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

DOE Grant No. DE-FG22-92PC92526

Quarterly Technical Progress Report No. 2
December 1, 1992 - February 28, 1993

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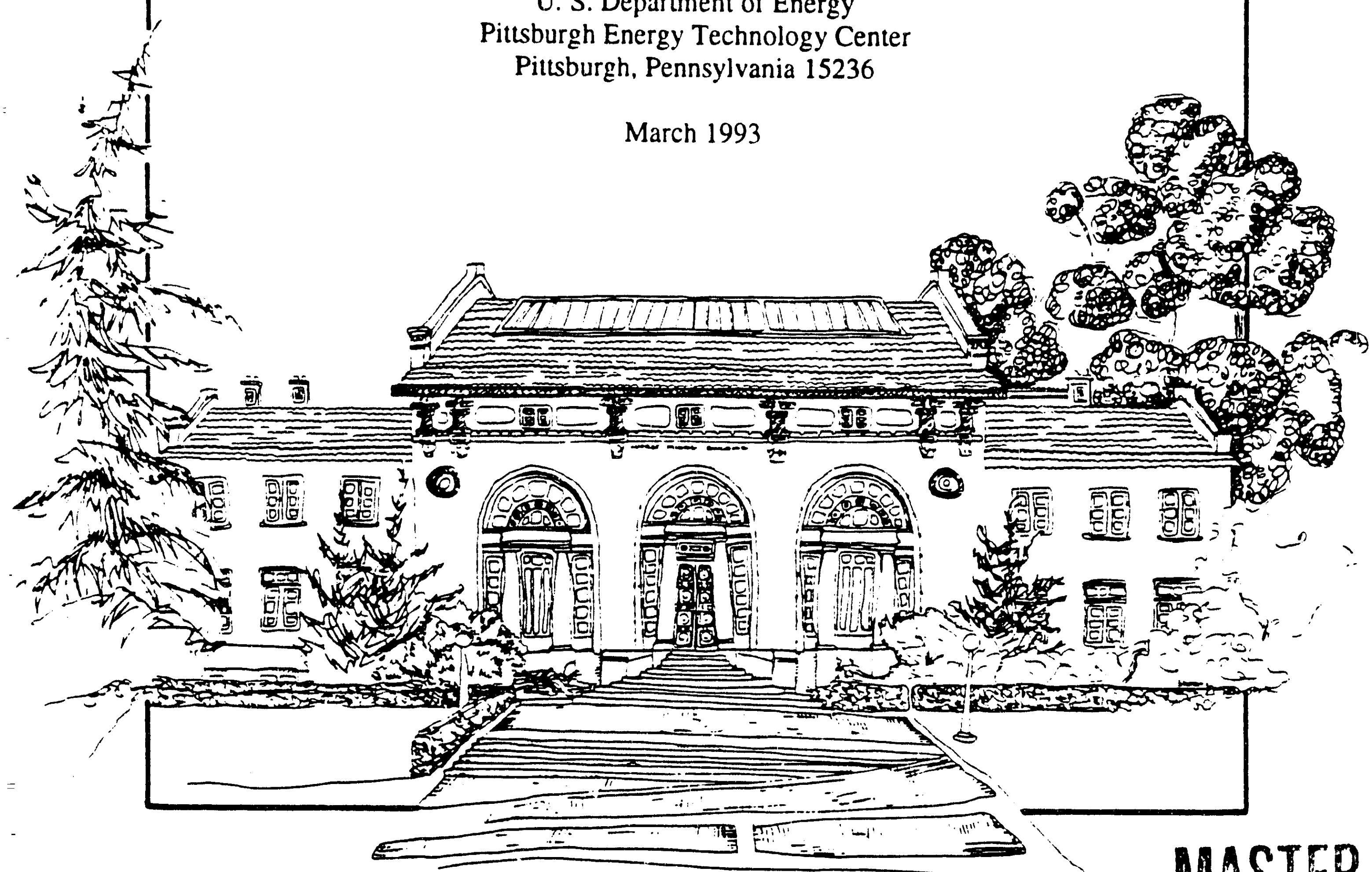

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INTRODUCTION

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 fully on its enormous low-cost coal resources.

In Quarterly Report No. 1, we presented preliminary results on the following topics:

i) calibrating the slurry viscometry apparatus,

ii) selecting a coal for initial study,

iii) standardizing experimental procedures for sample preparation, grinding and rheological measurements, and

iv) obtaining basic information regarding the rheological behavior and size distribution of coal ground in a ball mill under different grinding conditions.

