**CORRELATION OF STABILITY/RHEOLOGY
RELATIONSHIP WITH COAL**

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PROPERTIES AND CHEMICAL ADDITIVES.

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FINAL TECHNICAL REPORT

**PERIOD OF PERFORMANCE
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**U. S. Department of Energy
Pittsburgh Energy Technology Center
P. O. Box 10940
Pittsburgh, Pa 15236**

**Technical Project Officer
Doug Gyorke**

MASTER

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SUMMARY

Coal-water slurries have the potential of a near term replacement for fuel oil. In order to gain the fundamental understanding of the preparation and handling of coal-water slurries, experiments were performed to identify the relationship between the coal content of a given coal-water slurry and its physical and chemical properties.

The objectives of this program were:

- * Investigate the relationship between the chemical and physical properties of coal and the rheology of coal-water slurry
- * Define procedures for evaluating and preparing coal water slurries for a particular coal candidate, based on the characteristic coal properties
- * Develop improved methods of screening surfactants used in coal-water slurry preparation
- * Perform experiments designed to investigate the effect of characteristic coal properties on slurry quality, by examining the effect of the individual coal properties on slurry quality
- * Develop a statistical formulation to predict the coal content of a given coal water slurry content based on the coal characteristic properties

These objectives were accomplished by:

- * Performing a literature search to collect data on coals that have been used to prepare coal-water slurries

- * Selecting coal samples with varying properties necessary to meet the program objectives
- * Performing extensive coal analyses including state of the art surface property measurements
- * Performing rheological evaluations to include the effect of pH, additive type, additive concentration and particle size distribution measurements on the coal water slurries.

The coals selected and their key features were:

Kentucky #9	Low Organic Sulfur Content, Relatively Low Internal Moisture Content and greater than 10 % Ash content.
-------------	---

Adaville #1	Low Organic Sulfur Content, High Moisture content and Relatively Low Ash Content.
-------------	---

Illinois #6	Low Organic Sulfur Content, Relatively High Moisture Content, and High Ash Content
-------------	--

Elkhorn #3	Low Organic Sulfur Content, Low Moisture Content and Ash Content.
------------	---

Three other samples were later selected to test the results of the program. The samples selected were: Middle Kittaning, Upper Freeport and Pittsburgh coals.

Coal Characterization included:

Bulk Characterization	Those properties that are significant for the Utilization and Handling of the Prepared Slurries.
-----------------------	--

Bulk Properties	Proximate Analysis, Ultimate Analysis and
-----------------	---

Surface Properties

Particle Size Distribution

Fourier Transform Infrared Spectroscopy (FTIR), Electron Spectra For Chemical Analysis (ESCA), Heats of Immersion Measurements, Surfactant Adsorption and Zeta Potential Measurements.

The most important outcomes of this program were:

The development of a methodology to evaluate dispersants suitable for coal-water slurry preparation,

An experimental methodology of determining the influence of particle size distribution on coal-water slurry and

The development of a statistical expression to predict the coal content of coal-water slurry based on the coal properties, and an experimental verification of this expression.

INTRODUCTION

Coal water slurry (CWS) is a promising alternative to fuel oil [1]. One important advantage of using CWS fuel over direct conversion to pulverized coal is that fewer modifications to boiler, fuel handling , and environmental constraints are needed [2].

Despite the wide interest in CWS, there is very little information on the type of dispersing additives and their effect on the stability of CWS, since most of the information on additives are proprietary. Also, coal is not a uniform substance, but consists of carbonaceous material and a variety of inorganic matter. Therefore it is difficult to find what physico-chemical property(ies) of coal is (are) the essential factor(s) affecting the CWS rheology [3,4].

The utilization of coal-water slurries with high solids content require detailed rheological knowledge of the suspension and of the role played by chemical dispersants in influencing the chemistry of the solid-liquid interface.

Mathematical models, such as Bingham plastic model, Power law model or H. Buckley model have been used to define flow properties of such suspensions [5,6,7].

Rheology is defined as the study of the deformation of fluids. There are two types of fluids: Newtonian fluids and non-Newtonian fluids. In Newtonian fluids, shear stress is linearly proportional to the shear rate and viscosity is constant

with respect to the shear rate. Coal water slurries however, exhibit non-Newtonian behavior [8,9,10].

A typical set of curves for both Newtonian and non-Newtonian fluids are shown in Figure 1-1 [10].

A Bingham plastic fluid has the simplest rheological behavior among the non-Newtonian fluids because after an initial yield stress is reached, the curve exhibits the behavior of a Newtonian fluid. A pseudoplastic fluid exhibits a curvilinear relationship with decreasing apparent viscosity with increasing shear, whereas a dilatant fluid exhibits increasing viscosity as the shear rate is increased.

A general mathematical description of the time-independent rheological behavior of fluids which obey the power law model can be described by the relation:

$$\tau = \tau_0 + K(\gamma)^n \quad (1-1)$$

Where τ is the shear stress

τ_0 is the yield stress

γ is the shear rate (equal to the velocity gradient, du/dy)

K and n are empirical constants.

Various types of fluids can be represented by modified forms of mathematical expressions of equation 1-1 as follows:

Newtonian $\tau = \mu\gamma$ ($\tau_0=0$, $n=1$, $K=1$) (1-2)

Bingham plastic

Power Law $\tau = K(\gamma)^n$, ($\tau_0=0$) (1-3)

Yield Power law $\tau = \tau_0 + K(\gamma)^n$ (1-4)

- A Newtonian
 - B Pseudoplastic - shear thinning
 - C Dilatant - shear thickening
 - D Bingham
 - E Pseudoplastic, with yield value
 - F Dilatant, with yield value.
- τ_0 = yield value

FIGURE 1-1 CHARACTERISTIC SHEAR STRESS VS. SHEAR RATE FLOW

$n < 1$ yield pseudoplastic

$n > 1$ yield dilatant

The equations described above represent time-independent rheologic behaviors. Some sample fluids may also exhibit time-dependent behaviors. In a liquid suspension of nonspherical solid particles, the resulting viscous fluid possesses a structure of randomly packed configuration. When this fluid is sheared and flow starts, re-alignment of particles takes place. The gradual change of the structural configuration and particle orientation will result in a corresponding variation of the rheological behavior of the fluid and thus, a primary two time dependent viscosity relationship: rheopectic and thixotropic fluids can occur. Rheopectic fluids exhibit increasing resistance to flow with time, whereas the thixotropic fluids exhibit decreasing resistance to flow with time.

The rheological properties of coal-water mixtures depend primarily on the following parameters: Particle size distribution, interparticle interactive forces, attractive-repulsive forces, volume concentration and physico-chemical properties of the coal [11,12,23,14].

Effect of particle Interaction

Coal-water slurries are concentrated suspensions of coal particles in water. These systems are thermodynamically unstable. Thus, they exhibit the tendency to separate into two microphases, a solid phase and a liquid phase. One of the mechanisms by which the phase separation occurs arises from the

tendency of the particles to stick to each other to form clusters or aggregates.

The aggregation of the particles is due to long-range attractive forces which exists between the particles[15,16]. The need for dispersions in which there is either no sedimentation or in which the rate of sedimentation is very low is of very practical importance and are characterized as having sedimentation stability. Such stability is related to the repulsive forces between the coal particles. These repulsive forces can be imparted to the particles by one of the following mechanism:

- Repulsive interaction between electric double layers at the coal-liquid interface (Figure 1-2),
- Repulsion resulting from formation of structured solvation around the particles,
- Steric stabilization, which results from the adsorption of structured solvation layers around the particles and
- Repulsion resulting from macromolecules dissolved in the liquid phase [17,18].

Each type of coal constitutes a different system due to the coals characteristic properties. The chemistry of the coal surface plays an important role in any rheological process in which coal particles are incorporated in water. There are three main contributing effects to the surface properties of coal (19). These are:

- The hydrocarbon skeleton,

FIGURE 1-2 INTERPARTICLE POTENTIAL ENERGY

The number and type of functional groups on the coal surface,

The Ash content-> inorganic impurities.

Nature of Coal Surface

Coal particle surfaces are heterogeneous in nature. They consist of an organic part, i.e., of hydrocarbon portions with associated functional groups (mainly phenolic, carbonyl, and carboxyl groups), and an inorganic part (pyrite, clay minerals, which constitute the ash content [20,21]).

The oxygen content of the coal decreases with the rank of the coal; the higher the rank, the higher the carbon/oxygen ratio.

The C/O ratio of the coal surface is decreased by the process of aging or oxidation during which polar functional groups such as -COOH, -CO, and phenolic -OH are formed.

Therefore, it seemed desirable to conduct experiments to study the surface characteristics of the coal surface including oxidation of the coal particles and to relate this study to the rheological behavior of the coal-water slurry. The experiments conducted were Fourier Transform Infrared Diffuse Reflectance studies (FTIR), Electron Spectroscopy for Chemical Analysis (ESCA), Zeta Potential and Heats of Immersion studies of the coal particles in dispersant solution.

