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

Quarterly Progress Report
March 15, 1989- June 15, 1989

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INTRODUCTION:

Coal-water slurry (CWS) is being considered as a near term replacement for oil in both industrial and utility applications. Selecting an economical, yet technically compatible feedstock for producing highly loaded CWS is important to the commercialization of CWS technology (1). Previous work has shown that the dispersing additives can represent a significant portion of CWS preparation cost (2).

In an effort to establish a criteria for designing and preparing CWS for utilization, the relationships between coal properties and slurry quality must be determined. These relationships will enable the prediction of potential CWS quality for the particular coal candidate from some characteristic(s) of the coal.

The coal content at a given viscosity varies for different coal(3). Thus, to develop a viable coal selection strategy using chemical surfactants as additives, the adsorption of these surfactants by the coal particle surface must be established. This work therefore, intends to screen a number of chemical surfactants and dispersants which can be used in the preparation of coal water slurry. The information derived from this screening together with the coal properties will be used to help develop a prescription to predict the stability of coal slurries.

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:

All the items of equipment including the settling column have been received.

Characterization of the surfactants of the surfactants currently in use have been completed. Surface Analysis of the four coal samples (PSOC-1475, 1493, 1494 and 1487) have been performed by FTIR and ESCA.

Heats of immersion measurements of the coal particles as a function of:

Inherent Moisture content

Molecular weight of wetting agent

Oxidation time of coal

were made during this past quarter.

Also, Zeta Potential measurements of the coal samples in aqueous solutions of ammonium naphthalene sulfonate and Igepal as a function of:

coal content

and pH were made.

Collection of data from the literature in order to develop a correlation between the coal properties and slurry quality is

also in progress.

Characterization of Surfactants:

Surface Tension of the aqueous solutions of the surfactants-Cetyl trimethylAmmoniumBromide(CTAB), Dodecyltrimethylammonium bromide (D_{12} TAB), Decyltrimethylammoniumbromide (D_{10} TAB) and five non-ionic surfactants of the series, Nonylphenoxypoly(ethyleneoxy)ethanol, $[(C_2H_4O)_n C_{15}H_{24}O]$ were measured with a Fisher Surface Tensiometer Model 21. This instrument utilizes the du Nouy ring method and has a small electric motor to raise or lower the ring in the test solution more reproducible. A platinum-Iridium ring with a 6.0 cm circumference was used to measure the apparent surface tension. The critical micelle concentration of each of the surfactants were determined from Figs. 1-8 shows the plots of the surface Tension, as a function of the logarithm of the concentration of the surfactants. The critical micelle concentrations obtained for each of these surfactants are as shown in Table 1.

The plots do show that the surfactant are pure.

HEATS OF IMMERSION MEASUREMENTS:

Heats of immersion measurements were made on the coal samples, (PSOC-1475, 1487, 1493 1494) as a function of their equilibrium moisture content using an aqueous solution of 0.1%(wt/v) of dispersant A-23, ammonium naphthalene sulfonate, as the immersion fluid.

The experimental procedure has already been described (4).

The results obtained are shown in Table 2 and Fig.9. The plot shows that the heat of immersion decreases with increase in equilibrium moisture content.

The heat of immersion data, therefore, provides information on the hydrophilic nature of the coal surface.

Heat of Immersion as a function of oxidation time.

Table 3 and Fig.10 show the results of the heat of immersion of the oxidation time of Elkhorn #3 in 0.1%(wt/v) of A-23 as a function of time. In this study, the coal samples were ground to -100/+140 mesh size and allowed to sit in an air circulated oven maintained at 40°C over a period of five weeks. Samples were taken every week and the heat of immersion measurements made.

The results do show that the heat of immersion decreases exponentially with time. Sun and Wein (5) have observed that variations in coal properties due to oxidation might be due to the presence of humic acid on the coal surface. Humic acids are the major constituents of organic oxidation products and are formed on coal surfaces with various molecular weights. The variation of heat of immersion of the coal samples with oxidation time, might be due to increased formation of humic acid on the coal surface.

Heat of Immersion as a function of the Molecular weight of Surfactant.

0.1%(wt/v) of five non-ionic surfactants, Nonylphenoxypoly(ethyleneoxy)ethanol, $[(C_2H_4O)_n C_{15}H_{24}O]$ were used as the immersional fluids to determine the heat of immersion on Elkhorn #3 ground to +140 mesh size.