During the second quarter, our research efforts were directed towards the following:

i) study of the effect of the solids content on the rheological behavior of coal-water slurries,

ii) determination of the reproducibility of the rheological measurements using the Haake Viscometer and finding a more reliable way to calculate the viscosity from the flow curve,

iii) comparison of the rheological behavior of coal-water slurries measured with the Haake viscometer and the Brookfield viscometer, and

iv) study of the effect of the immobilization of water on the viscosity of coal-water slurries.

The details of these studies are given in the paragraphs that follow.

EFFECT OF THE SOLIDS CONTENT ON THE RHEOLOGICAL BEHAVIOR OF COAL-WATER SLURRIES

The solids content of coal-water slurries is very important for their utilization. At a given viscosity, the higher the solids content the better the properties of the coal-water slurry. In order to study the effect of solids content, Pittsburgh No. 8 coal was ground in a ball mill for 30 minutes following the procedure given in Quarterly Report No. 1. To obtain more reliable results, three samples were prepared for each slurry density. After conditioning at 20°C in a shaker for 16 hours, the shear stress of each slurry was measured as a function of shear rate using a Haake Rotovisco RV12 viscometer with a MV II Sensor System. The reported values are the average results of three measurements for the three samples.

Figure 1 presents the shear stress as a function of the shear rate (flow curve) for slurries containing 50, 55, 60 and 63 wt% solids. These slurries were prepared with coal that had been ground to 90 percent minus 200 mesh. No additives were used in preparing the slurries. Clearly, at the same shear rate, the shear stress of the slurries with high solids content is much higher than those of lower solids content. Furthermore, Figure 1 shows that the shapes of each flow curve change from a Bingham plastic type (linear relation) at 50 and 55 wt% solids contents to a pseudoplastic type (shear thinning) at solids contents of about 60 wt % or more. This figure also shows that a coal-water slurry with over 60 wt % solids content has quite a high yield stress. The presence of this yield stress can be explained by the formation of an interparticle network structure due to the attraction among particles at high solids content (1,2).

An attempt was also made to measure the shear stress of a coal-water slurry containing 65 wt % solids. However, the stress-shear rate curves for this system were very complex in that the yield stress was very high but as soon as the yield stress was overcome, the measured shear stress decreased significantly. This indicates that immediately after the yield stress is overcome, phase separation occurs in the sensor system, that is, having only water and/or a very light slurry in contact with the rotor of the sensor system. Therefore, it was impossible to obtain reliable results for the slurries containing 65 wt % solids content (in the absence of an additive). The maximum effective solids volume fraction, $\phi_{m,eff}$, can be estimated by plotting (1/apparent viscosity)$^{1/2}$ versus the volume fraction (ϕ) and extrapolating the resulting straight line to the zero ordinate (2,3,4). The quantity $\phi_{m,eff}$ gives a physical limitation of the coal sample, which results in the apparent viscosity of the slurry approaching infinity. Figure 2 shows that $\phi_{m,eff}$ for this coal sample was 59 vol % solids content (66 wt % solids content assuming the density of the coal to be 1.35 g/mm^3). In order to further decrease the viscosity of the slurries at a given solids content, it is necessary to increase $\phi_{m,eff}$ by grinding the coal sample to an optimum particle size distribution and to modify the surface properties of coal particles by adding chemicals to the slurry.

In Quarterly Report No. 1, we used a graphic method to determine the viscosity from the flow curves. However, that method is quite operator-dependent. In order to obtain more reproducible results, a less operator-dependent method should be used. The Heschel-Buckley equation has been reported to be one of the best equations for describing the rheological behavior of coal-water slurries (2,5,6). This equation has the following form:

$$\tau = \tau_0 + k D^m \tag{1}$$

where, τ is the shear stress, τ_0 is the yield stress, D is shear rate, and k and m are constants. By fitting the experimental shear stress to Eq. 1 as a function of shear rate, the two constants k and m can be determined. The viscosity of a slurry at different shear rates can be calculated from the first derivative of Eq. 1 after k and m have been evaluated.