SECTION II

SURFACE CHARACTERIZATION

2.1 FTIR Studies

The diffuse reflectance spectrum of each sample was measured in a KBr diluent. The diffuse reflectance of each coal as received is shown in Figures 2-1 through 2-4, and representative spectra of the coals after air oxidation are shown in Figures 2-5 through 2-8. The FTIR spectra of PSOC 1494 and 1493 (Figures 2-3 and 2-4) do show similarities. This shows that they have identical coal seam. The extent of the oxidation was monitored by observing changes in the intensity of the C-H stretching band between 3900 and 2700 cm^{-1} . The ratio of the aromatic and aliphatic -C-H stretching bands have been found to correlate well with the apparent rank of the high rank coals [21]. The measured infrared spectra, Figures 2-1 through 2-8, were used to determine the degree of hydrophilicity of the coal samples. Ye et al. [22] have defined hydrophilicity Index on the coal surface as:

$$\text{hydrophilicity Index} = \frac{(\text{C=O}) + 2(-\text{OH})}{(\text{R-H}) + (\text{Ar-H})} \quad (2-1)$$

The transmittance intensity corresponding to the groups appearing in the above relation were measured at the following wave numbers: 1710 cm^{-1} for C=O, 3400 cm^{-1} for -OH, 2700 cm^{-1} for R-H, and 2900 cm^{-1} for Ar-H. The transmittance intensities were converted into absorption intensities using the relation:

$$\text{Absorption} = \log (100/T) \quad (2-2)$$

where T is the percent transmittance.

The hydrophilicity index calculated from the FTIR spectra using

FIGURE 2-1 FTIR SPECTRA OF ELKHORN #3 (AS RECEIVED)

SAMP = BP51184714

WAVENUMBERS
RES = 8.0

P90C 1475 SSN 85-08-89/01
TUE MAY 89 15:58:18 1989

SCANS = 16

FIGURE 2-2 FTIR SPECTRA OF ADAVILLE #1 (AS RECEIVED)

SAMP = BP51184715

PSOC 1487 SSN 05-00-00/02

RES = 8.0

GRAVELING STATE U. (PELLET)

SCANS = 16

TUE MAY 16 16:30:33:00 1980

FIGURE 2-3 FTIR SPECTRA OF KENTUCKY #9 (AS RECEIVED)

SNAP = BP51184717

PSOC 1494 SSN 05-08-86/24

RES = 8.0

GRANBURY STATE U. (PELLET)

SCANS = 16

TUE MAY 16 12:26:26 1989

FIGURE 2-4 FTIR SPECTRA OF ILLINOIS #6 (AS RECEIVED)

SAMP = BP51184716

P50C 1493 SSN 05-08-00/03 GRAVELING STATE U. (PELLET)

DATE MAY 16 1988

the Relation above, are as shown in Table 2-1.

The hydrophilicity index compares the relative concentration of hydrophilic oxygen functional groups on or near the coal surface to the relative concentration of hydrophobic aliphatic and aromatic C-H groups. The values indicate that Elkhorn # 3 has the least hydrophilicity index and Kentucky # 9 and Adaville #1 have the highest hydrophilicity indices. The aromatic C-H and the aliphatic C-H stretching frequency absorptions at 2900 cm^{-1} and 2700 cm^{-1} indicate that Illinois #6, (PSOC-1493), has the lowest density of C-H on its matrix of the four coals examined.

Effect of Oxidation

Figures 2-5 through 2-8 show the FTIR spectra of the coal samples after a one year storage. Low Temperature oxidation of the coals has a number of important effects on the coal and thus the rheology of the coal-water slurries [14]. The oxidation of coal has been studied using a variety of analytical techniques including, Infrared spectroscopy [23], ESCA [24], UV fluorescence [25]. Although all these methods provide valuable information regarding the chemical and physical changes of the coal, infrared spectroscopy is the most suitable technique for studying oxidation on a molecular level [26]. Despite its relative insensitivity to small degrees of oxidation, it provides information concerning the molecular structure of the whole coal. Oxidation causes changes in the structure, and resulting transformations are seen in the infrared spectrum. The intensity of the carbon-hydrogen aliphatic stretching mode near 2900 cm^{-1}

Table 2-1

Intensities of Ar-C-H and R-C-H Absorption Frequencies of Coal

Samples			
Sample	2900 cm^{-1} Absorption	2700 cm^{-1} Absorption	Hydrophilicity Index
PSOC-1487	0.60	0.48	1.7
PSOC-1494	0.59	0.47	1.7
PSOC-1475	0.80	0.66	1.3
PSOC-1493	0.48	0.44	1.6

Table 2-2

Intensities of Ar-C-H and R-C-H Absorption Frequencies of Coal

After One Year Storage

Sample	2900 cm^{-1} Absorption	2700 cm^{-1} Absorption
PSOC-1487	0.35	0.29
PSOC-1494	0.38	0.34
PSOC-1475	0.30	0.28
PSOC-1493	0.45	0.22

decreases with increasing oxidation. A band attributable to a carbonyl moiety grows in near 1690 cm^{-1} , and there are differences in the C-O (ether) bands centered near 1200 cm^{-1} . By studying the evolution of these changes with increasing oxidation of the coal, the rate of oxidation of the coal samples and its effect on the rheology can be established.

In this study, the variation of the intensity of the C-H aliphatic stretching bands between 3000 cm^{-1} and 2700 cm^{-1} were measured a year apart. There were several reason for studying these bands. Fredricks and Moxon have shown that the C-H aliphatic mode stretching region was the spectral region most sensitive to oxidation [27]. Also, that spectral region is well isolated from other bands in the coal spectrum. The absorptivity of the aliphatic C-H stretching mode bands is intermediate in strength, so that those bands are not the strongest in the spectrum. This is advantageous because very strong bands tend to be overly sensitive to slight sample preparation and very weak bands are heavily influenced by noise in the spectrum. For this reason, the region between 3000 and 2700 cm^{-1} is ideal for the study of coal oxidation.

Comparison of the FTIR spectra of the coal samples taken a year apart, shows a decrease in the intensity of the absorption of the aliphatic C-H frequencies. This decrease can be attributed to the oxidation of the coal samples. The decrease is much more pronounced in the case of Elkhorn # 3. This may be due to the handling problem since this was stored for a much longer period

FIGURE 2-5 FTIR SPECTRA OF ELKHORN #3 (AFTER ONE YEAR)

FIGURE 2-6 FTIR SPECTRA OF ADAVILLE #1 (AFTER ONE YEAR)

FIGURE 2-7 FTIR SPECTRA OF KENTUCKY #9 (AFTER ONE YEAR)

FIGURE 2-8 FTIR SPECTRA OF ILLINOIS #6 (AFTER ONE YEAR)

Table 2-3

Percentage of Different Functional Groups at The Surface of the
Four Coal Samples: PSOC-1475, 1487, 1493, and 1494. 0

Coal Sample	<u>%C=C, C-C</u>	<u>% C-O</u>	<u>% C=O</u>	<u>% C=O</u>
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

Table 2-4.

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

Coal Sample	<u>%C=C, C-C</u>	<u>% C-O</u>	<u>% C=O</u>	<u>% (C=O)-O</u>
PSOC 1475	80.1	16.2	2.4	1.3
PSOC 1494	82.6	14.4	1.1	1.9
PSOC 1493	78.2	18.0	2.5	1.2
PSOC 1487	75.7	20.1	4.1	---

than the rest of the coal samples.

Tables 2-3 and 2-4 list data from ESCA analysis of these samples taken a year apart. The values 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. Comparison of the data in these two Tables 2-3 and 2-4 show considerable decrease in the C=C, C-C, and C=O contents and an increase in the percentage amounts of C-O, and C(=O)-O. This indicates oxidation of C-C and C=C groups to C-O and oxidation of C=O groups to C(=O)-O groups. The quality of the slurries prepared from these coal samples are discussed in Section IV.

2.2 Surface Charge and Electrokinetic Phenomena

The chemistry of the coal surface plays a significant role in the stability of coal water slurries [28,29,30]. Three main effects contributing to the surface properties are:

- The number and type of polar groups (carboxylic and phenolic),

- The ash content and

- The hydrocarbon skeleton.

The mineral matter of coal which constitutes the inorganic matter in coal is generally associated with the ash content in coal. There are two basic mechanisms that contribute to the

surface charge of the coal particles in aqueous media. The first is the dissociation of ionogenic groups on the coal surface, such as those having carboxylic, phenolic, and hydroxylic functionality. The surface charge is governed by the ionization of the acid groups

and for the surface containing hydroxyl groups which may be considered to be amphoteric, such as those that exist on the surface of inorganic oxides on the ash component of coal, the charging process may be represented by

Surface charge can also be generated by specific adsorption of ions from the solution phase [32]. These may be simple inorganic ions, surface active agents (anionic and cationic), hydrolyzable metal ions, and polymeric electrolytes. All these influence the electrophoretic behavior of the coal surface [33].

The zeta potential of the coal-water slurries were studied in various types of surface-active agents in order to determine the behavior of coal-water slurries and to gain knowledge of the surface charge effects resulting from adsorption of the dispersants on the coal particles.

2.3 Characterization of Surfactants:

Surface Tension of the aqueous solutions of the surfactants:

Table 2-5

Critical Micelle Concentration Of Surfactants

Determined From 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	$1.58 \times 10^{-4} \text{ M}$

Cetyl-trimethylAmmonium Bromide(CTAB), Dodecyltrimethylammonium bromide(D₁₂TAB), Decyltrimethylammoniumbromide (D₁₀TAB) and five non-ionic surfactants of the series

Nonylphenoxypoly(ethyleneoxy)ethanol, [(C₂H₄O)_nC₁₅H₂₄O] were

measured with a Fisher Surface Tensiomat 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 -Irridium ring with a 6.0 cm circumference was used to measure the apparent surface tension. The critical micelle concentration of each of the surfactants determined are as listed in Table 2-5.

