

ASSESSMENT OF THE HYDROPHOBICITY OF FINE COAL PARTICLES
IN VARIOUS AQUEOUS MEDIA BY VISCOSITY MEASUREMENTS.

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ABSTRACT

Viscosity measurements have been shown to provide a good indication of the relative hydrophobic and hydrophilic nature of fine coal particles in various aqueous media. Slurries of float and sink fractions of pulverized Upper Freeport run-of-mine coal in various electrolytes showed evidence of structure formation under the influence of shear. This structuring reaches a steady state at very high shear rates; by examining the viscosities at the higher shear rates, the inter-particle interaction effects and hydrodynamic effects may be distinctly determined. When the particles are more hydrophobic, the tendency for structure formation is greater. This is reflected in the response of the slurry to shear. Viscosity measurements of α -alumina particles in slurries of various pH, and corresponding zeta potential measurements, confirmed that the highest viscosity and the maximum structure formation occurred at the PZC, when the particle surfaces are most hydrophobic.

INTRODUCTION

The rheological properties of slurries are influenced both by the surface characteristics of the particles, and by the properties of the suspending liquid(1-4). Measurement of the appropriate rheological parameters offers a simple means of comparing the relative hydrophobicity of particles in different aqueous media and also of comparing the effect of different chemical treatments on the hydrophobicity of the particles. Current work in our laboratories involves surface modification by chemical pretreatment of coal during the size-reduction stage that typically precedes beneficiation in most advanced coal cleaning processes. The rheology measurements can be used to characterize the changes to the particle surfaces that have been brought about by the pretreatment.

THEORY

In the Einstein equation(5) for suspensions of non-interacting spherical particles, the viscosity increase due to the presence of the particles is a function only of the volume fraction of the particles. The equation is valid only for relatively dilute suspensions(6). In a simple shear field, this still represents Newtonian flow, in the sense that shear stress is linearly related to shear rate.

For more concentrated slurries, particle interactions also affect the viscosity of the suspension since various degrees of aggregation or 'structuring' of the particles will occur(7). If the particles are suspended in an aqueous medium and have strongly hydrophobic surfaces, the preference of the water molecules to associate with other water molecules, rather than with the particle surfaces, will promote aggregation. Ionic or polar surfaces on the

other hand, can associate more freely with the polar water molecules and are thus hydrophilic(8). The presence of an electrostatic charge at the surface reduces the tendency for such particles to aggregate. Aggregation causes the viscosity of the suspension to increase for two reasons. The particle assemblages tend to entrap liquid within themselves, increasing the effective volume fraction of the solids, and thus increasing the viscosity in accordance with the Einstein equation(9). Additional energy is also dissipated when the particle assemblages interact with each other during shear flow.

In most slurries containing particles of a few micrometers or smaller in size, the basic flow units are considered to be small clusters of particles and entrapped liquid called flocs(10,11). At rest, the flocs are grouped into larger flow units called aggregates. As shear is imposed on the slurry, the aggregates break down into individual flocs, until at sufficiently high shear, a linear shear stress-shear rate relationship is observed, as shown in Figure 1. This linear portion of the curve represents a steady-state energy relationship between the tendency of the flocs to form doublets, and the tendency of the shear forces to break-up the doublets. The curve is characteristic of pseudoplastic shear-thinning behavior. The Bingham yield stress, τ_B , is defined as the extrapolated intercept of the linear portion of the curve and the apparent viscosity, η , is the ratio of the shear stress to the shear rate at any point on the curve.

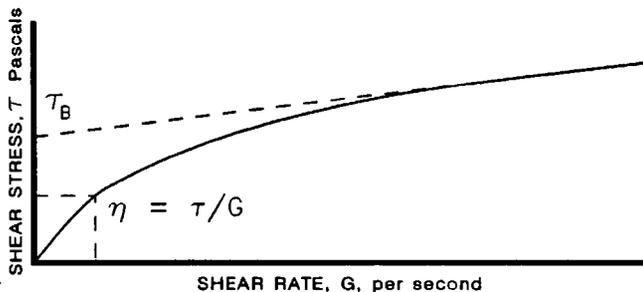


Figure 1. Typical shear stress-shear rate relationship showing pseudoplastic shear-thinning behavior.

Michaels and Bolger(10) found that τ_B increased with the square of the floc volume fraction (ϕ_F), and with the strength of the interparticle interactions. The relationship is expressed as:

$$\tau_B = \frac{A}{a d_F^2} \phi_F^2 \quad 1)$$

where A is a constant which depends on the net force of attraction between the particles. The parameter, d_F , is the average floc diameter, and 'a' is the distance between flocs and is thus a measure of the attraction between flocs. They also found that the ratio A/d_F^2 was constant and independent of the chemical composition of the liquid used. Thus τ_B depended only on 'a', which is a measure of the degree of interaction between flocs, and on ϕ_F , the floc volume. Since the tendency of particles to aggregate is

greater when they are more hydrophobic, this implies that greater hydrophobicity would yield a higher value of τ_b .