The results are as shown in Table 4 and Fig. 11. The plot shows that the heat of immersion decreases with increase in molecular weight of the non -ionic surfactant.

Traube,s rule (6) states that "The adsorption of organic substances from aqueous solutions increases strongly as we ascend the homologous series". Hansen and Craig (7) supported Traube,s rule by showing an increasing adsorption of fatty acids from water as the hydrocarbon chain length increased. It, therefore, appears that as the as the hydrophobicity of the hydrocarbon portion of the non-ionic surfactant increases, it's expulsion from water increases and thus increasing the interaction of the surfactant with the coal. This suggests that the high molecular weight surfactants should be preferred wetting agents in coal preparation.

Zeta Potential Measurements:

The zeta potential was determined using a Micromeritics Zeta Potential Analyzer. Operation allows the effective particle surface charge in a liquid solid sample to be measured by the application of a constant electric current applied across a 50% weight solids suspension. By determining the rate at which the particles migrate into a sample cell,

electrophoretic mobility and zeta potential can be determined.

Considerable time was spent in order to develop an effective technique in order to establish an equilibrium between the coal particles and the aqueous solutions of the various chemicals in order to obtain reproducible results. Allowing an equilibration time of between 24 -36 hours do give reproducible results.

Fig. 12 illustrates zeta potential as a function of pH for Elkhorn #3 coal using both 0.1% (wt/v) aqueous solutions of Coal-master A-23 and Igepal 890. As the pH increased, the magnitude of the zeta potential decreased. The plot shows a minimum at a pH of 8.48 when Igepal 890 is used as the wetting agent. The plots however, do show that the zeta potential in A-23, produces a slightly higher electrokinetic response than the measurements in non-ionic detergent, Igepal 890.

Zeta Potential provides a means of predicting colloidal behavior (7). The stability and the degree of flocculation of a system increase as the zeta potential decreases (7).

Thus, a correlation between the zeta potential and the state of flocculation suggests that, Igepal 890 will be most effective as a deflocculant at a pH 8.48 and that the ammonium naphthalene sulfonate will be slightly better.

Table 7 lists the percentages of the C=C, C-C, C-O, C=O, and $\overset{\text{O}}{\text{C}}=\text{O}$ found in the four coal samples being used in this study. Figs. 13-20 are the FTIR and ESCA plots obtained for each of these samples. The values in table 7, were obtained

by curve fitting analysis of the C 1s region with the four peaks due to different carbon containing groups: those containing C-C single bonds, carbon containing C=C bonds, carbon containing C-O bonds and carbon containing C=O bonds. The values do show that the total C-O bonds at the surface of the coal decrease in the order of PSOC1487> PSOC1493> PSOC1494> PSOC1475. The FTIR spectra of PSOC 1494 and 1493 do show identical similarities. This probably show that they have identical coal seam.

The presence of carbonyl and OH groups at the surface of the coal reflects the trends observed in the heat of immersion and zeta potential measurements as a function of pH.

COAL CHARACTERISTICS AND SLURRY QUALITY

The coal properties been examined in order to develop a relationship between slurry quality and the coal properties have been described in the first quarterly report.

Information on 32 different coals have been collected from the literature (8-11) and these have been used to establish a correlation between the coal content of a given slurry and the coal properties.

Figs. 21-26 show the relationship between the various coal properties examined and the coal content.

The data were fitted by a correlation of the form

$$CC = A_0 + \sum B_i X_i$$

where:

CC is the coal content

A_0 and B_i are constants

X_i are the plotted parameters

The equation obtained is of the form:

$$CC = 64.195 - 0.099 * \text{moisture} - 0.067 * \text{Ash} + 0.031 * \text{C/O} \\ + 0.590 * \text{FC/VM} - 0.046 * \text{Floatability} + 0.095 \text{ HGI.}$$

From the plots (Figs, 13-18), the coal content appears to increase with C/O, FC/VM, HGI, Ash, and decrease with the moisture content and floatability.

It appears that considerable increase in the oxygen and moisture content reduces the floatability and thus, a decrease in the coal content with increase in moisture content, is directly related to a decrease in hydrophobicity and hence the coal content. An increase in coal content with increase in the Ash content suggests that not all the mineral matter may be detrimental to the slurry quality.

