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Rheology of Coal-Water Slurries Prepared by the HP Roll Mill Grinding of Coal

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September 1 - November 30, 1993

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INTRODUCTION

Efforts to reduce dependence on imported oil and to rely more on its enormous low-cost coal resources should be of major importance to the United States. Consequently, the objective of this research is the development of improved technology for the preparation of coal-water slurries that have potential for replacing fuel oil in direct combustion.

According to this objective, Quarterly Report No. 1 presented preliminary results on the rheological behavior of coal-water slurries prepared from Pittsburgh No. 8 coal that had been ground in a ball mill under various conditions. Quarterly Report No. 2 summarized the results of studies on the effects of solids content, water immobilization and different viscometers, such as the Haake Rotovisco RV-12 and Brookfield Synchro-Lectric LVT, on the rheological behavior of coal-water slurries. In Quarterly Report No. 3, we compared the rheological behavior of Pittsburgh No. 8 coal-water slurries using different sensor systems. It was found that the Haake Rotovisco RV-12 with the MV-DIN sensor system performs better than with the standard MV-II sensor system at high solids content. Also, Quarterly Report No. 3 summarized the results of studies on the effect of chemical additives, namely nonionic surfactants (Triton X series) on the rheological behavior of coal-water slurries. The results showed that the addition of these nonionic surfactants reduces significantly the viscosity of the coal slurries at high reagent addition (0.75 - 1.0 wt%), with reagents having the larger number of ethylene oxide groups in their molecular structure being the most effective. In Quarterly Report No. 4, the results of studies on the role of the initial mixing procedure in the preparation of coal-water slurries were presented. That investigation resulted in modifying the experimental procedure to include a mechanical-mixing step. Further, Quarterly Report No. 4 also summarized our

findings on the effect of the storage time of ground coal samples and the addition of anionic surfactants, such as 2-TEPA, on the rheology of coal-water slurries. It was found that the storage time has little effect on suspension rheology, even after 30 days of storage. On the other hand, 2-TEPA seems to be an effective dispersant for the system, reducing the viscosity at high reagent addition (1 wt%).

Research conducted during the Fifth Quarter was aimed at the evaluation of the effect of a cationic surfactant, TMAE, on the rheology of coal suspensions and delineation of the effects of anionic, cationic, and nonionic surfactants on the aggregation stability of Pittsburgh No. 8 coal-water slurries. The purpose of these studies was to improve the understanding of the behavior of coal-water slurries in the presence of chemical additives.

EFFECT OF CHEMICAL ADDITIVES

To evaluate the effect of TMAE on the rheological behavior of Pittsburgh No. 8 coal-water slurries, experiments were carried out with slurries containing 60 wt% coal that had been ground to 95% minus 74 microns, using the mechanical-initial mixing step to introduce the reagent. TMAE is a reagent of the same family as 2-TEPA, containing sulfur and nitrogen functional groups in its molecule. TMAE, which is a hydrophilic cationic reagent of a short hydrocarbon chain as compared to the Triton X series of reagents, appears to strongly adsorb onto the surface of coal through its positively charged functional group. Since TMAE is a cationic surfactant, it can adsorb onto the negatively charged surface of the coal particles, causing a reduction in the magnitude of the Stern layer potential (or zeta potential).

Figure 1 presents the effect of TMAE addition on the flow curve of coal-water slurries made from Pittsburgh No. 8 coal. In this system, the rheological behavior of the system exhibits a pseudoplastic behavior with yield stress for all reagent dosages tested. The plots show that the reagent initially increases the shear stress for a given shear rate up to an addition of 0.5 wt%, indicating the flocculation of the particles. Further increase in the amount of reagent decreases

Figure 1. Flow curves (rheograms) of Pittsburgh No. 8 coal-water slurries at 60 wt% solids content for different TMAE additions, using the MV-DIN sensor system at 20°C.

the shear stress for a given shear rate to values obtained in the absence of this reagent. This decrease in the shear stress must be related to reagent adsorption at the coal-water interface. Maximum flocculation would occur when at reagent additions that bring about reversal of the zeta potential, and redispersion would occur when the double layer at the coal surface becomes recharged. Thus TMAE can flocculate the particles at low surface coverage and weakly flocculate or redisperse them at high surface coverage as the net charge builds up on the positive side. Another possible contribution to the observed behavior could be the formation and rearrangement of flocs of suitable shape (oblates) that may allow the suspension to flow; thus, decreasing the viscosity of the coal-water slurries [1, 2].

