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QUARTERLY REPORT

ROLES OF ADDITIVES AND SURFACE CONTROL IN SLURRY ATOMIZATION

by

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ABSTRACT

This quarterly report describes the effects of anionic dispersant and nonionic surfactant on the rheology of micronized (Mass Median Diameters of 4 μm and 10 μm) coal water slurries (CWSs). We found that the micronized CWS is pseudoplastic (shear thinning) at a low additive concentration of either anionic dispersant or nonionic surfactant because coal particles aggregate under the influence of the interparticle van der Waals attraction. At a high additive concentration, the micronized CWS becomes Newtonian, and turns dilatant (shear thickening) at an even higher concentration of nonionic surfactant. The Newtonian behavior results as the interparticle van der Waals attraction is counterbalanced by the interparticle electrostatic repulsion; the dilatant behavior may be attributed to the cross linking of the nonionic surfactant molecules adsorbed on the coal particle surface. No dilatant behavior has been observed when using anionic dispersant.

MATERIALS AND MEASUREMENTS

Micronized Upper Freeport coal, ranked high volatile bituminous A and supplied by the Pittsburgh Energy Technology Center, is used in this study. While the Run-of-Mine (ROM) Upper Freeport coal contains 16.7 % ash, one batch has been cleaned by microbubble flotation to an ash content of 5.4% on dry basis. Other analyses of the cleaned Upper Freeport coal are: 82.8% carbon, 5.1% hydrogen, 0.7% nitrogen, 1.2% sulfur, and 4.8% oxygen. The volume mean and mass median diameters are 15.8 μm and 10.0 μm for the ROM coal and 4.9 μm and 4.0 μm for the cleaned coal. The particle size distributions of both coals are shown in Fig. 1. Both the ROM and the

cleaned coals are irregularly shaped and have densities of 1.39 g/cc and 1.33 g/cc, respectively. Irregularly shaped sand particles with a density of 2.60 g/cc and greater than 85% spherical glass bead GL5 with a density of 2.39 g/cc, both sieved to 20-40 μm by Alpine Air-Jet Siever, are also used for comparison. Their particle size distributions are also shown in Fig. 1 (inverse triangles for sand and solid circles for glass bead).

Two additives, one anionic and the other nonionic, are used separately to disperse coal particles in deionized water for CWS preparations. The anionic dispersant used is Coal Master A23M from Henkel Corp. containing 44 wt% naphthalene sulfonic acid formaldehyde polymer, ammonium salt. The nonionic surfactant used is Tergitol NP-40, Nonylphenol polyethylene glycol ether from Union Carbide.

While the particle size distribution is measured using the Malvern Particle Sizer 2600C, the slurry viscosity is measured using the Burrell-Severs capillary rheometer A120. The liquid viscosities are also measured by the Haake rotational viscometer RV20. The zeta potential of particles in deionized water is measured using the Malvern Zeta Sizer IIc.

RESULTS AND DISCUSSIONS

In our earlier publications¹, we have shown that the flow behavior index of an Upper Freeport coal slurry containing aqueous solution of a variety of alcohols (such as glycerol, ethylene glycol, and isopropanol) at a constant solid volume fraction varies linearly with the Hamaker constant. The slurry becomes less pseudoplastic (greater flow behavior index, n) and the zeta potential in deionized water becomes more negative as the coal surface is oxidized. While the Hamaker constant is a good measure of the interparticle van der Waals attraction², the zeta potential in deionized water is a qualitative measure of interparticle electrostatic repulsion as

it is related to particle surface charge density³. The less pseudoplastic behavior of oxidized Illinois #6 CWS was attributed to the interparticle electrostatic repulsion between neighboring charged particles which prevents particle aggregation⁴. In order to further verify this mechanism, an anionic dispersant (Coal Master A23M) is adsorbed onto the surface of a coal particle to increase its surface charge density. We found that as the anionic polymer concentration increases from 0.36% to 0.74% by weight of coal, the zeta potential of the Upper Freeport coal in deionized water decreases from +4 mV to -35 mV. As a result, the flow behavior index of the Upper Freeport CWS at 0.48 volume fraction increases from 0.83 (pseudoplastic) to 1.0 (Newtonian). Likewise, as shown in Fig. 2, the pseudoplastic Upper Freeport CWS at 0.46 volume fraction becomes nearly Newtonian (n equals 0.94) as the anionic polymer concentration increases from 0.32 % to 0.49 % by weight of coal. The relative viscosities of the pseudoplastic Upper Freeport CWS at 0.46 volume fraction containing 0.32 wt% anionic polymer (open diamonds) are only slightly lower than those of the Upper Freeport coal slurry consisting of an aqueous solution of 50 wt% isopropanol (liquid viscosity of 0.04 P) at the same volume fraction (open triangles).

Fig. 2 also shows that the relative viscosities of the Upper Freeport coal in water/glycerol (28/72 wt/wt with liquid viscosity of 0.28 P) slurry are in line with those of the sand in ethylene glycol/glycerol (80/20 wt/wt with liquid viscosity of 0.35 P) slurry, both at 0.45 volume fraction (solid circles and solid diamonds, respectively). They are considerably lower than those of the Upper Freeport coal slurry containing an aqueous solution of 50 wt% isopropanol at 0.46 volume fraction (open triangles). The substantial increase in the relative viscosity (open triangles vs solid circles), much more than what can be accounted for by the increase in the volume fraction

from 0.45 to 0.46, can be attributed⁵ to the nearly one order of magnitude decrease in the viscosity of the suspending liquid (0.28 P vs 0.04 P). Note that the zeta potential in deionized water for the Upper Freeport coal is +4 mV, and therefore the primary force affecting the rheology of these Upper Freeport coal slurries is the interparticle van der Waals attraction. Note that the relative viscosity of the glass bead GL5 suspension in ethylene glycol/glycerol (80/20 wt/wt with viscosity of 0.35 P) at 0.55 volume fraction is also shown in Fig. 2 (open circles) for comparison.