Figure 3 replots the results given in Figure 1 on log-log scale, along with the fitting lines according to Eq. 1. It can be seen from Figure 3 that the empirical Heschel-Buckley equation describes the experimental results quite well. The standard deviation for the three measurements is also shown in Figure 3 with the error bars. For shear rates between 7 s^{-1} and 230 s^{-1}, the standard deviation increases from 2.6 - 4.7 percent at 50 and 55 wt% solids content to 8.8 - 9.8 percent at 60 and 63 wt% solids content, which seems to be below those reported by other researchers (5). However, the standard deviation increases to over 10 percent at both the low

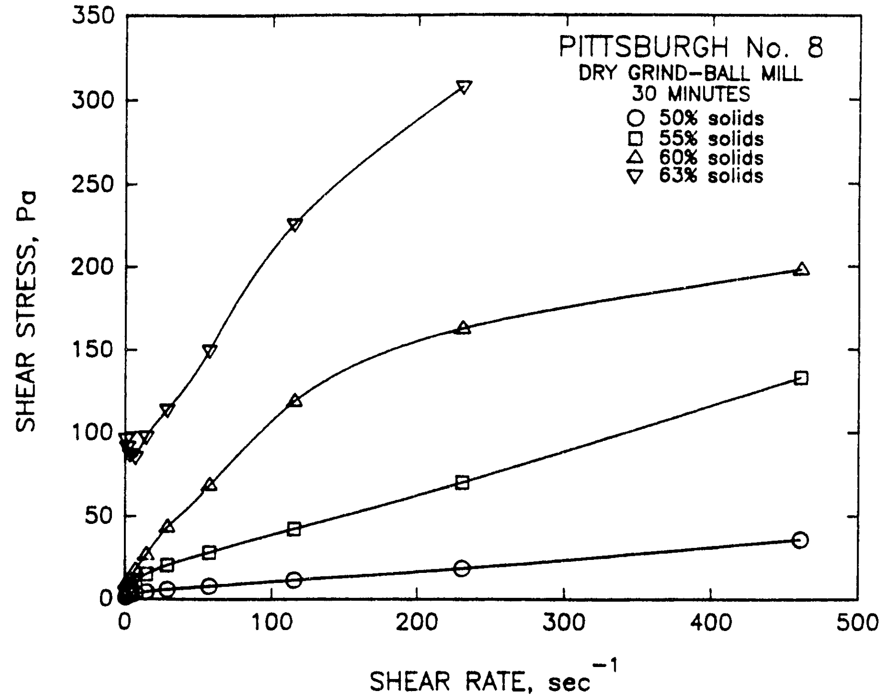

Figure 1. Flow curves (rheograms) for Pittsburgh No. 8 coal-water slurries of different solids contents at 20°C.

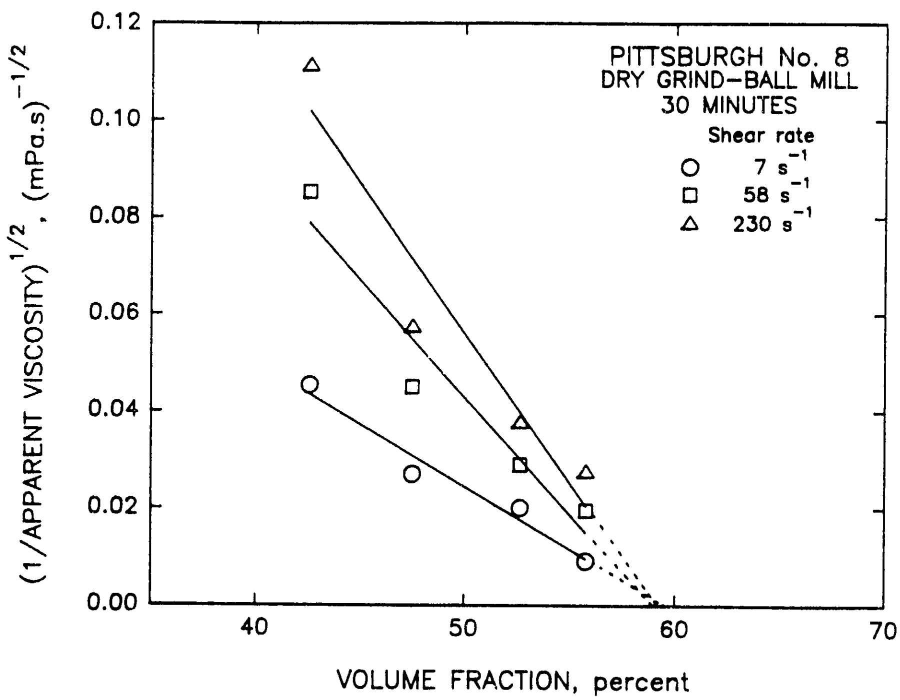

Figure 2. Plot of (1/apparent viscosity)$^{1/2}$ as a function of the volume fraction of particles for Pittsburgh No. 8 coal-water slurries at three different shear rates at 20°C.

end (0.9 - 3.6 s^{-1}) and high end (461 s^{-1}) of the shear rate, which may be due to the limitation of the viscometer used. Because of the small values of the error bars for slurries at 50 and 55 wt% solids content, they cannot be seen in this figure.