Figure 2 presents the change in viscosity as a function of reagent addition for shear rates of 10 sec^{-1} , 83 sec^{-1} , 165 sec^{-1} , and 330 sec^{-1} . As can be seen from the results given in this figure, the viscosity increases as the reagent addition increases up to 0.5 wt% and then decreases upon

further addition of the reagent. It is important to observe that after an 0.5% addition of the reagent, the viscosity values never go below those obtained in the absence of this reagent.

EFFECT OF CHEMICAL ADDITIVES ON THE AGGREGATION STABILITY IN COAL-WATER SLURRIES

To study the effect of chemical additives on the aggregation stability of coal-water slurries and to clarify the explanation suggested for the effect of anionic, cationic and nonionic surfactants on the rheological behavior of Pittsburgh No. 8 coal-water slurries, flocculation tests were performed through such indirect measurements as the relative sedimentation volume and the size distribution of flocs. These measurements were selected because the range of particle size and the high solids content of these slurries do not allow us to use light scattering techniques. Figure 3 presents the relative sedimentation, expressed as a volume percentage of the initial slurries volume, as a function of reagent addition for the anionic 2-TEPA and cationic TMAE surfactants. For these tests, the slurries were prepared according to the standard procedure (Quarterly Report No. 4), both in the absence and presence of the reagents. The samples were then transferred to a centrifuge tube and the height of the mud line was recorded after which these samples were centrifuged at 16,000 rpm for 30 minutes, the new sediment height recorded. As was demonstrated by previous researchers [1], the height of the sediment increases as the aggregation stability of the slurry decreases; that is, the flocculation of the system increases. Figure 4 shows that in the case of 2-TEPA the relative sedimentation volume steadily decreases as the reagent addition is increased. Therefore, these results indicate that the system is dispersed by the presence of this reagent, in agreement with the results of the rheological measurements (see Quarterly Report No. 4). In the case of TMAE, Figure 3 shows that relative sedimentation volume decreases slightly at 0.25 wt% addition, increasing continuously at higher reagent dosages. Thus, the possible explanations of a weak flocculation and/or a rearrangement of flocculated coal particles may be correct.

Figure 2. Viscosity of Pittsburgh No. 8 coal-water slurries at 60 wt% solids content as a function of TMAE addition for four different shear rates, using the MV-DIN sensor system at 20°C.

Figure 3. Relative sedimentation volume as a function of 2-TEPA and TMAE additions for Pittsburgh No. 8 coal-water slurries (60 wt% solids) centrifuged at 16,000 rpm for 30 minutes.

Determination of the effect of 2-TEPA and TMAE on the particle size distribution in the slurries was studied using the Microtrac Particle Size Analyzer and the Andreasen pipette technique. In the case of the Microtrac results, the particle size distribution did not show any significant difference, both in the absence and presence of either of these reagents (see Figures 4 and 5). Possibly, the high energy applied to the system in the centrifuge pump and in the measuring chamber of this apparatus destroys the weak flocs formed and maintain the particles dispersed during the measurements. To avoid the dispersion of the system, experiments with an Andreasen pipette, which is a simple gentle sedimentation technique, were carried out. Figure 6 presents the apparent particle size distribution for ground Pittsburgh No. 8 in the absence and presence of 2-TEPA. This figure shows that the observed Stokes' diameter or sedimentation diameter decreases with increasing reagent addition, indicating that this reagent disperses the system. Under the conditions used, the particles must be slightly aggregated in the system without added 2-TEPA. These results are in agreement with the rheological data which show that the viscosity decreases as the reagent addition increases. On the other hand, the results given in Figure 7 for the case of TMAE indicate no change in the sedimentation diameter (except for apparent aggregation in the absence of reagent). Since sedimentation techniques are based on determining the settling rate of particles according to Stokes' law (which is based on the equilibrium between gravity and drag forces), the presence of weak flocs could reduce the density of the aggregate, resulting in a settling rate for the aggregate equivalent to that for the particles in the absence of the reagent. Another possible explanation for the behavior of the system in the presence of TMAE could be related to the shape of the flocs formed. The settling rate of the aggregates can decrease if they form an oblate floc (nonspherical), which increases the drag force when settling. Apparently, the presence of oblate aggregates could explain the observed decrease in viscosity at high TMAE addition due to the alignment of the flocs in the direction of the flow [2]. Therefore, the apparent change in floc diameter due to reagent that promotes a weak flocculation of the system, such as in the case with TMAE, could not be detected by the Andreasen pipette technique. This can be seen by the results given in Figure 8,

