850	49.1	6759	51.2	2300

*The Data in column 5 was obtained by taking the difference between columns 1 and 3, dividing by the coal weight and multiplying by the

Molecular weight of Igepal 990 (4,625).

Table 2
Stability Measurement of 65% Coal Slurry
(Elkhorn # 3, pH=10, 0.25% by weight of Igepal 990)

Time (days)	<u>Coal Content.</u>		
	Port #1	Port #2	Port #3
0	65	65	65
1	60	63	66.8
3	58	60.6	68.8
5	56.1	58	70
7	55	56	71
9	54	55	71
11	53.2	54.6	72
14	53	54	73

REFERENCES

1. Fuerstenau, D. W., Resenbaum, J. M. and J. Laskowski, Colloids and Interface Science, (1983), 8, 153-174.
2. Adamson, A.W., "Physical Chemistry of Surfaces", Wiley Interscience, New York, 4th edition, Chapter 2 (1982).
3. Davies, J. T. and E. K. Rideal, "Interfacial Phenomena", Academic Press, New York, 2nd edition, (1963), 39-52.
4. Rosen, M. J. "Surfactants and Interfacial Phenomena". Wiley Interscience, New York (1978).
5. Widanyi, E. and Wightman, J. P., Colloids and Surfaces (1982), 4, 209-212.
6. Fuller, E. L., Journal of Colloid and Interface Science, (1980), 75(2), 577-583.

FIG. 1. A PLOT OF COAL CONTENT AS A FUNCTION OF TIME

KEY: CURVE 1..... BOTTOM PORT
CURVE 2.....MIDDLE PORT
CURVE 3.....UPPER PORT

ADSORPTION ISOTHERM (G MOLE/G COAL)

Fig. 2 A PLOT OF SURFACE TENSION AS A FUNCTION OF
LOG(SURFACTANT CONCENTRATION)

FIG. 3. A PLOT OF ADSORPTION (g MOLE SURFACTANT/ g COAL)
AS A FUNCTION OF EQUILIBRIUM SURFACTANT CONCENTRATION.

THICKNESS

DIA 3"
1/4" THICKNESS

SECTION

SCALE 3"-1'

FIGURE 4

UN BY:	DATE:	SCALE:	DBL. CYL.	GRAMBLING
AR, KENNETH	10-6-88	1"-1'	GLASS	STATE UNIV.

END

DATE
FILMED

3127192

I