2.4. Zeta Potential

The theory of the electrical double layer associated with a charged particle in an aqueous electrolyte solution has been well documented. Essentially, the charge is assumed to be smeared out uniformly over the particle surface, and this is balanced by ions, regarded as point charges, which are of opposite sign and distributed in the medium around the particle.

The dissociation constant expressions in equations 2-2 and 2-3, can be represented by:

$$K_{\text{acid}} = \frac{[\text{COO}^-] a_{\text{H}^+}^{(s)}}{[\text{COOH}^+]} \quad (2-6)$$

and for Equation 2-7,

$$K_{\text{phenolic}} = \frac{[\text{O}^-] a_{\text{H}^+}(\text{s})}{[-\text{OH}]} \quad (2-7)$$

where $a_{\text{H}^+}(\text{s})$ is the activity of the hydrogen ions at the surface of the coal and is related to the activity in the bulk (a_{H^+}), i.e., the pH by the relation:

$$a_{\text{H}^+}(\text{s}) = a_{\text{H}^+} \exp(-e\psi_0 / kT) \quad (2-8)$$

where ψ is the potential at the solid liquid interface, e is the electronic charge, k is the Boltzmann constant and T is the absolute temperature.

The surface has an electrostatic potential ψ , and on moving away from the surface the potential decays exponentially to zero in the bulk liquid. The shear plane, which corresponds to the boundary of the layer of bound solvent, is the location of the zeta potential.

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 maximum of 50% by weight solids suspension. By determining the rate at which the particles migrate into a sample cell, electrophoretic mobility and zeta potential can be determined.

In order to obtain reproducible results, considerable time was spent in developing an effective technique to establish an equilibrium between the coal particles and the aqueous solutions of the various solutions. It was found that an equilibration time

of between 24-36 hours gave reproducible results.

Measurements were found to be very sensitive to the solid concentration of the slurry. Thus, solids concentration of 25% and 50% by weight were used. The 25% by weight solids' concentration were much more reproducible. Therefore, more measurements were made at this solids concentration. In addition, the effect of aging of the coal samples on the zeta potential was also noted. Measurements in a constant ionic medium of 0.001 M KNO_3 helped eliminate any anomalies, due to changes in ionic strength of the aqueous phase as a result of leaching of ions from the coal into the aqueous phase, or varying the pH of the suspension, in the measured values

Figures 2-9 through 2-12 are plots of zeta potential of 50% by weight solid concentration as a function of pH for the coals used in this study using both 0.3% (wt/wt) aqueous solutions of three different dispersants. The zeta potential decreased with an increase in pH and the iso-electronic point (iep) varied from coal to coal. The coals having a high ash content, (Illinois #6, Kentucky # 9) exhibit iso-electronic points (iep) at low pH values. For all the coals, there was a shift in the iep to lower pH's with respect to aging. This change is due to the oxidation of the coal samples (FTIR and ESCA Analysis show increase oxidation of the coal samples). The plots show the zeta potential is pH and dispersant dependent. The increase in the zeta potential with pH for each of the coal samples showed a minimal decrease after a pH of 8, indicating a levelling effect after a

FIGURE 2-9 ZETA POTENTIAL VS. PH, ELKHORN #3

FIGURE 2-10 ZETA POTENTIAL VS. PH, ADAVILLE #1

FIGURE 2-11 ZETA POTENTIAL VS. PH, KENTUCKY #9

FIGURE 2-12 ZETA POTENTIAL VS. PH, ILLINOIS #6

pH of 8. This indicates that a better electrokinetic response is exhibited by the slurries above a pH of 8 and that the electrokinetic response is better in anionic dispersants.

Zeta Potential provides a means of predicting colloidal behavior (34). The stability and the degree of deflocculation of a system increase as the zeta potential decreases. Thus, a correlation between the zeta potential and the state of flocculation suggests that Igepal will be most effective as a deflocculant at a pH above 8 and that the ammonium naphthalene sulfonates will be slightly better.

2.5 Adsorption Isotherm of the Surfactant:

Adsorption studies of the various surfactants: Igepal 990, Igepal 890, Igepal 720, Coal master A-23 and Coal Master-A-23-S on Elkhorn #3 was studied. The adsorption studies of Igepal surfactants gave reproducible results. The amount of the surfactant adsorbed from an aqueous solution on the coal particles was obtained by measuring the concentration of the surfactant in aqueous solution before and after equilibration with the coal samples. 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 (35,36). 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. Initially,

it was very difficult to obtain reproducible results from this measurement. 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 25% (wt/wt) 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 [concentration] below the concentration of 10^{-4} M. A calibration curve of surface tension as a function of log [concentration] was therefore established prior to the adsorption measurements.

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

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

$$\frac{\Delta X_2}{m} = X_1 - X_2 \quad (2-9)$$

ΔX_2	Change in surfactant concentration after adsorption
X_1, X_2	concentration of surfactant before and after adsorption

FIGURE 2-13 ADSORPTION ISOTHERM, IGEAL 890 AND 990

Figure 2-14 shows the adsorption isotherm for the adsorption of non-ionic surfactants (Igepal 890 and 990) onto Elkhorn #3.

The plot shows three distinct regions of adsorption. This suggests that three different mechanisms of adsorption may be involved. In region I, the equilibrium concentration is very low, and thus the amount of surfactant 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 is likely to lie parallel to the surface of the coal [37,38,39].

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 [40,41]. 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.

2.6 Heats of Adsorption (Immersion)

In the original proposal, it was proposed to measure the heat of adsorption of ammonia gas by the coal particles in order to help determine the underlying energetics of molecular interactions at the coal interface. Thus, a literature search was made to find out whether heats of adsorption or heats of immersion have been related to the hydrophobicity of the coal surface and hence the stability of coal-water slurry. Most of the heat of information reported in the literature, have been related to the spontaneous heating and swelling of the coal samples [42,43,44]. Thus, it seemed desirable to measure not only the heats of adsorption of ammonia on the coal, but also the heat of immersion of the coal particles in various dispersant solutions and relate the data to the rheology of the coal-water slurry.

The heat of immersion measurements of the coal samples were conducted in an adiabatic solution calorimeter (Parr Instrument Company, 211 Fifty-Third Street, Moline, Illinois 61265). The Parr 1451 is a multi-purpose calorimeter especially suited for enthalpy changes which occur in solutions between 20° C and 29°C, including heats of wetting. Endothermic and exothermic enthalpy changes can be measured over a range of 2 to 1000 calories at a detectability limit of less than 0.2 calories and the temperature resolution is 0.001 C.

The calorimeter equivalence was determined by measuring 100 mL of 0.1 M HCl into the calorimeter Dewar flask. Approximately 0.500 grams of Tris (Tris-hydroxymethyl-aminomethane) was added

to the sample cell and the rotating cell assembly was assembled for immersion into the 0.1 M HCl solution. Enough time was allowed for the sample and surrounding solution to come to thermal equilibrium. The push rod was depressed and the TRIS was dropped into the 0.1M HCl where the reaction was allowed to progress with stirring. A thermogram was recorded on a strip chart recorder. The energy equivalence was calculated from this thermogram.

The heat of immersion measurements were made by substituting coal in place of Tris and the dispersant solution in place of 0.1N HCl. The heats of immersion were produced from the thermograms.

Heats of Immersion Measurements

Heats of immersion measurements were made on the coal samples, (PSOC-1475, 1487, 1493 and 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 results obtained are shown in Figure 2-16. The plot shows that the heat of immersion decreases with increase in equilibrium moisture content. The heat of immersion data can also provide information on the hydrophilic nature of the coal surface.

Heat of Immersion as a Function of oxidation time:

Figure 2-17 shows 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

FIGURE 2-14 HEAT OF IMMERSION AS A FUNCTION OF EQUILIBRIUM MOISTURE

FIGURE 2-15 HEAT OF IMMERSION AS A FUNCTION OF OXIDATION TIME

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 (45) have observed that variations in coal properties due to oxidation of the coal surface and have explained this to 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

Five non ionic surfactants, Nonyl phenoxy poly (ethyleneoxy) ethanol, $[(C_2H_4O)_n C_{15}H_{24}O]$ (0.1% wt/v) 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 Figure 2-18. The plot shows that the heat of immersion decreases with increase in molecular weight of the non-ionic surfactant. Traube's rule [46] states that "The adsorption of organic substances from aqueous solutions increases strongly as we ascend the homologous series". Hansen and Craig [47] supported Traube's rule by showing an increasing adsorption of fatty acids from water as the hydrocarbon chain length increased. Therefore, it appears that

FIGURE 2-16 HEAT OF IMMERSION AS A FUNCTION OF MOLECULAR WEIGHT OF SURFACTANT

FIGURE 2-17 HEAT OF IMMERSION AS A FUNCTION OF PARTICLE SIZE

as the hydrophobicity of the hydrocarbon portion of the nonionic surfactant increases, its' expulsion from water increases, thus increasing the interaction of the surfactant with the coal. This suggests that the high molecular weight non ionic surfactants should be preferred wetting agents in coal-water slurry preparation.

Also, the heats of immersion measurements (Figure 2-19), do show that the heat of immersion decreases as the particle size decreases. This is an indication that a decrease in the particle size increase the degree of wetting.