Figure 4 presents viscosities calculated as a function of shear rate for each solids content. As can be seen, the slurry behaves as a Bingham plastic fluid at 50 wt% solids content, (the viscosity is independent of shear rate), whereas slurries containing over 55 wt% solids behave as pseudoplastic fluid. The viscosity of the coal-water slurries at high solids content decreases as the shear rate increases. This behavior is related to the progressive destruction of the interparticle structure as the shear rate increases (1,2). As was expected, the viscosity of a slurry increases significantly as the solids content is increase at a fixed shear rate, as can be seen from the results given in Figure 5, where the viscosity is plotted as a function of the solids content at three different shear rates. The increase in observed viscosity with the increase in solids content is due to the hydrodynamic effects, that is, the decrease in available water for the coal particles to flow at high solids content, as well as the non-hydrodynamic effects, such as the interparticle interaction (especially for fine particles).

COMPARISON BETWEEN THE BROOKFIELD AND HAAKE VISCOMETERS

In order to compare the rheological behavior of coal-water slurries determined with different viscometers, a Brookfield Synchro-Lectric LVT viscometer with a No. 4 spindle was also used in this investigation. Because the Brookfield Synchro-Lectric viscometer does not have a controlled-temperature bath, measurements were performed in a controlled-temperature room at 21°C after conditioning the slurries in a shaker at 20°C for 16 hours. Calibration of this viscometer was conducted according to the manufacturer's instructions, using glycerol as a standard (8,9,10). For the Brookfield viscometer, only the shear rates can be calculated at each speed and it is impossible to calculate the shear stress. The reason is that the shear rate is a function of the geometry of the sensor system only, whereas the shear stress depends on both the

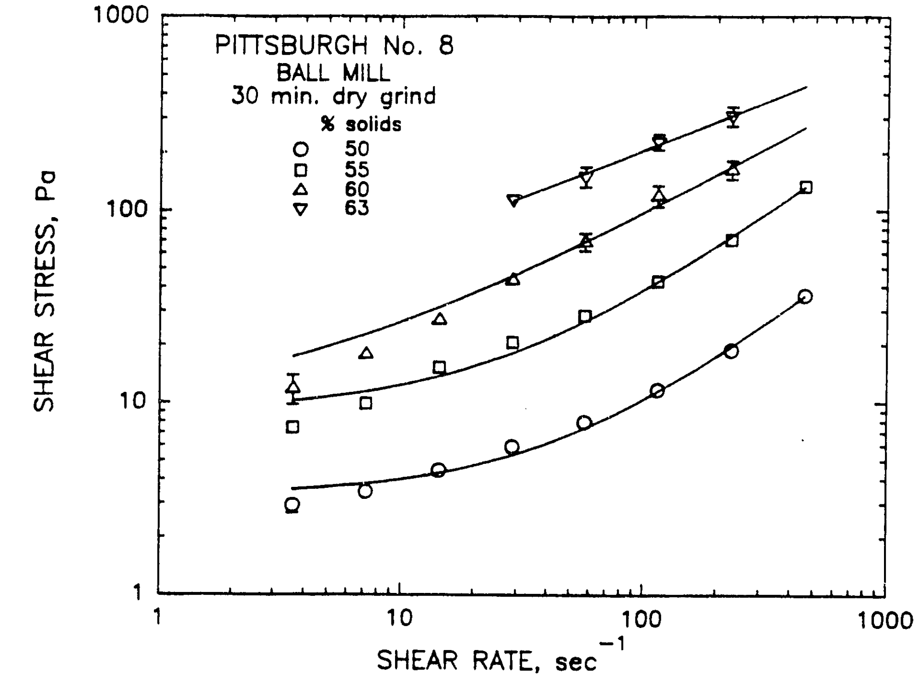

Figure 3. Shear stress as a function of shear rate for Pittsburgh No. 8 coal-water slurries of different solids content at 20°C, along with the measured standard deviation and the fitting curves of the Heschel-Buckley equation.