Hunter and co-workers(11), who extended the "aggregate-collision" theory of Michaels and Bolger(10), showed that τ_b varied as the square of the zeta potential of the particles in the suspension. τ_b was a maximum when the zeta potential was zero. The tendency for particles to aggregate is also a maximum at this point.

EXPERIMENTAL

To study the effects of the different treatments on the surface properties of the organic and mineral portions of Upper Freeport run-of-mine coal, the coal was first ground to an average particle size of about 10 μm , separated into an organic-rich fraction which had only 4.9% ash, and a mineral-rich fraction which had 55.3% ash. This was done by centrifugal float-sink separation using a liquid of specific gravity 1.4. The organic and mineral-rich fractions were filtered, vacuum dried, and then used to form a variety of different slurries each of which had the same solid concentration (volume fraction). However, the pH of the suspending solutions was different. For each fraction, one additional slurry was made using a 0.1M solution of sodium dithionite. The viscosities of the slurries were measured using a Haake concentric cylinder viscometer. The viscosities of the suspending electrolytes were measured using a Cannon-Fenske capillary viscometer, and very little variation among them was noticed.

As a further test of the method, viscosity and pH measurements were also made on slurries of α -alumina particles, which had more homogenous surfaces. The alumina was obtained from Fisher Scientific Company, and was further ground to an average particle size of about 10 μm .

RESULTS

The results of beneficiation tests on separate samples of the same Upper Freeport run-of-mine coal used in this work are given in an accompanying paper(12). Separation was carried out by oil agglomeration, microbubble frit flotation, and microbubble foam flotation. They were made at different pH levels and also in the presence of 0.1M sodium dithionite. In each case the coal which had been pretreated with sodium dithionite ($\text{Na}_2\text{S}_2\text{O}_4$) yielded substantially better results than when only pH control was used. To understand the changes to the surfaces of the particles that might have caused such a response, the viscosity curves obtained in this work were examined.

The shear responses of the mineral-rich fractions of Upper Freeport coal in the various electrolytes are shown in Figure 2. The only difference between the curves is in the liquid used for making each slurry. The curves are all typical of shear thinning behavior. The initial nonlinear portion of the curves represents increasing break-up of aggregates. When these are all destroyed, the curve becomes linear and represents a steady-state relation between the formation and break-up of floc doublets. The slopes of the linear part of the curve is a function only of the

floc volume. These slopes, and hence the floc volumes of the slurries, are essentially equal. This is not unreasonable since each slurry has the same particle concentration, and was subjected to the same shear cycle in the viscometer.

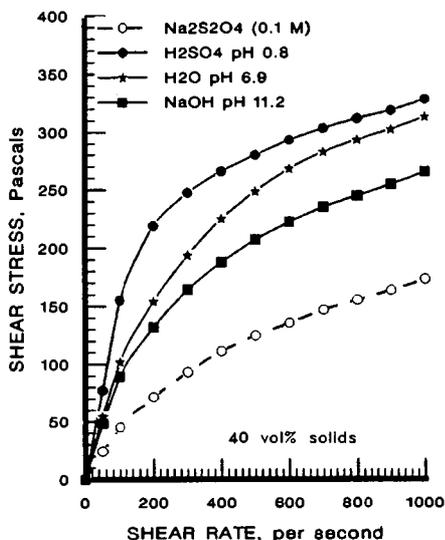


Figure 2. Shear response of slurries of the mineral-rich fraction.

Table 1. τ_B values for slurries of the mineral-rich fraction.

pH	τ_B , Pascals
0.8	245
6.9	204
11.2	162
0.1M Na ₂ S ₂ O ₄	85

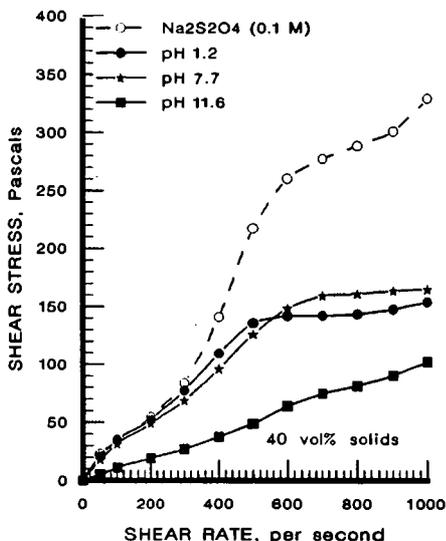


Figure 3. Shear response of slurries of the organic-rich fraction.