SECTION III

COAL CHARACTERISTICS AND SLURRY QUALITY:

The primary goal was to determine those coal properties which most directly impact on the quality of CWS. In this way, an understanding, which will allow a general relationship between coal properties and the coal content of a given coal-water slurry to be established, can be gained. In order to correlate the relevant coal properties with the coal content, the interaction relation between coal properties (carbon, nitrogen, hydrogen, sulfur, oxygen contents, HG index, fixed carbon, particle size distribution and hydrophobicity index) and the capacity to prepare good quality slurry were examined using multivariate analysis [48,49,50].

Data Collection and Analysis

Data on coal properties and stability/rheology of various coal-water slurries were collected from selected literature [51,52,53,54,55]. The coal-water slurries were normalized to slurries containing more than 60% coal content. The operating variables considered in this study were : carbon, nitrogen, hydrogen, sulfur, oxygen content, HG index, fixed carbon, ash, moisture, particle size distribution and hydrophobicity index. The difference between the sums of hydrogen (H), carbon (C), sulfur (S) and oxygen (O), nitrogen (N), moisture (M), ash (A) were determined for each coal and assigned as the hydrophobicity index.

The coal properties were selected by how much each

individual property affected the percentage of the total variation, R^2 . This was done by regressing all the independent coal properties on the coal content, and removing the variables one at a time to examine their effect on the R^2 value. The predicted relationship was determined from the variables which influenced the R^2 significantly. Table 3-1 lists the coefficients of the independent variables with the coal Content. From the correlation of the independent variables and the dependent variable, coal content, the HG Index, C/O, FC/VM, and the moisture are highly correlated. The plots of these variables with the coal content are shown in Figures 3-1 through 3-6.

The correlation matrix of these variables and the coal content are as shown in Table 3-2, and The R-square values are listed in Table 3-3.

From the R- square values, regression on HG index, FC/VM, C/O and moisture provides the best fit with an R-square value of 0.8455. The regression equation established is of the form:

$$CC = 64.195 - 0.099 * \text{moisture} - 0.067 * \text{Ash} + 0.031 * \text{C/O} + 0.590 * \text{FC/VM} - 0.046 * \text{Hydrophobicity} + 0.095 \text{ HGI.} \quad (3-1)$$

The standard error of prediction was calculated to be 7.73. This equation was therefore used to find the optimal value of the coal-water slurry solids loading of the coals used in this study.

Figure 3-7 is a surface response plot of the effect of moisture and C/O on CWS. The plot shows that the coal content decreases with increase in the moisture content.

Table 3-1

VARIABLE	REGRESSION COEFFICIENT
Ash	0.5489
Sulfur	0.0203
FC/VM	0.6880
Hydrogen	-0.3754
Nitrogen	0.3442
HG Index	0.8154
C/O	0.7362
Moisture	-0.7396

Table 3-2

CORRELATION MATRIX OF SIGNIFICANT VARIABLES.

	HG Index	C/O	Moisture	FC/VM	Slurry
HG index	1.0000				
C/O	0.66023	1.0000			
Moisture	0.63785	-0.72981	1.0000		
FC/VM	-0.57665	-0.72981	-0.53311	1.0000	
Slurry	0.81550	0.73622	0.74073	1.0000	

TABLE 3-3

**INDEPENDENT REGRESSION VARIABLES AND CORRESPONDING R-SQUARE
VALUES FOR THE REGRESSION.**

Variables in Regression	R-Square
HG index, FC/VM, C/O. Moisture	0.7455
HG index, FC/VM, C/O	0.7422
HG index, FC/VM, moisture	0.7689
HG index, C/O, Moisture	0.7462
FC/VM, C/O, Moisture	0.5779
HG index, FM/VM	0.7220
HG index, C/O	0.6052
HG index, moisture	0.6459
FC/VM, C/O	0.5695
C/O, Moisture	0.5419
HG index	0.6650
FC/VM	0.4734
C/O	0.5421
Moisture	0.5470

FIGURE 3-1 COAL CONTENT VS. MOISTURE CONTENT

FIGURE 3-2 COAL CONTENT VS. C/O RATIO

FIGURE 3-3 COAL CONTENT VS FC/VM RATIO

FIGURE 3-4 COAL CONTENT VS. FLOATABLE MATTER (CALCULATED)

FIGURE 3-5 COAL CONTENT VS. HARDGROVE GRINDABILITY INDEX

FIGURE 3-6 COAL CONTENT VS. ASH CONTENT

FIGURE 3-7 SURFACE RESPONSE OF COAL CONTENT AS A FUNCTION OF MOISTURE AND C/O RATIO

SECTION IV

SLURRY PREPARATION AND RHEOLOGICAL CHARACTERIZATION

4.1 Table 4-1 shows the proximate and ultimate analysis of the coal samples used initially in this study. Also listed in this table are the predicted coal content calculated from equation 3-1. The coal-water slurries utilized in this study, had the following general specifications:

- * 52-71% by weight of coal depending on Coal type
Additive type
- * Packing of the coal particles
99% through 80 mesh and 100% less than 50 mesh
- * Less than 2% increase in solids content measured at the bottom of a settling column after 24 hours
- * Power Law index of less than 1.3
- * 0.3% Concentration of the Additive based on coal weight.
pH of 10.

The analysis of the flow properties of the CWS was conducted in the laboratory by :

- * Measuring the viscosity as a function of shear rate
- * Viscosity as a function of time
- * Viscosity as a function of pH
- * Viscosity as a function of Additive concentration
- * Viscosity as a function of additive type
- * Viscosity as a function of Packing concentration
- * Viscosity as a function of temperature

FIGURE 4-1 PERCENT SIZE UNDER VS. PARTICLE SIZE

* Stability as a function of time

4.2 Coal Sample Preparation

The coal samples were ground to a typical distribution as shown in Figure 4-1 and carefully screened to obtain size fractions of: -400 mesh, +400/-325 mesh, +325/-270 mesh, +270/-200 mesh and +200/-100 mesh using standard U.S sieve screens. Blended distributions of these particle size fractions were formulated and the particle size distributions measured, using a Microtrac Particle Size Analyzer, Model 2600. Typical particle size distributions obtained are as shown in Table 4-2 and Figures 4-2 through 4-5.

4.3 Determination of Packing Concentration

It has been established that highly loaded mixtures can be achieved by blending particles of various sizes in appropriate fractions [13]. It has also been mentioned earlier that the coal content of CWS can be predicted from equation 3-1. This equation does not however take into consideration the particle size distribution. In order for the predictive relationship to be significant, it was found necessary to examine the influence of the particle size distribution.

One of the most important parameters influencing the viscosity of CWS is the particle size distribution [56,5758]. In a mixture formed of a broad distribution of particles, the void space between densely-packed coarse particles will be filled by the fluid and fine particles which will act together as a lubricant between the coarse particles [56]. This effect is very

Table 4-1

Proximate and Ultimate Analyses of the Coal Samples

	PSOC-1494	PSOC-1487	PSOC-1493	PSOC-1475
	Kentucky #9	Adaville#1	Illinois#6	Elkhorn#3
Proximate				
<u>Analysis</u>				
% Moisture	7.12	18.99	9.43	3.37
% Ash	10.97	4.55	13.74	3.22
% Volatile	35.77	34.67	34.34	36.03
% Fixed Carbon	46.14	41.78	42.50	57.38
<u>ULTIMATE ANALYSIS</u>				
% Ash	10.97	4.55	13.74	3.22
% Carbon	65.32	57.96	59.98	78.38
% Hydrogen	3.98	4.09	3.74	5.20
% Nitrogen	1.14	0.84	1.15	1.44
% Total Sulfur	4.50	1.06	4.51	0.95
% Oxygen	6.97	12.50	7.41	7.45
C/O	9.37	4.64	8.09	10.45
FC/VM	1.29	1.21	1.24	1.59
Flotability	47.61	26.01	33.14	68.10
HG Index	72.0	61.1	62.2	58.70
Free Swell.Index	5.0	0.0	3.0	5.0
Predicted				
Coal Content	68.4	56.85	67.7	67.4

Table 4-2

Particle Size Distributions

	PSOC-1494	PSOC-1487	PSOC-1493	PSOC-475
	Kentucky #9	Adaville#1	Illinois#6	Elkhorn#3
Size				
(Microns)				
564	100	100	100	100
261.6	87.1	100	97	99.9
160.1	65.7	100	71.4	88.6
112.8	65.7	99.8	57.4	81.0
84.8	65.7	93.8	51.4	74.5
64.6	49.4	88.8	48.2	68.2
50.2	46.6	78.2	42.7	61.3
39.0	43.8	66.0	38.0	55.1
30.3	36.3	55.7	34.6	49.6
23.7	32.5	47.9	31.4	45.0
18.5	31.0	41.7	28.3	41.1
14.5	29.1	31.3	23.8	31.3
11.4	24.7	22.6	18.1	22.6
9.1	19.0	18.6	14.2	18.6
7.2	16.4	15.2	10.8	15.2
5.8	9.2	9.5	6.5	10.1
Packing				
Concentrations:	82.6	72.1	80.1	78.5

important in the resulting viscosity of the mixture, because excess of coarse particles may create an unstable suspension.

Flow properties of mixtures will also be affected by the shape of particles, such that the greater deviation from a uniform spherical shape the larger the viscosity will be. An important parameter which is closely related to the particle size distribution is the maximum packing of solids.

