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

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Quarterly Technical Progress Report No. 6

December 1, 1993 - February 28, 1994

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INTRODUCTION

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. This should be of major importance to the United States in its efforts to reduce dependence on imported oil and to rely more on its enormous low-cost coal resources.

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 significantly reduces 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. The 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.

In Quarterly Report No. 5, the evaluation of the effect of a cationic surfactant (TMAE) and an anionic surfactant (2-TEPA) on the rheological behavior and the aggregative stability of Pittsburgh No. 8 coal-water slurries was presented. The results indicated that for a given shear rate the addition of the cationic reagent TMAE causes the viscosity to increase up to 0.5 wt% addition, indicating flocculation of the particles in the system. Increasing the TMAE addition over 0.5 wt% caused the slurry viscosity to decrease for a given shear rate, with the viscosity obtained at 1 wt% addition being similar to that without any addition of the reagent. In contrast, 2-TEPA seems to be an effective dispersant for the system, reducing the viscosity at high reagent addition (1 wt%). Furthermore, the results of the relative sedimentation volume and the floc size distribution of the coal-water slurries show that the anionic 2-TEPA disperses the system, whereas the cationic TMAE flocculates it. This seems to be related to electrostatic interactions between the surface of the coal particles and the surfactants.

Research conducted during the Sixth Quarter was to study the effect of nonionic surfactants (Triton X series) on the aggregative stability of coal-water slurries by measuring the relative sedimentation volume and the floc size distribution. Grinding of Pittsburgh No. 8 coal in the high-pressure roll mill and deagglomeration of the ground product by stirring in the methanol suspensions were also conducted.

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

Following the experimental procedure delineated in Quarterly Report No. 5, flocculation tests with nonionic surfactants such as Triton X-165, Triton X-305 and Triton X-405 were conducted to study the effect of chemical additives on the aggregative stability of coal-water slurries. The Triton series of nonionic surfactants are oxyethylenic octylphenol compounds

[C₈H₁₇-C₆H₄-(O-CH₂-CH₂)_n-OH]. These surfactants have different numbers of ethoxy groups: n=16 for Triton X-165, n=30 for Triton X-305, and n=40 for Triton X-405, with a molecular weight of 889 g/mole, 1515 g/mole and 1945 g/mole, respectively [1]. For these tests, the slurries were prepared according to the standard procedure (Quarterly Report No. 4), both in the absence and presence of these reagents. For the relative sedimentation volume tests, the samples were 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 and the new sediment height recorded (see Quarterly Report No. 5). As was demonstrated by previous researchers [2], the height of the sediment increases as the aggregative stability of the slurry decreases; that is, the flocculation of the system increases. Figure 1 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 volume, leveling off at around 1 wt% Triton X-165 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 decreases slightly up to an addition of about 0.5 wt%, but decreasing sharply between 0.5 and 0.75 wt% addition. At 1.0 wt% addition, the sedimentation volume increases again.

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 hydration layer on the coal particles as the number of ethylene groups increases [1,3]. At low reagent addition, the effective particle diameter may increase, but still allowing the particles to interact between them and thereby increasing the relative sedimentation volume (flocculation of the system). However, as

the surface coverage increases, the sedimentation volume of a coal-water slurry would tend to decrease due to the decrease in the particle-particle interactions (dispersion of the system). This is in agreement with the viscosity data given in Figure 2, where the viscosity of Pittsburgh coal-water slurries are plotted as a function of Triton X series addition. This effect is more pronounced as the number of ethylene oxide groups on the surfactant molecule increases. At high reagent addition, a bilayer (reverse micelles) may be formed over the surface, increasing the hydrophobic nature of the particle by facing the aromatic part of the adsorbed molecules 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 sedimentation volume of the slurries would tend to increase at reagent additions higher than this critical concentration. Similar to the case of the sedimentation volume results, the rheological measurements shows a slight increase in the viscosity at 1 wt% Triton X-405 addition. Another possible explanation for observed results at high reagent additions might be the presence of steric effects due to the adsorption of these large molecules. Under these conditions, the distance between particles could be where the secondary minimum is located in the interparticle-potential-energy diagram, thereby causing a weak flocculation of the system. This could explain the difference in the behavior of the system between Triton X-165 (16 ethylene oxide groups) and Triton X-305 and Triton X-405 (30 and 40 ethylene oxide groups, respectively).