Table 2. τ_B values for slurries of the organic-rich fraction.

pH	τ_B , Pascals
1.2	130
7.7	150
11.6	11
0.1M Na ₂ S ₂ O ₄	217

The Bingham yield stress, τ_B , found by extrapolating the linear portion of each curve to zero shear rate, is different for each slurry. The values of τ_B are given in Table 1. The Bingham yield stress is a function of both the floc volume and the strength of the net attractive interaction force between flocs. Since the floc volumes are essentially equal for each slurry, τ_B should be directly related to the strength of the particle interactions. Lower values of τ_B indicate a lower net particle-particle interaction (or more correctly, a greater tendency for particle-medium association), a

lesser tendency towards flocculation, and hence a stronger hydrophilic character of the particle surfaces. Clearly, the particles in the slurry treated with sodium dithionite were most hydrophilic; the curve for this slurry is significantly lower than those slurries in which only pH was varied.

Figure 3 shows the shear response of the slurries formed with the organic rich fractions. Although some shear thickening appears at intermediate shear rates, the slurries still showed shear thinning at low and high shear. This type of behavior is not unusual for hydrophobic systems(3,13). For these slurries, the plastic viscosities are not so nearly equal as they were for the mineral-rich slurries. A clear interpretation of the result is difficult and will not be attempted until more data are available. However, the substantial difference in the τ_B values shown in Table 2, for the slurry treated with sodium dithionite, would seem to overshadow any effect of the floc volume difference in reaching a conclusion that the particles in the sodium dithionite slurry were most hydrophobic.

These results suggest that the improved beneficiation results obtained by using sodium dithionite was due to alteration of surfaces of both the organic-rich and mineral-rich coal particles, since the organic-rich particles became more hydrophobic and the mineral-rich particles became more hydrophilic. In other words, the surface characteristics of the two fractions were altered in different ways. Additional evidence, given in the companion paper(12) to this work, is that both sulfur and ash reduction was improved. Reduction of a sulfide surface by an appropriate reductant is known to improve sulfur rejection, but its effect on either carbonaceous surfaces or ash surfaces is less clear and additional work will be required to explain this result.

Figure 4 shows the shear response of α -alumina slurries at various pH values and is included to demonstrate the variation of τ_B with particle interaction effects on slurries made up of particles with more homogenous surfaces. At the point of zero zeta potential, (see Figure 5) the value of τ_B (Table 3) is a maximum, showing maximum particle-particle interaction, minimum particle-liquid interaction, and therefore maximum hydrophobicity. This is only expected, since the particles being least charged can least interact with the polar aqueous medium, and also have the least particle-particle repulsion.

Table 3. Yield Stress (τ_B) at various pH for α -alumina slurries. The corresponding zeta potential values (ζ) are also shown.

pH	ζ , mV	τ_B , Pascals
6.4	+10	76.6
8.3	0	102.4
9.8	-27	33.6
10.0	-29	18.1

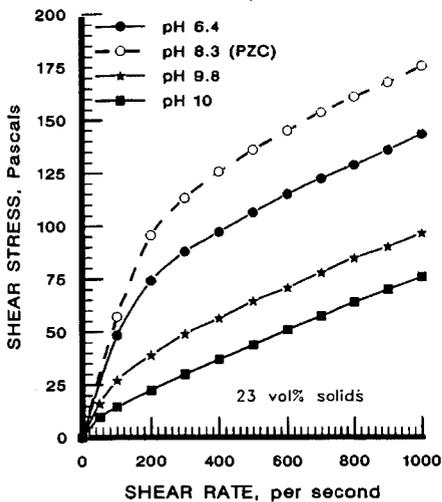


Figure 4. Shear response of slurries of α -alumina.

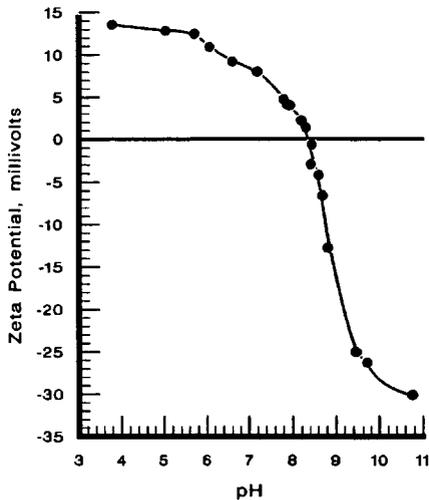


Figure 5. Zeta potential of α -alumina particles at different pH.

CONCLUSIONS

Rheological measurements have been used to study the hydrophobic/hydrophilic behavior of coal and mineral particles in various aqueous media, in an effort to explain why the use of sodium dithionite as an additive during grinding of a coal slurry produced improved beneficiation results. The measurements suggest that this was due to a beneficial effect on the surface properties of both the organic and mineral fractions of the coal. The organic fraction became more hydrophobic and the mineral fraction became more hydrophilic in the slurries containing 0.1M sodium dithionite. These results do not necessarily contradict the contact angle measurements reported earlier(12), if the possibilities of kinetic effects are taken into account. The time taken to prepare the dispersed slurries for viscosity measurements could allow for relatively slow changes to the particle surfaces. These effects would not be expected to show up in the contact angle measurements which did not allow for extended coal-sodium dithionite solution contact. The exact mechanisms that effect these changes are not known at this time. However, additional studies are underway.

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