Figure 4. Particle size distribution for Pittsburgh No. 8 particles in the absence and presence of 2-TEPA conditioned according to the standard procedure, using the Microtrac Particle Size Analyzer.

Figure 5. Particle size distribution for Pittsburgh No. 8 particles in the absence and presence of TMAE conditioned according to the standard procedure, using the Microtrac Particle Size Analyzer.

Figure 6. Particle size distribution for Pittsburgh No. 8 coal-water slurries in the absence and presence of 2-TEPA conditioned according to the standard procedure, using the Andreasen pipette technique.

Figure 7. Particle size distribution for Pittsburgh No. 8 coal-water slurries in the absence and presence of TMAE conditioned according to the standard procedure, using the Andreasen pipette technique.

which presents the sedimentation mean diameter as a function of 2-TEPA and TMAE addition for Pittsburgh No. 8 coal-water slurries. These plots show that 2-TEPA disperses the system, whereas the cationic TMAE does not show any apparent change in the mean sedimentation diameter.

In the case of nonionic surfactants, the mechanism of interaction of these reagents with the surface of coal is not electrostatic (except for shielding charged sites on the surface by adsorbed neutral molecules). Apparently, the Triton X series of reagents are absorbed by hydrophobic interaction with the hydrophobic sites on the surface of coal, probably through their aromatic groups. Consequently, the hydrophilic ethylene oxide groups of these nonionic surfactants orient towards the bulk liquid, tending to increase the water layer on the coal particle [3, 4]. Under these conditions, the viscosity of a coal-water slurry would tend to decrease as the surface coverage increases and as the number of ethylene oxide groups on the surfactant molecule is increased. At high reagent addition, the formation of a bilayer (reverse micelles) over the surface seems to increase the hydrophobic nature of the particle by facing the aromatic part of the molecule towards the bulk liquid. This effect may take place at a critical reagent concentration, which decreases as the number of ethylene oxide groups increases. Therefore, the viscosity of a coal-water slurry would tend to increase at reagent additions higher than this critical concentration. Since previous rheological data (see Quarterly Report No. 3) suggested that Triton X-165, Triton X-305, and Triton X-405 were the most effective chemical additives, these three reagents were chosen for evaluation of the effect of nonionic surfactants on the aggregation stability of the system. Again, the standard experimental procedure was used for the preparation of the suspension, followed by the centrifugation of the sample at 16,000 rpm for 30 minutes.

Figure 9 presents the relative sedimentation volume of Pittsburgh No. 8 coal-water slurries as a function of the addition of Triton X-165, Triton X-305, and Triton X-405. Up to an addition of 0.5 wt%, Triton X-165 does not cause any significant change in the relative sedimentation volume. But higher reagent additions cause a sharp decrease in sedimentation

Figure 8. Sedimentation mean diameter as a function of reagent addition for Pittsburgh No. 8 coal-water slurries conditioned according to the standard procedure in the absence and presence of 2-TEPA and TMAE.

Figure 9. Relative sedimentation volume as a function of Triton X series of reagents addition for Pittsburgh No. 8 coal-water slurries (60 wt% solids) centrifuged at 16,000 rpm for 30 minutes.

volume. According to the mechanism suggested, it seems that at low surface coverage this reagent is not able to increase the hydration layer significantly, maintaining the system weakly flocculated. However, at higher reagent additions, it appears that the aggregation stability of the system increases, possibly due to a thick hydration layer over the coal particles. Since the number of ethylene oxide groups in Triton X-165 is 16, the amount of reagent added was not enough to form a bilayer (reverse micelles) over the surface. Therefore, no increase of the relative sedimentation volume was observed even at 1 wt% addition. In the case of Triton X-305 and Triton X-405, which contain 30 and 40 ethylene oxide groups, respectively, the relative sedimentation volume steadily decreases up to an addition of about 0.75 wt% but then has increased again at 1.0 wt% addition. Based on the explanation suggested, the increase in aggregation stability (dispersion of the system) may be due to the thickening of the hydration layer above 0.75 wt% addition. However, at higher reagent additions, the system tends to weakly flocculate (increase in the relative sedimentation volume). Possibly, the formation of a bilayer (reverse micelles) is responsible for this behavior.