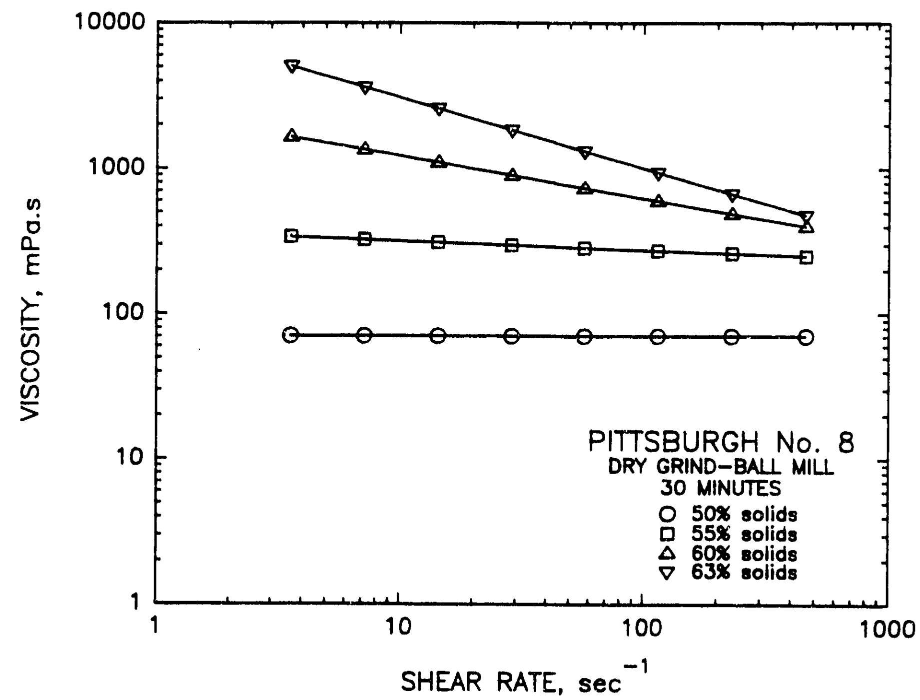

Figure 4. The viscosity of Pittsburgh No. 8 coal-water slurries of different solids contents as a function of shear rate at 20°C.

geometry of the sensor system and the torque at each shear rate. As a consequence, only the apparent viscosity measured with both viscometers can be compared at the same shear rates.

Figure 6 shows the apparent viscosity of slurries having solids contents of 50 and 55 wt% as a function of shear rate measured with both the Brookfield Synchro-Lectric LVT and the Haake Rotovisco RV12 viscometers. As can be seen from the plots given in this figure, the results obtained with both viscometers show that the apparent viscosity of the slurries decreases with increasing shear rate. The apparent viscosity of both slurries is quite close in the overlapping range of the shear rate of the two viscometers. However, at higher solids contents (60 and 63 wt%), the apparent viscosities measured with the Brookfield viscometer are much lower than those measured with the Haake viscometer. The spindle of the Brookfield viscometer seems to slide due to its small diameter (0.320 cm) at higher solids contents. It appears that the Haake Rotovisco RV12 viscometer with a MV II sensor is superior to the Brookfield Synchro-Lectric LVT viscometer with a spindle No. 4 for coal-water slurries because it can determine the shear stress, the apparent viscosity and the absolute viscosity in a wider range of shear rate at more precise temperature-controlled environments.

EFFECT OF WATER IMMOBILIZATION

When coal particles contact with water during the preparation and conditioning of coal-water slurries, water molecules will interact with the surface of coal particles, which in turn will influence the rheological behavior of coal-water slurries. These may include water penetration into the pores of coal particles, interactions with oxygen functional groups on the coal surface, development of electrical double layer, etc. (2). Preliminary investigation of the effect of these phenomena on the rheology of a coal-water slurry was conducted by first conditioning a slurry at 60 wt% solids for 0.25, 0.5, 0.75, 1 and 16 hours, and then measuring their rheological behavior with the Haake viscometer. In this study, special attention was given to the short conditioning times (between 0.25 to 1 hour).