An analytical method developed by Lee [57] proposed calculation of the packing of n-component mixtures, whose compositions were assumed to be independent of the size ratio of the spherical particles. This assumption was improved subsequently by Patton [58] through the use of a parameter whose value varies with the size ratio. The equation derived by Patton is given by:

$$(\phi_m)_i = \sum_{j=1}^{nf} \sum_{i=1}^{nf} \Phi_{ij} \phi_j$$

where nf is the number of size fractions, ϕ_j refer to the respective volume fractions, $\phi_{ii} = \phi_{jj} = 0.639$ and Φ_{ij} represent the coefficients to be used in relating a larger particle group to a smaller one and vice versa. The following expression was developed for these coefficients:

$$\Phi_{ij} = 0.639 + \left[\frac{(\phi_{mo} - 0.639)}{1.15 - 1.017\phi_{mo}} \right]$$

FIGURE 4-2

PARTICLE SIZE DISTRIBUTION (-200 MESH)

FIGURE 4-3
PARTICLE SIZE DISTRIBUTION
(-325 MESH)

FIGURE 4-4

PARTICLE SIZE DISTRIBUTION (-200/270 MESH)

FIGURE 4-5

PARTICLE SIZE DISTRIBUTION (-80 MESH)

*where, ϕ_{mo} is the maximum packing concentration for binary mixtures.

In Equation (4-2), positive sign applies when a coarse size fraction is blended with a finer size fraction, and the negative size applies otherwise.

The maximum packing concentrations calculated for a number of blended distributions using a program developed at the Adelphi Center for Energy Studies based on equation 4-2 algorithm is as shown in Table 4-3. The packing concentrations calculated increased with an increase in the number of fines (-325 mesh) to a value of 40 % fines by weight. Above a value of 40% fines, the packing concentration decreased.

4.4 Rheological Testing

A Haake RV-20 concentric cylinder viscometer and an Extrusion Rheometer were used to determine the rheological properties of the CWS at low and high shear rates. In The RV-20, the slurry is sheared in the annular gap between a rotating bob and a stationary cup. The torque necessary to rotate the bob at a given speed is measured by a torsion spring. The drive unit consists of a driving motor, a tachometer-generator, and a reduction gear. The stator is surrounded by a temperature tempering vessel (enclosed in a steel container to prevent moisture loss) connected with a constant temperature bath. The temperature can be controlled to $\pm 0.01^{\circ}\text{C}$.

The viscometer is integrated with an IBM ps/2 data acquisition and analysis system. The signals from the viscometer

Table 4-3

Weight Fractions And Packing Concentrations

WT %>200 MESH	WT% -200/325 MESH	WT %<325 MESH	PACKING CONCENTRATION
53.7%	8.5%	37.8%	83.4%
47.7%	9.4%	42.9%	83.1%
41.7%	9.0%	49.3%	83.6%
43.6%	9.4%	47.0%	76.4%
53%	8.3%	39.7%	85.3%
36.2%	15.4%	48.4%	72.1%
26.5%	18.1%	55.4%	73.4%
9.6%	15.6%	74.8%	69.6%
58.1%	2.2%	39.7%	85.2%

is monitored twice per second and converted to torque and rotational speed values. Viscosity as a function of shear rate was computed using one of the following flow models:

$$\tau = \tau_0 + \mu_p \dot{\gamma} \quad (\text{Bingham law}) \quad (4-3)$$

$$\tau = K \dot{\gamma}^n \quad (\text{Power law}) \quad (4-4)$$

$$\tau = \tau_0 + K \dot{\gamma}^n \quad (\text{H.-Bulkley law}) \quad (4-5)$$

Where:

τ_0 is the yield value

K is the flow consistency number

n is the flow behavior index.

n = 1 for a Newtonian flow

< for a pseudoplastic material

and > for a dilatant material.

Figure 4-6 shows a typical flow curve for a CWS formulated at 65% solids (Elkhorn #3) content generated in this viscometer. The shear rate, to which the sample was subjected, was continuously increased from zero to a maximum determined by the viscosity of the CWS (curve 1). Curve 2 decreased to zero, curve 3 increased to a maximum, and curve 4 decreased to zero. The viscosity measurements were taken from curve 3, which represents the fluid after it has been sheared and its structure broken down.

4.5 Effect of Surfactant Concentration on the Viscosities of the Slurries

Figure 4-7 shows a variation of the viscosity measured as a function of surfactant concentration. There was a gradual decrease in the viscosity as the surfactant concentration was

FIGURE 4-6 TYPICAL CWS VISCOMETER FLOW CURVE

FIGURE 4-7 VISCOSITY VS. SURFACTANT CONCENTRATION

FIGURE 4-8 VISCOSITY VS. PH

increased. Beyond a concentration level of 0.25% (wt/wt) of surfactant, there was no marked difference in the viscosity values obtained. Thus, a concentration level of 0.3% (wt/wt) was used in all measurements.

4.6 Viscosity as a Function of pH

Figure 4-8 shows a plot of the variation of viscosity as a function of pH. Zeta Potential measurements (Figures 2-8 through 2-11) indicate that better electrokinetic response is attained above a pH of 10. The viscosity measurements show that there is levelling effect above a pH of 8. Thus all subsequent rheological measurements were performed above a pH of 8.

4.7 Types of Additives:

Tables 4-4 through 4-7, lists the measured rheological properties of the CWS prepared from the four parent coals listed in Table 4-1. The slurries were prepared using various additives. Figures 4-9 is a plot of apparent viscosity as a function of the molecular weights of the non-ionic surfactants used. Among the Igepal series (610-990), the Igepal 990 provided the lowest viscosity. The values obtained are comparable to those obtained using the ammonium sulphonates (A-23, A-23-s), sodium polyanthene and naphthalene sulfonates. The maximum amount of solids attainable with Igepal 990 used as an additive, is less than those obtained using the anionic additives and more than that obtained using the cationic additive (CTAB). Based on preliminary studies, it was noted that the slurries containing cationic dispersants gave poor stability. Thus, all subsequent studies

FIGURE 4-9 : VISCOSITY VS. MOLECULAR WEIGHT OF ADDITIVES

FIGURE 4-10 VISCOMETER FLOW CURVE OF CWS IN DIFFERENT ADDITIVES

Table 4-4

Rheological Properties of Elkhorn #3 (pH=10)

Additive	Coal Content	η_{100}	n	τ_0	R^2	Φ_{max}
0.25%						
Igepal 610	63%	557	0.714	250	0.9912	78.5
0.25%						
Igepal 720	63%	460	0.882	150	0.9967	78.5
0.25%						
Igepal 890	63%	305	1.11	90	0.9987	78.5
0.25%						
Igepal 990	63%	224	1.067	30	0.9996	78.5
0% Additive	63%	448	0.775	150	0.9924	78.5
0.25% A-23	63%	236	0.991	0	0.9989	78.5
0.25% A-23-S	63%	213	0.991	0	0.9900	78.5
0.25% sodium polyanthene sulfonate	63%	198	0.9924	0	0.9986	78.5
0.25% sodium naphthalene sulfonate	63%	235	0.986	0	0.9966	78.5
0.25% Armogard 6000	63%	292	0.888	35	0.9912	78.5
0.25% Lignin Sulfonate	63%	264	1.023	25	0.9896	78.5
0.25% Nopcosperse	63%	225	0.881	25	0.9803	78.5

Table 4-5
Rheological Properties of Kentucky #9

	η_{100}	n	τ_0	R^2	
0.25% Igepal 990					
in 64 % Slurry	252	0.741	80	0.9995	10
0.25% Igepal 990					
in 62 % Slurry	234	0.916	90	0.9984	10
0.25% Igepal 990					
in 60% Slurry	165	0.992	70	0.9977	10
0.25% Igepal 990					
in 59% Slurry	121	0.900	30	0.9976	10
61% Slurry					
(No additive)	289	0.948	225	0.9946	10
0.25% A-23					
in 61% slurry	286	0.784	100	0.9988	8.65
0.25% Igepal 990					
in 56% Slurry	95	1.150	35	0.9940	10
0.25% A-23					
in 64% Slurry	324	0.661	90	0.9982	10
64% Slurry					
(No Additive)	485	1.045	220	0.9953	10

Table 4-6

Rheological Properties of Adaville #1

Description of	η_{100}	n	τ_0	R^2	pH	
<u>Slurry</u>						
61% Slurry						
(No Additive)	587	0.714	20	0.9996	10	
0.25% Igepal 990						
in 66% Slurry	680	0.778	235	0.9886	10	0.25%
Igepal 990						
65% Slurry	414	1.042	30	0.9996	10	
0.25% Igepal 990						
in 61% Slurry	236	1.009	45	0.9980	10	
0.25% Igepal 990						
in 64% Slurry	325	0.851	30	0.9990	10	
0.25% Igepal 990						
in 60 % Slurry	158	0.921	20	0.9990	10	
0.25 % Igepal 990						
in 63% Slurry	292	0.941	0	0.9965	10	
62% Slurry						
(No Additive)	364	1.026	45	0.9984	10	
60% Slurry						
(No Additive)	194	1.017	15	0.9991	10	
0.25% A-23						
in 65% Slurry	337	1.025	15	0.991	10	

Table 4-7

Rheological Properties of Illinois #6

Description of	η_{100}	n	τ_0	R^2	pH
Slurry					
0.25% A-23					
in 60% Slurry	180	0.973	20	0.9989	10
0.25% A-23S					
in 58% Slurry	110	1.160	50	0.9954	10
0.75% Lig. Sulfate					
in 64% Slurry	314	1.249	80	0.9987	10
0.25% A-23 in					
63% Slurry	438	0.700	25	0.9994	10
0.25 A-23S in					
64% Slurry	186	1.202	100	0.9967	10
0.25% Igepal 990					
in 63% Slurry	450	1.212	180	0.9881	10
0.25% Igepal 990					
in 61% Slurry	291	0.981	75	0.9960	10
0.25% Igepal 990					
60% Slurry	212	0.881	45	0.9886	10
0.25% Igepal 990					
in 59 % Slurry	186	1.075	55	0.9866	10
0.25% Igepal 990					
in 58% Slurry	154	1.012	30	0.9920	10
0.25 % Igepal 990					
in 57% Slurry	127	1.032	65	0.9951	10

were performed using a non-ionic or anionic dispersant.