The effect of Triton X-165, Triton X-305 and Triton X-405 on the size distribution of flocs in the slurries was studied using the Andreasen pipette technique. In these experiments, the coal-water slurries were first prepared according to the standard procedure at a solids content of 60 wt%. Then, 3 wt% solids suspensions were prepared for performing the Andreasen pipette experiments. Figures 3, 4 and 5 present the apparent particle size distribution in the absence and presence of Triton X-165, Triton X-305 and Triton X-405, respectively. An assumed density of flocs equal to the density of coal was used in determining floc size distributions. Although the size distributions thus calculated were not the true size distributions, they did provide a technique for comparing the flocculation response of different experiments. These figures show

Figure 1. 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.

Figure 2. Effect of addition of different nonionic surfactants on the viscosity of Pittsburgh No. 8 coal-water slurries containing 60 wt% solids content at a shear rate of 83 s^{-1} .

Figure 3. Apparent particle size distribution for Pittsburgh No. 8 coal-water slurries in the absence and presence of Triton X-165 conditioned according to the standard procedure, using the Andreasen pipette technique.

Figure 4. Apparent particle size distribution for Pittsburgh No. 8 coal-water slurries in the absence and presence of Triton X-305 conditioned according to the standard procedure, using the Andreasen pipette technique.

that the observed Stokes diameters or sedimentation diameters with the addition of the nonionic surfactants up to 0.5 wt%, indicating flocculation of the system. However, at higher nonionic surfactant addition, the sedimentation diameter decreases, indicating dispersion of the system. These results are in agreement with those obtained by the relative sedimentation volume technique. However, the results of the particle size distribution measurements do not indicate the degree of flocculation of the system that is shown by the sedimentation volume tests at 1 wt% addition. Similar to the case of the cationic TMAE reagent reported in Quarterly Report No. 5, the apparent change in floc diameter due to the weak flocculation of the system could not be detected by the Andreasen pipette technique.

The sedimentation mean diameters for Pittsburgh No. 8 coal-water slurries in the presence of Triton X-165, Triton X-305 and Triton X-405 are presented in Figure 6. This figure shows that the sedimentation mean diameter increases with the addition of Tritons from 30 μm in the absence of reagents to about 35-38 μm at 0.5 wt% (flocculation) and then decreases to about 25-27 μm with the addition of 1 wt% (dispersion). Apparently, the addition of Triton reagents over 0.5 wt% results in the dispersion of the system due to the shielding of the particles by these nonionic surfactants, reducing particle-particle interactions.

Figure 7 presents the apparent size distributions obtained using the Andreasen pipette technique for 1 wt% addition of the three Tritons. Since the sedimentation mean diameter in the absence of reagents is 30 μm , this figure shows that all nonionic surfactants of the Triton X series disperse the system at 1 wt% addition. However, it seems that the formation of some aggregates from 10 μm particles is possible since the sedimentation mean diameter is around 25 μm and particles of 10 μm diameter are absent.

The viscosity of Pittsburgh No. 8 coal-water slurries as a function of shear rate in the presence of 1 wt% added the Tritons is given in Figure 8. Since in the absence of these nonionic reagents the viscosity of the coal-water slurries is 1510 mPa.s, the addition of the Tritons significantly reduces the viscosity of the suspensions. The results indicate that the viscosity

Figure 5. Apparent particle size distribution for Pittsburgh No. 8 coal-water slurries in the absence and presence of Triton X-405 conditioned according to the standard procedure, using the Andreasen pipette technique.

