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RHEOLOGICAL PROPERTIES ESSENTIAL FOR THE ATOMIZATION OF COAL WATER SLURRIES (CWS).

Quarterly Progress Report
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OVERALL OBJECTIVE:

The overall objective of this project is to perform experiments to understand the effect of high shear and extensional properties on the atomization of coal-water slurries (CWS). In the atomization studies, the mean drop size of the CWS sprays will be determined at various air-to CWS. A correlation between the extensional and high shear properties, particle size distributions and the atomization will be made in order to determine the influence of these parameters on the atomization of CWS.

Work Done

During the past quarter, further rheological testing of the CWS were performed. The CWS samples were prepared and stored in sealed containers for a period of three months before testing. The testing included low and high shear measurements. Also, zeta potential measurements were performed in order to determine changes in the electokinetic response. The CWS tested were prepared from PSOC-1527 (Middle Kittaning), PSOC-1472 (Lower Banner), PSOC 1475 (Elkhorn #3).

Surface Charge and Electrokinetic Phenomena.

Origin of charge

The chemistry of the coal surface plays a significant role in the stability of coal water slurries [1,2,3]. 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

$$\text{-COO-H} \Longrightarrow \text{COO}^- + \text{H}^+ \qquad (1\text{-}1)$$

$$\text{Phenolic-OH} \Longrightarrow \text{phenolic-O}^- + \text{H}^+ \qquad (1\text{-}2)$$

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

$$\text{M-OH} \Longrightarrow \text{M-O}^- + \text{H}^+ \qquad (1\text{-}3)$$

$$\text{M-OH} + \text{H}^+ \Longrightarrow \text{M-OH}_2^+ \qquad (1\text{-}4)$$

Surface charge can also be generated by specific adsorption of ions from the solution phase [4]. 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 [5].

Zeta Potential

The theory of the electrical double layer associated with a charged particle in an aqueous electrolyte solution has been well documented [5]. 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 electrophoretic behavior of the coal surface [5].

Zeta Potential

The theory of the electrical double layer associated with a charged particle in an aqueous electrolyte solution has been well documented [5]. 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 1-1 and 1-3, can be represented by:

$$K_{acid} = \frac{[COO^{-}]\ a_{H}^{+(s)}}{[COOH^{+}]} \qquad (1-5)$$

and for Equation---

$$K_{phenolic} = \frac{[O^{-}]a_{H+(s)}}{[-OH]} \qquad (1-6)$$

where $a_{H}^{+(s)}$ 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:

$$aH^{+\,(s)} = aH^{+}\exp(-e\psi_{o}\ /kT) \qquad (1-7)$$

where $\gamma$is the potential at the solid liquid interface, e is the electronic charge, k is the Boltzmann constant ant 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.

Measurements were performed in a constant ionic medium of 0.001 M KNO_3 in order to eliminate any anomalies in the measured values due to changes in ionic strength of the aqueous phase as a result of leaching of metal ions from the coal into the aqueous phase, or varying the pH of the suspension.

Figure 1 is a plot 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 Coal master A-23M. The zeta potential decreased with increase in pH and the iso-electronic point (iep) varied from coal to coal. The coals having a high ash content, (PSOC-1472) exhibit iso-electronic points (iep) at low pH value. For all the coals, there was a shift in the iep to lower pH's with respect to aging.

Low Hear Testing

The flow behavior exhibited in the shear rate regime of between 0-220 /s indicated that there was very slight settling of the slurries when the concentration was between 58-63%. The flow behavior however, changed from pseudoplastic to dilatant due to aging of the samples. The results are as shown in Table 1.

High Shear Testing

The high shear behavior of the slurries were studied using a HVA-6 capillary viscometer and 100 mm capillary tube of 0.8 mm inside diameters. The results also show no significant variation in the flow behavior with respect to aging of the slurries.

References

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Table 1.

RHEOLOGICAL PROPERTIES OF CWS (Fresh Sample).

COAL SAMPLE PSOC-1527 &1472 (Φ_{th}=76.5%)

Coal	R^2	n	τ_o	K	$\frac{\Phi_{exp}}{\Phi_{th}}$	η_{100} (mPas)
PSOC1472	0.94	0.98	13.41	0.56	82%	484
PSOC1472	0.97	0.93	14.5	0.82	85.3	763
PSOC1472	0.99	0.81	54.34	10.43	78.2	302
PSOC1472	0.97	0.85	37.2	0.06	77.3	286
PSOC1527	0.98	0.92	0	1.18	85.0	502
PSOC1527	0.99	1.12	3.24	0.24	80.2	400
PSOC1527	0.94	0.64	0	1.14	78.8	220
Rheological Properties of CWS After a 3-Month Storage Period.						
PSOC1472	0.95	1.13	18.6	1.14	82%	502
PSOC1472	0.98	1.21	21.6	3.20	85.3	721
PSOC1472	0.99	0.97	47.2	7.23	78.2	350
PSOC1527	0.96	0.91	13.2	3.18	85.0	512
PSOC1527	0.87	1.41	1.24	1.24	80.2	378
PSOC1527	0.90	0.89	0.54	4.14	78.8	257

$\Phi_{th}$is the theoretical calculated packing.

Figure 1. Zeta Potential of CWS as a Function of pH.