PLAN FOR THE NEXT QUARTER:

The adsorption studies are inconclusive. These measurements will be continued in the next quarter. Also viscosity as well as, stability studies will be performed.

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Table 1.

A List Of Surfactants and Their Critical Micelle Concentrations (CMC) as Determined by Surface Tension Measurements.

Surfactant	Critical Micelle Concentration (CMC)
Decyltrimethylammonium Bromide (D ₁₀ TAB)	$6.15 \times 10^{-2} \text{ M}$
Dodecyltrimethylammonium Bromide (D ₁₂ TAB)	$1.66 \times 10^{-2} \text{ M}$
Cetyltrimethylammonium Bromide (CTAB)	$9.55 \times 10^{-4} \text{ M}$
Igepal-430	$2.55 \times 10^{-5} \text{ M}$
Igepal 610	$1.96 \times 10^{-4} \text{ M}$
Igepal 720	$2.08 \times 10^{-4} \text{ M}$
Igepal 890	$1.47 \times 10^{-4} \text{ M}$
Igepal 990	$1.58 \times 10^{-4} \text{ M}$

Table 2.

Heat of Immersion as a Function of Equilibrium Moisture
Content of Coal Samples.

Heat of Immersion (Cal/gm)	Coal Sample and Moisture Content.	
-10.67 $\pm$ 1.81	[PSOC-1475]	6.09%
-14.94 $\pm$ 1.61	[PSOC-1494]	7.80%
-21.63 $\pm$ 2.86	[PSOC-1493]	11.08%
-24.64 $\pm$ 4.17	[PSOC-1487]	18.82%

Table 3.

Variation of the Heat of Immersion of the coal particles
(PSOC-1475) as a Function of oxidation time.

Heat of Immersion	Oxidation Time
(cal/gm)	(Number of Weeks)
-14.46 $\pm$ 2.13	0
-16.27 $\pm$ 3.71	1
-18.31 $\pm$ 2.91	2
-21.08 $\pm$ 1.71	3
-22.23 $\pm$ 3.16	4
-21.94 $\pm$ 2.87	5

Table 4.

A Variation of the Heat of Immersion as a Function of the Molecular weight of [0.1% (wt/v) Aqueous solution] the Surfactant.

Heat of Immersion (Cal/gm)	Surfactant (Mol.wt)
-2.84 $\pm$ 1.21	Igepal-430 (396)
-4.68 $\pm$ 1.51	Igepal 610 (550)
-11.54 $\pm$ 1.41	Igepal 720 (750)
-16.31 $\pm$ 3.17	Igepal 890 (1983)
-20.19 $\pm$ 4.33	Igepal 990 (4625)

Table 5.

Variation of Zeta Potential of 50% (wt/v) of coal slurry (PSOC-1475) in 0.1% (wt/v) aqueous solution of Igepal 890 as a Function of pH.

Zeta Potential(mv)	pH
5.55 $\pm$ 1.73	2.07 $\pm$ 0.01
-0.14 $\pm$ 0.11	5.20 $\pm$ 0.01
-7.84 $\pm$ 1.34	8.48 $\pm$ 0.01
-1.37 $\pm$ 0.84	9.30 $\pm$ 0.01
-2.39 $\pm$ 1.01	10.93 $\pm$ 0.01

Sodium Hydroxide or Hydrochloric Acid was used to adjust the pH.

Table 6.

Variation of the Zeta Potential of 50% (wt/v) of Coal Slurry (PSOC-1475) in 0.1 % (wt/v) aqueous solution of Ammonium Naphthalene Sulfonate as a Function of pH.

Zeta Potential	pH
-0.97 $\pm$ 0.67	5.63 $\pm$ 0.01
-2.27 $\pm$ 1.43	6.45 $\pm$ 0.01
-4.04 $\pm$ 0.81	7.44 $\pm$ 0.01
-8.67 $\pm$ 2.15	8.31 $\pm$ 0.01
-15.42 $\pm$ 2.38	9.56 $\pm$ 0.01
-16.67 $\pm$ 1.83	10.93 $\pm$ 0.01

Ammonium Hydroxide was used to adjust the pH.