Figure 4-10 shows the flow behavior of 63% CWS in various additives. The CWS exhibits a newtonian behavior when Daxad 19 is used as an additive. All the other additives impart a pseudoplastic flow behavior to the CWS. The CWS prepared with CTAB, however, exhibits a dilatant behavior at high shear rates and has a high yield point.

The adsorption studies show that compared to Igepal 890, Igepal 990 is strongly adsorbed on the coal surface. The strength of adsorption of the higher molecular weight Igepal and its ability to produce lower viscosity slurries, show that the higher molecular weight additives are much more effective in producing low viscosity CWS.

4.8 Effect of Particle Size Distribution on Rheology of CWS.

Figure 4-11 shows the effect of particle size distribution on the flow behavior of the slurries. Table 4-8 lists the rheological data evaluated from these flow curves. The particle size distribution was formulated according to the information contained in Table 4-8, and all the slurries contained 65% solids content and 0.3% A-23 dispersant.

Rheological analysis of the flow curves show that the flow behavior changed from dilatant to pseudoplastic as the packing concentration increased. Also, the viscosity was found to decrease with increase in the packing concentrations of the slurries. This is an indication that a wider distribution is indeed necessary for more efficient packing.

FIGURE 4-11 VISCOMETER FLOW CURVE OF CWS WITH VARYING PACKING CONCENTRATIONS

Table 4-8
Rheological Properties Of 65% (PSOC-1475) CWS
With Varying Packing Concentrations.

PACKING	n	τ_0	K	R^2	η_{100} (mPas)
69.6	1.036	3.25	0.276	0.99	335
72.1	0.970	2.01	0.340	0.97	320
73.4	0.907	1.76	0.322	0.98	301
76.4	0.884	4.10	0.827	0.97	248

Table 4-9
Rheological Properties of 63% CWS of The Four Parent Coals:
PSOC-1475, 1494, 1493 and 1487.

Sample	n	τ_0	K	R^2	η_{100} (mPas)
1494	0.680	24.0	0.676	0.86	445
1493	0.729	11.3	1.42	0.98	527
1487	0.913	0.250	0.879	0.93	293
1475	0.916	0.082	0.238	0.99	180

4.9 Coal Content and Viscosity

Figure 4-12 shows the variation of the coal content as a function of viscosity measured at η_{100} , and the rheological properties are listed in Tables 4-4 through 4-7. The plot shows that the Elkhorn #3 provides the best slurry quality and Illinois # 6 gave the poorest slurry quality. The rheological behavior is similar to that of Kentucky #9. The heat of immersion data (Figure 2-17) coupled with the ESCA and FTIR measurements, show that Elkhorn # 3 is more hydrophobic than Illinois #6. The evaluation of the effect of coal properties on the slurry quality (chapter 3) indicates that the moisture content correlates well with the slurry quality. The hydrophilicity of the coal sample reduces the tendency of the hydrocarbon tail of the dispersant to be adsorbed on the coal surface and thus, reduces the efficiency of the dispersant.

Figure 4-13 is a plot of apparent viscosity as a function of coal content prepared with various additives. The plot shows that MCG-23ALS impacts low viscosities to the slurries and that A-23 and A-23S have an identical effect on the CWS.

4.10 Effect of Shear Rate on Flow Behavior

Figure 4-14 is the flow behavior of 63% solids loading of the four coals listed in Table 4-1. Their rheological properties are listed in Table 4-10. All the samples exhibit a pseudoplastic behavior with yield at this slurry concentration. PSOC-1493 and 1494 however, have higher yield values and viscosities relative to PSOC-1487 and 1475.

FIGURE 4-12 VISCOMETER FLOW BEHAVIOR OF 63% CWS OF (PSOC-1475,
1487, 1493, AND 1494)

FIGURE 4-13 APPARENT VISCOSITY VS. COAL SLURRY COAL CONTENT

FIGURE 4-14 APPARENT VISCOSITY VS. COAL SLURRY CONTENT IN DIFFERENT ADDITIVES

The predictive relationship developed in this study, indicate that the C/O ratio and the moisture content affect the slurry quality and behavior. Also, the acidic functional groups on the coal surface have an adverse effect on the electrokinetic behavior of the slurry [12,14,29]. ESCA analysis of these samples show a higher degree of carboxylic functional groups on PSOC-1494 and 1493 relative to PSOC-1475 and 1487. The differences in the flow patterns observed are thus due to a combination of these properties.

High shear Rheology of 65% solids content of PSOC-1475 was determined using an Extrusion Rheometer. This device determines the apparent viscosity of the slurry under flowing conditions. The CWS volume flow rate, Q , and pressure drop, ΔP , were measured for laminar flow through a tube of Length, L , and radius, R . The shear stress, τ_p , and the shear rate, $\dot{\gamma}$, were obtained from the pipeline flow data as follows:

The shear stress at the pipe wall, τ_p , can be defined as:

$$\tau_p = \frac{R}{2} \left(\frac{\Delta P}{L} \right) \quad (4-4)$$

against a pipe flow characteristic, Γ , given by:

$$\Gamma = \frac{4}{\pi R^3} (Q) \quad (4-5)$$

where $\Delta P/L$ is the pressure gradient along the tube of length, L

Q is the volumetric flow

and R is the tube inside radius.

Γ relates to $\dot{\gamma}$ through the Rabinowitsch-Mooney relation [62]:

$$\dot{\gamma}_p = (1/4)\Gamma[(3+(d \ln \Gamma / d \ln \tau_p)] \quad (4-6)$$

The apparent viscosity of the suspension then is given by

$$\eta = \tau_p / \dot{\gamma}_p \quad (4-7)$$

The data obtained from the Extrusion Rheometer are shown in Table 4-11. Figure 4-15 is the rheogram generated from this data. Rheological analysis shows that the rheogram can be described by the relation:

$$\tau = 1.4 + 0.84 (\dot{\gamma})^{0.96} \quad (4-8)$$

The apparent viscosities of the slurry as a function of shear rate are listed in Table 4-12. There is a decrease in viscosity with an increase in shear rate to a value of 4000 s^{-1} due to the existence of yield stresses, but the viscosity remains fairly constant after a shear rate of 4000 s^{-1} .

4.11 Effect of Temperature

The viscosity as a function of shear rate was measured at 20, 30, and 50°C or a maximum temperature tolerated by the CWS. From these tests, the effect of temperature on the Newtonian behavior of each CWS was determined. The variation of viscosity of 67% solids of PSOC-1475 as a function of temperature is shown in Figure 4-16. The viscosity of CWS was found to decrease with increase in temperature between 19°C and 50°C . However, with Igepal 990 as an additive, there was an increase in viscosity between 45°C and 60°C . It is apparent that the flow behavior of the slurry in the low temperature range is governed by the behavior of water. Above 45°C , the flow behavior is dependent on

Table 4-10

Extrusion Rheometer Flow Data.

Weight of Slurry/s	Pressure (psig)	Shear Rate(s^{-1})	Shear Stress(mPa)	Viscosity mPa.s
1.6195	10	1181	7860	665
2.55	20	1866	15721	642
5.4995	30	4008	23581	588
7.3921	40	5391	31441	583
9.999	50	7292	39302	539
11.615	60	8471	47162	557
14.237	70	10383	55022	530
15.4417	80	11262	62882	558
17.4041	90	12692	70743	557
20.2955	100	14801	78603	531

FIGURE 4-15 TYPICAL HIGH SHEAR FLOW BEHAVIOR OF CWS

the additive. The change in flow behavior can be caused by changes in the solubility behavior or changes in the interaction of the additive with the coal particles at higher temperatures [46]. This may explain the increase in viscosity with increase in temperature when Igepal 990 was used as a dispersant.

4-12 Stability

Experiments were performed to study the static stability of the coal slurries. 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 6ft in height and 3 inches in diameter. This had three ports from which coal samples could be drawn and the coal content at each level determined. The variation of coal content at the three ports are as shown in Figure 4-17.

The slurry samples were maintained in the cylinders for an initial period of 35 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. Elkhorn # showed good stability at a solids concentration of 66%. Above this concentration level, a hard pack solid formed after 3 days. The slurries prepared from the other coals; Illinois #6, Kentucky #9 and Adaville #1, were stable only at concentration levels up to 62% solids concentration.

Also, a method which is based on measurement of the low-shear rheology of the slurry was used [63]. Slurries that exhibited poor stability had viscometer flow behaviors identical to that shown in Figure 4-18.