Figure 6. 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 Triton X165, Triton X-305 and Triton X-405.

Figure 7. Apparent particle size distribution for Pittsburgh No. 8 coal-water slurries in the presence of 1 wt% reagents addition conditioned according to the standard procedure, using the Andreasen pipette technique.

Figure 8. Viscosity for Pittsburgh No. 8 coal-water slurries as a function of shear rate in the presence of 1 wt% reagents addition conditioned according to the standard procedure.

Figure 9. Apparent particle size distribution for Pittsburgh No. 8 coal-water slurries in the absence of reagents conditioned according to the standard procedure, using the Andreasen pipette technique and Microtrac Particle Size Analyzer.

in the presence of Triton X-165 is around 600 mPa.s, decreasing to around 200 mPa.s upon the addition of the Tritons of higher molecular weight. The decrease in the viscosity may be due to the shielding of the coal particles with the reagents with the ethylene oxides groups oriented towards the bulk liquid. Possibly, the slightly higher value of the viscosity for slurries containing Triton X-405 in comparison with Triton X-305 might be due to the formation of reverse micelles or by steric effects. However, comparison of the results obtained from the relative sedimentation volumes with the apparent particle size distributions seems to suggest that the Andreasen sedimentation technique only indicates the tendency towards either a more flocculated or dispersed system.

To determine the reproducibility of the Andreasen pipette tests, the average of the apparent particle size distribution for tests performed in the absence of reagents for two different grinds of Pittsburgh No.8 coal is presented in Figure 9. The results of the Microtrac Particle Size Analyzer reported in Quarterly Report No. 5 are also included for comparison. Figure 9

shows similar unimodal-apparent particle size distributions with a mean particle size of around 30 μm obtained from the Andreasen pipette technique for the two grinds, indicating that this technique is able to detect the aggregation of particles in such systems. In case of the Microtrac, the high energy applied to the system in the centrifugal pump and in the measuring chamber of this apparatus tends to break the weak flocs formed and maintain the particles dispersed during the measurements. Because of this, the measured particle size distribution obtained using the Microtrac did not show any significant difference, both in the absence and presence of reagents.

HIGH PRESSURE ROLL MILL GRINDING OF COAL

One of the most exciting innovations in comminution in recent years is the development of the high-pressure roll mill [4]. Schoenert's research showed that the most efficient utilization of energy for the comminution of brittle solids is achieved when a single particle is broken slowly under pure compression. The next most efficient method is the compressive loading of a bed of particles in a piston-die arrangement. In this mode, comminution occurs primarily by very high, localized interparticle stresses generated within the particle bed. Energy consumption for a comparable degree of size reduction via the compression loading route is only about one-half of that for ball milling. Based on these results, Schoenert conceived of a device to carry out this process continuously and invented the high-pressure roll mill. Figure 10 shows a schematic representation of this mill, which comprises two-counter rotating rolls mounted on a strong frame. The bearings of one roll are fixed, while the other roll can slide laterally for adjustment of the gap. The milling force is applied by hydraulic or spring press loading of the movable roll. The rolls are choke fed from a feed hopper mounted directly above the roll gap. The ground product often comes out in the form of lightly compressed flakes or briquettes which are then broken up by a deagglomerator, such as by agitating it in water or by passing the material quickly through a hammer mill or ball mill. Since the first full industrial operation of the high-pressure roll mill in 1985, it has within only a few years proven to be the most efficient grinding mill in

Figure 10. Schematic representation of the comminution in a high-pressure roll mill.

the field of cement clinker grinding [5]. It is now also being used for grinding many other materials and ores with substantive energy savings of up to 50%. However, very little is known about the size reduction of coal in this machine.