Table 7.

Percentage of Different Functional Groups at The Surface of the Four Coal Samples: PSOC-1475, 1487, 1493, and 1494.

Coal Sample	<u>%C=C, C-C</u>	<u>% C-O</u>	<u>% C=O</u>	<u>% $\overset{\text{O}}{\text{C}}=\text{O}$</u>
				O
PSOC 1475	88.5	8.0	1.4	2.1
PSOC 1494	86.7	10.5	0.9	1.8
PSOC 1493	82.6	14.6	1.2	1.7
PSOC 1487	80.9	14.2	2.7	2.1

FIG. 1. A PLOT OF SURFACE TENSION AS A
FUNCTION OF LOG[D TAB]

FIG. 2. A PLOT OF SURFACE TENSION AS A
FUNCTION OF LOG [CTAB]

FIG. 3. A PLOT OF SURFACE TENSION AS A
FUNCTION OF LOG[D TAB]

FIG. 4. A PLOT OF SURFACE TENSION AS A FUNCTION OF LOG[IGEPA 430]

FIG. 5. A PLOT OF SURFACE TENSION AS A
FUNCTION OF LOG [IGEPAL 610]

FIG. 6. A PLOT OF SURFACE TENSION AS A FUNCTION OF
LOG [IGE PAL 720]

FIG. 7. A PLOT OF SURFACE TENSION AS A
FUNCTION OF LOG [IGEPA 890]

FIG. 8. A PLOT OF SURFACE TENSION AS A FUNCTION OF
LOG [IGEPAL 990]

FIG. 9. A PLOT OF HEAT OF IMMERSION AS FUNCTION OF EQUILIBRIUM MOISTURE CONTENT OF COAL SAMPLES

FIG. 10. A PLOT OF HEAT OF IMMERSION AS A FUNCTION OF OXIDATION TIME.

FIG. 11 A PLOT OF HEAT OF IMMERSION AS A FUNCTION OF THE MOLECULAR WEIGHT OF THE WETTING AGENT

FIG. 12 A PLOT OF ZETA POTENTIAL AS A FUNCTION OF pH

A ---- AMMONIUM NAPHTHALENE SULFONATE (A-23)
B-----IGEPAL 890

FIG. 13: ESCA SPECTRA OF PSOC 1487

PSOC 1487

FIG. 14: FTIR SPECTRA OF PSOC 1487

SAMP = BP51184715
PSOC 1487 SSN 05-08-00/02 BALTRIS GRAMBLING STATE U. (PELLET)
TUE MAY 16 00:33:08 1989
RES = 8.0

FIG. 15: FTIR SPECTRUM OF PSOC 1494

Kentucky #9
high moisture
high ash

Kentucky #9 same coal seam as Illinois #6
∴ virtually the same

PSOC 1494

SAMP = BF51184717

WAVENUMBERS

RES = 8.0

PSOC 1494 SSN 05-08-89/04 BALTRUS GRABLING STATE U. (PELLET)

TUE MAY 16 13:26:26 1989

SCANS = 16

Fig. 16: ESCA Spectrum of PSOC 1494

FIG. 17: FTIR SPECTRUM OF PSOC 1475

FIG. 18: ESCA SPECTRUM OF PSOC 1475

PSOC 1475

% TRANSMITTANCE

Illinois #6
high moisture
high ash
1766 1743

SAMP = BPS1184716

WAVENUMBERS

RES = 0.0

SCANS = 16

P30C 1409 99N 05-08-08/03 BALTIMORE GRAVELING STATE U. (PELLET)

TUE MAY 16 11:23:40 1989

FIG. 21. A PLOT OF COAL CONTENT AS A FUNCTION OF FLOATABILITY

FIG. 22. A PLOT OF COAL CONTENT AS A FUNCTION OF FC/VM RATIO

FIG. 23. A PLOT OF COAL CONTENT AS A FUNCTION OF C/O RATIO

FIG. 24. A PLOT OF COAL CONTENT AS A FUNCTION OF
ASH CONTENT

FIG. 25. A PLOT OF COAL CONTENT AS A FUNCTION OF EQUILIBRIUM MOISTURE

FIG. 26. A PLOT OF COAL CONTENT AS A FUNCTION OF HG INDEX

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