FIGURE 4-16 VISCOSITY VS. TEMPERATURE

FIGURE 4-17 CWS STABILITY- COAL WEIGHT VS. TIME

FIGURE 4-18 VISCOMETER FLOW BEHAVIOR OF UNSTABLE CWS
 TEST #: 1493-5
 RHEOLOGY DETERMINATION
 FUEL: 0.75% LIG. SULFATE IN 64% SLURRY FH=9.5

TEMPERATURE: 20
 MEASURING SYSTEM: MV11150
 INSTRUMENT CONSTANTS:
 $R1 = 1.511$ $R2 = 2.097$
 $L1 = 6.007$
 ACCELERATION: 200 rpm/min

CURVE #1 _____
 CURVE #2
 CURVE #3 _____
 CURVE #4 _____

SECTION V

VERIFICATION OF PREDICTIVE RELATIONSHIP

5.1 The concept, methodologies and formulations developed in described in the preceding sections were tested with further experiments on three additional coal samples. The three coal samples: Middle Kittaning, (PSOC-1339), Upper Freeport, (PSOC-1527), and Pittsburgh, (PSOC-1531) were selected and further experiments performed to test the validity of the model proposed. The proximate and ultimate analyses of these coals are as listed in Table 5-1. Also listed in Table 5-1 are the expected coal content calculated, using equation 3-1. The samples were both dry and wet ground.

5.2 Coal Analyses

FTIR, ESCA and Zeta Potential measurements were performed on these samples. The FTIR spectra obtained are as shown in Figures 5-1 through 5-3- and the ESCA values for the coal samples are listed in Table 5-2. The Zeta Potential, Heats of Immersion and natural pH measured values are also listed in Table 5-2.

5.3 The predictive model developed in chapter 3, does not include the effect of the packing concentration of the coal particles. The experiment described in section 4.8 shows that the particle size distribution does indeed govern the behavior of the slurry. Thus, to minimize the effect of the particle size distribution, the coal samples were ground to a distribution as shown in Table 5-2 and again, carefully screened to obtain size fractions of: -400 mesh, +400/-325 mesh, +325/-270 mesh, +270/-

Table F-1

	PSOC-1339	PSOC-1527	PSOC-1531
	M. Kittaning	Upper Freeport	Pittsburgh
Proximate			
<u>Analysis</u>			
% Moisture	0.80	0.46	1.65
% Ash	19.50	27.52	6.29
% Volatile	18.09	23.14	36.98
% Fixed Carbon	61.60	46.10	55.08
<u>ULTIMATE ANALYSIS</u>			
% Ash	19.50	27.52	6.29
% Carbon	71.65	60.66	78.05
% Hydrogen	3.77	3.59	4.88
% Nitrogen	1.12	1.11	1.51
% Total Sulfur	0.49	0.83	1.38
% Oxygen	3.31	4.97	7.87
C/O	21.65	12.21	9.92
FC/VM	3.41	1.93	1.49
Flotability	51.18	31.02	66.99
HG Index	63	78	60
Free Swell.Index			
Predicted			
Coal Content	69.12	69.84	67.42

Table 5-2

Percentage of Different Functional Groups at The Surface of the
Three Coal Samples: PSOC-1339, 1527, 1531.

Coal Sample	<u>%C=C, C-C</u>	<u>% C-O</u>	<u>% C=O</u>	<u>% C=O</u>
PSOC 1339	77.4	19.1	1.4	2.1
PSOC 1527	83.3	14.0	1.2	1.5
PSOC 1531	84.9	11.1	2.3	1.8

FIGURE 5-1. FTIR SPECTRA OF MIDDLE KITTANING (AS RECEIVED)

FIGURE 5-2 FTIR SPECTRA OF UPPER FREEPORT (AS RECEIVED)

FIGURE 5-3 FTIR SPECTRA OF PITTSBURGH (AS RECEIVED)

200 mesh, +200/-140, and +140/80 mesh using standard U.S sieve screens. Several blended distributions of these particle size fractions were formulated in order to attain an expected packing concentration of greater than 80.

Earlier calculations show that particle size distribution as shown in Table 5-3 will result in a packing efficiency of 85.

Weight fractions that will result in a packing concentration of 85 were blended and used in all subsequent slurry preparations. Thus, by standardizing the particle size distribution for all the coal samples, the dominant effect of the particle size distribution on the coal-water slurry was removed. This allowed the effects of the various coal properties to be recognized.

The rheological measurements and stability measurements were performed using procedures described in section 4.4. The results obtained are as shown in Figure 5-4 and the experimental coal content obtained are listed in Table 5-4.

Table 5-1 also lists the expected coal content expected from these coals. The experimental $\phi_{\max}$ determined for PSOC-1527 and PSOC-1339 are in agreement with ϕ_{expected} . The $\phi_{\max}$ for PSOC-1531 is however, lower than expected.

Effect of Additive Type

The following additives were also evaluated for their effectiveness in this test program:

1. Coal master A-23-S, Diamond Shamrock Chemical Co., Anionic high molecular weight condensed polynuclear hydrocarbon.
2. PC-876, West Vaco Chemical Co., ammonium lignosulfonate.

Table 5-3

Particle Size Distribution Desired.	
Sieve Size (microns)	% Retained
450	0.0
300	17.0
212	13.0
150	11.0
106	10.0
75	8.0
63	4.0
53	3.0
45	4.0
<45	30.0

$\phi(\max) = 85.6$ ---

3. Combination of A-23-S and PC-876.
4. Lomar D from Diamond Shamrock
5. MCG-23A-LS from Morrison chemicals group
6. Daxad 19 from Grace corporation
7. Igepal 990 from Gaf corporation
8. A-23 from Henkel Corporation

The selection and dosage rates were determined from earlier studies in this program. The additives were combined with the optimum amount of NH_4OH to a pH level as determined from zeta potential measurements of the coals in these additives.

All the CWS at 65% solids showed good stability for a period 5 days when a combination of 1:1 sodium polyanthrene sulfonate and MCG-23A-LS, A-23 and Lomar D or A-23 and Daxad 19 were used as additives. The flow curves generated from the Haake viscometer using these formulated additives, had low yield points in comparison with those obtained using the pure additives. All the CWS prepared with CTAB or CTAB in combination with the additives listed above, showed very poor stability with time. Slurries prepared with 1:1 combination of either; MCG, A-23, A-23S with Daxad 19 produced lower viscosities at a shear rate of η_{100} compared to those containing either of the pure additives.

Figure 5-5 is a plot of the apparent viscosity of CWS prepared from PSOC-1531 in different additives as a function of the coal content. The plot shows that MCG-23A-LS impacts lower viscosity to the slurries. The viscosities measured using the cationic additive, (CTAB), were higher than those obtained using

FIGURE 5-4 APPARENT VISCOSITY VS. COAL SLURRY COAL CONTENT

Table 5-4.

Rheological Properties of PSOC 1339 Middle Kittanning

Coal Content	Power Index n	Yield Point τ_0	η_{100}	Flow Const. # (k)	Additive	pH
55%	0.62	7.0	230	0.82	N	10
59%	0.81	9.22	447	1.95	N	5
59%	0.59	5.57	379	1.60	N	10
66%	0.97	1.20	152	0.14	B	10
67%	0.88	1.2	321	1.3	B	10
67%	1.44	0.8	1372	2.6	N	10
67%	1.05	11.2	635	0.80	I	10
67%	0.92	2.60	346	.43	A	10
73%	1.28	.04	653	.02	B	10
73%**	1.18	0.04	505	.30	B	10

Additives:

A---> A-23	Polynaphthalene Ammonium Sulphonate from Henkel Corp.
AS--> A-23S	Polynaphthalene Ammonium Sulphonate from Diamond Shamrock
B--> MCG-23A-LS	Polynaphthalene Ammonium Sulphonate from MCG corporation.
N--->	No Additive
I--->Igepal 990	Non-Ionic Detergent from GAF corporation.

Table 5-5.

Rheological Properties of PSOC 1527 Middle Kittanning

Coal Content	Power Index	Yield Point	η_{100}	Flow Const. #	Additive pH	
	n	τ_0		(k)		
56%	0.76	0.08	55	2.43	A	10
57%	0.64	2.36	93	0.34	A	10
60%	0.64	2.36	93	0.34	A	10
60%	0.50	40.70	514	1.23	N	10
63%	0.60	6.40	155	0.69	A	10
67%	0.94	15.40	293	0.22	AS	10
67%	0.84	28.60	328	0.13	B	10
67%	0.75	31.26	425	0.45	C	10
69%	0.66	45.91	809	1.96	A	10

Additives:

A---> A-23	Polynaphthalene Ammonium Sulphonate from Henkel Corp.
AS--> A-23S	Polynaphthalene Ammonium Sulphonate from Diamond Shamrock
B--> MCG-23A-LS	Polynaphthalene Ammonium Sulphonate from MCG corporation.
N--->	No Additive

Table 4-1.

the anionic dispersants. There was no significant difference in CWS viscosities prepared using either the dry or wet ground sample.