The relative viscosities of the Newtonian CWSs (anionic concentration equal to and greater than 0.74 wt% polymer) are fitted to the Krieger/Dougherty (K/D) rigid sphere model⁶ using the maximum packing fraction ϕ_M obtained from sedimentation as the sole parameter:

$$\eta_r = (1 - \phi/\phi_M)^{-[\eta]\phi_M}$$

where the intrinsic viscosity $[\eta]$ equals 2.5 in the Einstein equation for dilute suspensions of non-charged spheres, and equals 2.67 for latex⁶ and noncolloidal nonaqueous suspensions of polystyrene spheres, glass beads, and irregularly shaped sand⁴. As shown in Table I, the measured relative viscosities are considerably higher than what are predicted by the K/D Model using an intrinsic viscosity of 2.67. In order to determine any significant role the interparticle electrostatic repulsion may play, the sedimentation and rheology studies of two slurries using 1.73 wt% polymers, one anionic and the other nonionic, were carried out. As shown in Table I, the maximum packing fraction of the CWS containing the anionic dispersant is only slightly lower (0.58 vs 0.61) while its relative viscosity is substantially higher as compared with the CWS containing the nonionic surfactant. Additional experimentation is in progress to determine the underlying mechanisms.

It should be noted that the dilatent behavior observed by the Haake rotational viscometer and recently reported in the literature⁷ on coal dispersions using an anionic dispersant (ammonium salt of a condensed naphthalene sulfonate, 0.98 wt% on coal basis for 2.9 μm coal at 0.48 - 0.55 volume fractions) has never been observed in this study when using the anionic dispersant. In contrast, dilatent behavior with a flow behavior index of 1.2 in the shear rate range of 800 s^{-1} to 8000 s^{-1} has been observed when the concentration of the nonionic surfactant NP-40 in the micronized CWS (0.45 volume fraction of coal with MMD of 4 μm) exceeds 0.94 wt% on coal basis. Note that at the same concentration of the nonionic surfactant on coal basis, the CWS of 10 μm MMD is found to be Newtonian even at a higher volume fraction (0.50 vs 0.45). The surface area available for adsorption of the surfactant molecules is considerably larger for the 4 μm coal than for the 10 μm coal. As a result, more surfactant molecules are adsorbed on the coal surface for the 4 μm coal even though the surfactant concentration on coal basis is the same. The adsorbed surfactant molecules cross link under high shear in the absence of interparticle electrostatic repulsion and, thus, particle aggregation takes place in a similar manner as flocculation. As particles aggregate, the slurry viscosity increases⁸. Therefore, the slurry with excess nonionic surfactant shows shear thickening.

At nonionic surfactant concentrations ranging from 0.023 wt% to 0.19 wt% on coal basis, the micronized (MMD 4 μm) CWSs at 0.45 volume fraction are found to be pseudoplastic with flow behavior indices ranging from 0.70 to 0.75. Their relative viscosities are shown in Fig. 3 as a function of the Particlet number which equals the time required for a particle to diffuse a distance comparable to its radius multiplied by the shear rate. Also shown in Fig. 3 are the relative viscosities of the

pseudoplastic CWSs of coal with 10 μm MMD at 0.50 volume fraction and the nonionic surfactant concentrations ranging from 0.175 wt% to 0.87 wt% NP-40 on coal basis. This figure clearly shows that the relative viscosity of a pseudoplastic CWS (both 4 μm and 10 μm sizes) is independent of the nonionic surfactant concentration. However, it should be noted that coal is hydrophobic and a minimum amount of surfactant is required for slurry stabilization.

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TABLE I

COMPARISON OF THE RELATIVE VISCOSITIES OF NEWTONIAN SLURRIES

Solid	Vol. frac.	Dispersant [#] coal basis	η_r Expt.	ϕ_M	η_r Model [*]
Up. Fr. coal MMD 4 μm	0.48	anionic polym. 0.74 wt%	1150	-	164 ^{**}
Up. Fr. coal MMD 4 μm	0.45	anionic polym. 1.15 wt%	450	0.49	26.6
Up. Fr. coal MMD 10 μm	0.50	anionic polym. 1.73 wt%	1600	0.58	21.6
Up. Fr. coal MMD 10 μm	0.50	nonionic polym. 1.73 wt%	70	0.61	16.3
Sand, 20-40 μm	0.45	Silicone oil	22	0.50	22

[#] Dispersant is used in coal water slurries only, and water is replaced by silicone oil in the case of sand suspension.

^{*} The intrinsic viscosity $[\eta]$ is taken as 2.67⁶.

^{**}Maximum volume fraction of 0.49 is assumed.

Fig. 1 Particle Size Distributions

Fig. 2 Comparison of the Rheology of Various Coal Slurries, Sand and Glass Bead Suspensions

Fig.3 Rheology of Micronized Coal Water Slurries

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