SUMMARY

The effect of the cationic reagent, TMAE, on the rheology of Pittsburgh No. 8 coal-water slurries was studied. The results indicate that the presence of TMAE causes the viscosity to increase for a given shear rate up to 0.5 wt% addition, indicating flocculation of the particles in the system. Increasing the TMAE addition over 0.5 wt% decreases the viscosity for a given shear rate, with the viscosity obtained at 1 wt% addition being similar to that obtained without any addition of the reagent.

The effect of the addition of anionic, cationic and nonionic surfactants on the aggregation stability of coal-water slurries was investigated by determination of sedimentation volume and the floc size distribution. In the case of the anionic 2-TEPA, the sedimentation volume steadily decreases as the surfactant is added to the system, indicating dispersion of the particles. This

effect is in accordance with the rheological results, which show that the viscosity decreases with increasing 2-TEPA additions (see Quarterly Report No. 3). For cationic surfactants, such as TMAE, the sedimentation volume increases as the TMAE addition is increased, indicating flocculation of the coal particles.

Particle size distributions were measured by the Microtrac Particle Size Analyzer and the Andreasen pipette technique. Because of the intense agitation in the pump of the Microtrac Particle Size Analyzer, no difference was observed in the absence and presence of both 2-TEPA and TMAE reagents. However, with the Andreasen pipette, which is a gentle sedimentation technique, the results show differences in the measured particle size distribution as 2-TEPA or TMAE is added to the system. The 2-TEPA mean sedimentation diameter constantly decreases as the reagent addition increases, indicating dispersion of the system. On the other hand, the TMAE mean sedimentation diameter shows no apparent change at any reagent addition. The reason for this behavior is that anionic surfactants absorb through hydrophobic bonding to the coal surface and thereby increase the negative charge at coal-water interface, thereby dispersing the particles (increasing the aggregation stability) due to electrostatic repulsion. This results in increased viscosity of the slurry. However, with cationic surfactants, the behavior of the system involves first a reduction in the negative charge at the coal-water interface, followed by an apparent charge reversal at higher additions of the positively charged reagent. Flocculation of the coal particles at low surface dosage (decrease of the aggregation stability) would be expected due to the reduction in the net negative charge on the particles, thereby increasing the viscosity. However, as the surface coverage increases, two possible phenomena might take place: i) the coal particles acquire a positive surface charge and redisperse; and ii) there could be reformation and rearrangement of flocs, such as oblate flocs that allow the suspension to flow.

Sedimentation volume measurements for nonionic surfactants show that for Triton X-165, Triton X-305 and Triton X-405, the sedimentation volume decreases for reagent additions up to 0.75 wt%. However, at higher additions, the sedimentation volume levels off for Triton X-165, but increases for both Triton X-305 and Triton X-405. These results are in agreement with

the viscosity measurements reported previously (see Quarterly Report No. 3).

The results suggest that the aromatic part of nonionic surfactants may adsorb onto hydrophobic sites of the coal surface, with the ethylene oxide groups oriented towards the bulk water. As the amount of reagent increases, the formation of a bilayer (reverse micelles) may occur, partially restoring the hydrophobicity of the coal, thereby promoting the flocculation of the coal particles. Under these conditions, both the viscosity and the sedimentation volume should decrease at low reagent addition and increase over a certain critical concentration due to the formation of reverse micelles. The critical concentration will depend on the number of ethylene oxide groups of the surfactant, decreasing as the number of ethylene oxide groups increases.

FUTURE WORK

Efforts to characterize the rheology of coal-water slurries will be continued. For this purpose, flocculation studies of coal slurries will be carried out. In addition, electrokinetic studies will be performed on coal, using the acousto-electrophoresis apparatus. The effect of high-pressure roll mill grinding of the coal on the rheological behavior of slurries will be initiated.

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