Since the objective of this project is to study the rheology of coal-water slurries prepared by the high-pressure roll mill grinding of coal, grinding behavior of coal in this mill was studied during this quarter. Our laboratory-scale, choke-fed high-pressure roll mill consists of two counter rotating steel rolls of 200 mm diameter and 100 mm length. One roll is fixed in a housing while the other roll can slide freely laterally in parallel with the adjacent roll for adjustment of the roll gap. A milling force of up to 150 kN can be applied to the movable roll by a spring-loaded press. The rolls are driven by a 50 hp variable speed dc motor. The roll speed can be varied between 0.1 to 3 m/s and the roll gap from 0 to 6 mm. Mill torque is measured by a 1000 Nm torque transducer attached to the drive shaft and is linked with a computer system that is programmed to operate the mill while recording mill torque, roll speed and roll gap simultaneously.

In the grinding experiments, the coal feed was minus 1/4-inch sample of Pittsburgh No. 8 coal. The amount of energy invested in grinding per pass through the rolls can range from 0.5 to about 4 kWh/tonne. The specific energy input is increased by increasing the load on the spring-loaded press. The roll speed was varied in the range of 15 to 20 rpm and the feed rate was varied in the range of about 20 to 100 grams per second depending on the milling force applied.

Because of its plastic nature, bituminous coal is readily briquetted or agglomerated by the intense localized stresses encountered during comminution in the high-pressure roll mill. The degree of briquetting depends on the nature of coal and the compressive stresses. Therefore, to ascertain the true extent of grinding that has taken place in the roll gap prior to the briquetting of the ground mass, a deagglomeration procedure had to be developed, a technique that would not further comminute the coal. Preliminary tests showed that the agglomerates were generally strong enough to resist complete disintegration during wet-sieving or by ultrasonic treatment in a water slurry. It was then decided to use methanol which had been earlier identified as a good dispersing agent for coal because of its wetting properties. However, it soon became apparent that breaking up the agglomerates completely by just soaking them in methanol was also not possible. To overcome this problem, the agglomerates were stirred in a methanol suspension (100 grams of coal plus 100 ml of methanol) at 900 RPM for different time intervals in a beaker. After the stirring, the size distribution of the samples were obtained by first wet sieving minus 200 mesh, then drying the material and dry sieving the plus 200 mesh for 20 minutes on a series of Tyler sieves, using a Ro-Tap sieve shaker. For comparison, the size distributions of the ball milled coal product (in a 10-inch ball mill with 1-inch balls) and minus 8-mesh fraction in the feed were also analyzed using the same deagglomeration procedure.

Figure 11 shows the effect of the time of stirring coal-methanol suspensions on the amount of material reporting to the minus 200-mesh fraction. It can be seen that the percentage of minus 200-mesh material produced from the Pittsburgh No. 8 coal by deagglomerating the briquetted product from the high-pressure roll mill increases significantly at short stirring times. Since agglomerates are not expected to be formed in the ball mill or in the minus 8-mesh coal

Figure 11. Percentage of minus 200-mesh material in the high-pressure roll mill product, ball mill product and minus 8-mesh coal feed as a function of stirring time.

feed, the small increase in minus 200-mesh fraction in those two samples probably results from attrition, such as the breakage of the weak corners of particles during stirring. After about 30 minutes of stirring, the rate of increase of the minus 200-mesh Pittsburgh No. 8 fraction in the high-pressure roll mill product is similar to other products presented in Figure 11. The initial rapid increase in the amount of high-pressure roll milled Pittsburgh No. 8 product reporting to the minus 200-mesh fraction after short stirring times probably results primarily from the disintegration of the agglomerates, and the continued increase during the next 30 minutes of stirring represents the breakage of cracked and weak corners of particles.