The rheological properties are as shown in Table 5-5. Also, rheological evaluations were undertaken minimizing the effect of pH, effect of additive type and concentration and the effect of optimum PSD on CWS rheology. Slurry quality was determined from the ratio of the maximum amount of coal which is present in a given CWS as determined experimentally, ϕ_{m-exp} , to the maximum theoretical amount obtainable as calculated from the particle size distribution, ϕ_{p-th} . This was compared with the coal content as calculated from the coal properties using equation 3-1. The slurry content at ($\phi_{exp}/\phi_{th}=86\%$) showed good fluidity and stability. Rheological analysis showed a pseudoplastic behavior. Above a value of ($\phi_{exp}/\phi_{th}=86\%$), the slurries became more dilatant.

The purpose of this verification was to ascertain the coal properties that affect the rheology/stability of coal water slurries. There are a number of experimental data reported in the literature on coal-water slurry suspensions [3-10]. However, depending on the objectives of those studies, various different parameters related to the behavior of the CWS were focussed on while neglecting other parameters. Only a few were found to contain the appropriate information needed in this study. Thus, the results of the relationship developed in section III, is not very significant. However, it revealed the coal properties that

Table 5-6

RHEOLOGICAL PROPERTIES OF CWS.

COAL SAMPLE PSOC-1531 ($\Phi_{th}=76.5\%$)

Additive	R^2	n	τ_0	K	$\frac{\Phi_{exp}}{\Phi_{th}}$	η_{100} (mPas)
0.15%MCG +0.15%A-23	1.00	0.89	13.41	0.56	86%	482
0.15%MCG + 0.15% A-23S	1.00	0.93	17.52	0.82	86.3	763
0.15%MCG + 0.15 % LGS	0.99	0.61	54.34	10.43	88.9	1365
0.15%MCG + 0.15%DXD	0.97	1.4	37.2	0.06	87.2	949
0.15%MCG + 0.15%SPS	0.97	0.92	0	1.18	92.3	635
0.15%MCG + 0.15%SPS	0.99	1.12	3.24	0.24	87.7	421
0.15%MCG + 0.15%CTAB	1.00	0.64	0	1.14	85.8	220
0.15%MCG + 0.15%LD	0.99	0.85	4.02	.35	86.1	214.6
0.15%A23 + 0.15A23S 0	0.98	0.39	0	3.76	85.7	223.1
0.15%A23 + 0.15%LS	1.00	0.7021	0	0.88	84.4	226.8
0.15%A23 + 0.15%CTAB	0.97	0.6472	0	0.76	85.6	147.9
0.15%A23 + 0.15%SPS	1.00	1.008	0	6.75	85.9	207.1
0.15%A23 + 0.15%DXD	1.00	1.048	2.12	0.138	86.6	183
0.15%A23 + 0.15%LD	0.99	1.173	0.69	0.886	88.1	183.5

RHEOLOGICAL PROPERTIES OF CWS.						
COAL SAMPLE PSOC-1531 ($\Phi_{th}=76.5\%$)						
Additive	R^2	n	τ_o	K	$\frac{\Phi_{exp}}{\Phi_{th}}$	η_{100} (mPas)
0.3% MCG	0.98	1.16	5.92	0.023	82.4	85.4
0.3% A23	0.98	1.04	3.44	0.067	78.95	92.7
0.3% A23-S	0.94	0.95	1.17	0.02	75.8	68.0
0.3% A23-S	1.00	0.87	13.54	0.58	86.9	467
0.15%A23 + 0.15%LD	0.98	1.2	4.39	0.0317	89.4	139.2

affect quality of CWS.

Thus, to gain further understanding, the interaction of the experimentally determined coal content in this program and their properties: FC/VM, C/O, Ash, Moisture, Hardgrove grindability index, and floatability were examined using multivariate analysis. The purpose was to implement the available physical properties of both the coal and the dispersant used in the formulations and determine the new relationship which will predict the coal content of the slurries consistent with the measured values.

Table 5-6 lists the coefficients of the independent variables considered, and the plots of these variables with the coal content are shown in Figures 5-4 through 5-9.

The correlation matrix of these variables and the CWS are as shown in Table 5-7, and The R-square values are listed in Table 5-8.

The regression equation obtained is of the form:

$$\begin{aligned} \text{CC} = & 190.91 - 5.34 * \text{moisture} - 4.83 * \text{Ash} + 1.68 * \text{C/O} + 3.54 * \text{FC/VM} \\ & - 2.28 * \text{Hydrophobicity} + 0.72 \text{ HGI.} \end{aligned} \quad (5-1)$$

The R^2 value was determined to be 0.9982 and the standard error of prediction was calculated to be 1.25 within 95% confidence level.

This equation is more significant than the equation developed in chapter 3. This stems from the fact that the data used in developing equation 3-1, were not obtained under homogeneous conditions. The packing concentrations and the

additives also varied. However, in developing equation 5-1, the effect of the particle size distribution was eliminated by using a blended distribution in which the packing efficiency was constant. Calculated CWS coal content agreed very well with the experimentally measured values.

The properties used in establishing this relationship between CWS were:

The moisture Content

Ash Content

C/O Ratio

FC/VM

Hydrophobicity

HG index

The correlation coefficients between these variables and CWS show that there is significant relationship between these variables and CWS. Also the plot in Figure 5-10 shows that the level of ash in the coal does not appear to impact on CWS preparation.

Table 5-7

VARIABLE	REGRESSION COEFFICIENT
Ash	0.4421
Sulfur	0.0203
FC/VM	0.8210
Hydrogen	-0.3754
Nitrogen	0.3442
HG Index	0.8234
C/O	0.1033
Moisture	-0.656

Table 5-8

CORRELATION MATRIX OF SIGNIFICANT VARIABLES.

	HG Index	C/O	Moisture	FC/VM	FL
HG index	1.0000	0.5412	-0.4810	0.6259	.4300
C/O	0.5412	1.000	-0.7130	0.6240	0.5410
Moisture	0.6385	-0.7281	1.000	-0.5671	0.3031
FC/VM	0.6259	0.6240	-0.53311	1.0000	.6447
FL	0.4300	0.5410	0.74073	1.0000	1.000
Ash	0.2080	0.5340	0.4811	0.6153	0.4300

TABLE 5-9

INDEPENDENT REGRESSION VARIABLES AND CORRESPONDING R-SQUARE
VALUES FOR THE REGRESSION.

Variables in Regression	R-Square
Moisture	0.4303
Moisture, Ash, C/O, FC/VM, Floatability, HG index	0.9982
FC, Floatability, C/O	0.6432
Moisture, Ash, C/O	0.556
Moisture, Ash, C/O, FC/VM	0.8892
Moisture, Ash, HG index, FC/VM	0.7193
Moisture, Ash, FC/VM, Floatability	0.7611
Moisture, Ash, Floatability	0.4462
Moisture, Ash, FC/VM	0.6700
Moisture, Ash, C/O	0.5562

FIGURE 5-5 COAL CONTENT VS. MOISTURE CONTENT

FIGURE 5-6 COAL CONTENT VS. C/O RATIO

FIGURE 5-7 COAL CONTENT VS. FC/VM RATIO

FIGURE 5-8 COAL CONTENT VS. FLOATABLE MATTER (CALCULATED)

FIGURE 5-9 COAL CONTENT VS. HARDGROVE GRINDABILITY INDEX

FIGURE 5-10 COAL CONTENT VS. ASH CONTENT

CONCLUSIONS

The results the study of the effect of coal properties on CWS, stability tests, rheology tests, heats of immersion , FTIR, ESCA, and electrokinetic studies have led to the following conclusions which relate to the preparation and use of CWS. These conclusions are:

- * The parent coals used to make the slurries determine the basic CWS properties
- * The heats of immersion study in the additives, show that heat of immersion data can be used to screen additives suitable for CWS preparation.
- * Heat of immersion of the coal particles as a function of particle size can give information on the degree of wetting of the coal particles
- * Adsorption studies show that, the high molecular weight additives are much more strongly adsorbed on the coal particles
- * FTIR and ESCA data were found to be valuable techniques in elucidating changes in the coal particle surface due to oxidation
- * Optimum particle size distribution can be determined experimentally which can result in maximizing the coal content in a given CWS.

- * An experimental technique of examining the influence of particle size distribution on the rheology of CWS, indicate a range of rheological behavior depending on particle size distribution. Solids with low packing efficiency have relatively high time-independent yield points and exhibit a dilatant flow behavior, whereas CWS having a high packing efficiency, exhibit a pseudoplastic flow behavior.
- * Chemical additives exert strong influence on the behavior of CWS. The anionic additives are much more suitable in CWS preparation compared to the cationic or non-ionic additives. The CWS prepared with cationic additives exhibited poor stability.
- * The CWS showed a newtonian behavior at high shear rates
- * Using Multivariate analysis, a statistical expression which relates the parent coal properties to the coal content in a given CWS has been established.
- * Test results using this expression shows that, the expression is very significant.
- * The behavior of CWS at high temperatures is dependent on the additive type. With Igepal 990 as an additive, the slurry viscosity increases with increase in temperature, whereas, with A-23 as a dispersant, the viscosity decreased with increase in temperature.
- * The coal treatment method (wet ground or dry ground) does not appear to affect the quality of the CWS.

RECOMMENDATIONS FOR FUTURE WORK

- * Continue to determine the effectiveness of the predictive model which has been established in this program.
- * Perform Rheological Analysis of the CWS over considerable shear and temperature range.
- * Formulate new methods of dispersing ultra fine coal particles in order to obtain high solids content with desirable fluidity.
- * Explore the atomization characteristics of the CWS in order to determine the atomization quality and practical significance.

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