The apparent amount of minus 200-mesh fine coal particles in the HPRM product will depend on the deagglomeration process used in determining the size distributions. Figure 12 shows how the stirring time (15 and 30 minutes) affect the results for the apparent amount of minus 200-mesh coal produced as a function of the specific energy expended in the high-pressure roll mill. From this plot two conclusions may be drawn. One, the amount of minus 200-mesh coal produced depends mainly on the energy invested in the high-pressure roll mill

Figure 12. Percentage of minus 200 mesh fraction produced as a function of specific energy expended in the high-pressure roll mill grinding of Pittsburgh No. 8 coal.

grinding but the procedure adopted for deagglomeration of the briquettes does have an effect on the measured results. Two, irrespective of the deagglomeration procedure, it is evident that the percent of fines generated increases more or less linearly with the specific grinding energy consumed in the initial stages and tends to level off at high energy inputs.

Figure 13 shows the size distribution of Pittsburgh No. 8 coal that had ground in the high-pressure roll mill with different energy inputs, using the 30 minute of stirring procedure for deagglomeration. As expected, the size distribution curves shift toward finer size with increased energy investment in the high-pressure roll mill. However, even at 3.74 kWh/t of energy input, the ground product contained only 30 percent of minus 200-mesh particles, which is much lower than 80 percent of minus 200-mesh particles required in the coal-water slurries for direct combustion in power plants. Therefore, deagglomeration and/or further grinding of the high-pressure roll milled product in ball mill or rod mill will be studied in the next quarter.

Figure 13. Size distribution of Pittsburgh No. 8 coal (S1) ground in the high-pressure roll mill at different pressures.

SUMMARY

The effect of the addition of nonionic surfactants on the aggregative stability of coal-water slurries was investigated through determination of sedimentation volumes and floc size distributions. Sedimentation volume measurements for nonionic surfactants show that for Triton X-165, Triton X-305 and Triton X-405, the sedimentation volume decreases slightly with added reagent up to 0.5 wt% addition, decreasing sharply for reagent additions between 0.5 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.

The Andreasen pipette technique, which is a gentle sedimentation technique, show differences in the measured particle size distribution as Triton X-165, Triton X-305 and Triton X-405 is added to the system. The results indicate that in the case of the Triton reagents the sedimentation mean diameter increases with added reagent up to an addition of 0.5 wt%, indicating flocculation of the system. Above this reagent addition, the sedimentation mean

diameter shows a sharp decrease as the Triton addition is increased, indicating dispersion of the system. These results agree with those of the relative sedimentation volume experiments. However, it appears that the apparent particle size distribution can only indicate the tendency towards a more flocculated or dispersed system. The comparison of the apparent particle size distributions measured by the Andreasen pipette technique and the Microtrac Particle Size Analyzer indicate that the system is flocculated in the absence of chemical additives.

Because of its plastic nature, bituminous coal is readily briquetted or agglomerated by the intense localized stresses encountered during comminution in the high-pressure roll mill. The degree of briquetting depends on the nature of the coal and the compressive stresses. We have found that the briquettes can readily be deagglomerated by stirring the comminuted products in a methanol suspension. Our results show that the amount of minus 200-mesh coal produced depends mainly on the energy invested in the high-pressure roll grinding. The percentage of fines generated increases more or less linearly with the specific grinding energy consumed in the initial stages and tends to level off at the high energy inputs higher than 3 kWh/t. Even at 3.74 kWh/t of energy input, the ground product contained only 30 percent of minus 200-mesh particles, which is much lower than 80 percent of minus 200-mesh particles required in the coal-water slurries for direct combustion in power plants. Therefore, future work will encompass grinding of the high-pressure roll milled product in ball mill or rod mill, using hybrid HP roll mill/ball mill circuit for feed preparation.

FUTURE WORK

Efforts to characterize the rheology of coal-water slurries will be continued. For this purpose, electrokinetic studies will be performed on coal, using the acousto-electrophoresis apparatus. Hybrid grinding of the high-pressure roll mill product in a ball mill will be studied and the effect of the high-pressure roll mill grinding of the coal on the rheological behavior of slurries will be evaluated during the next quarter.

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