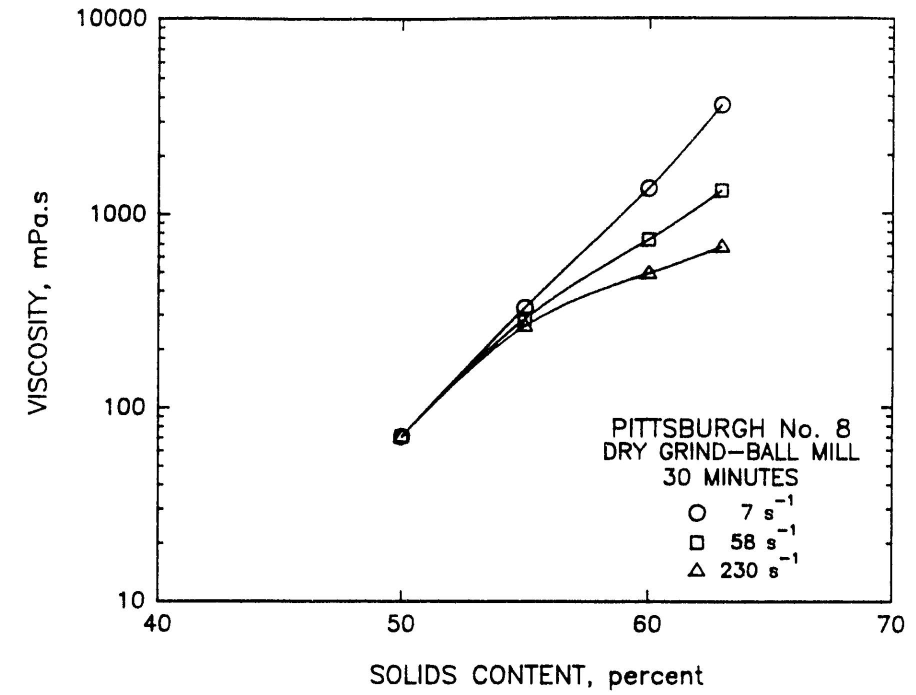

Figure 5. Effect of the solids content on the viscosity of Pittsburgh No. 8 coal slurries at three different shear rates at 20°C.

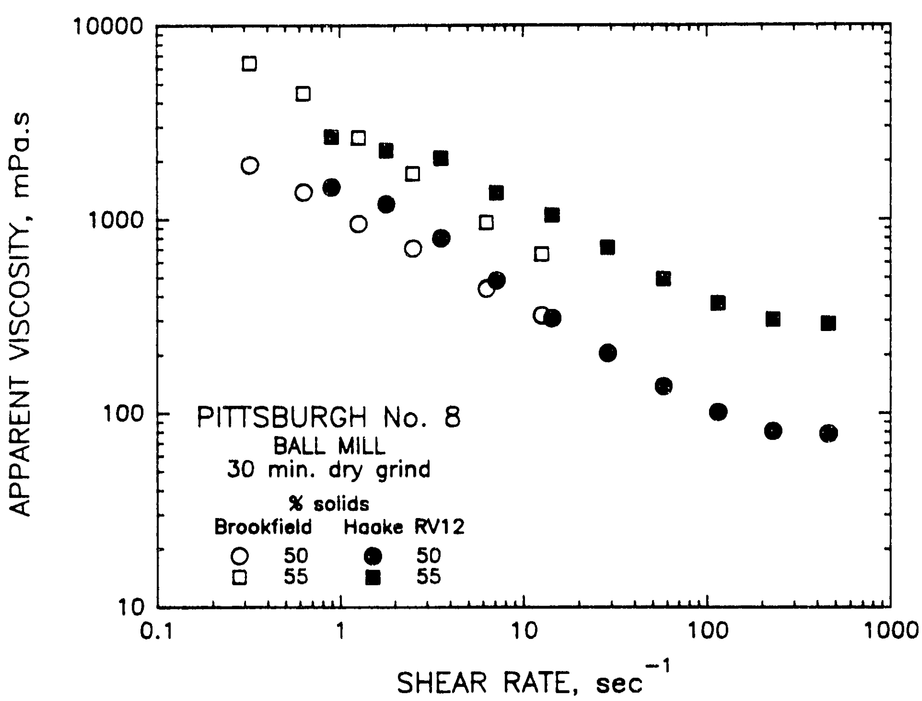

Figure 6 Comparison of the apparent viscosity as a function of shear rate for Pittsburgh No. 8 coal slurries measured with the Brookfield Synchro-Lectric LVT viscometer and the Haake Rotovisco RV12 viscometer.

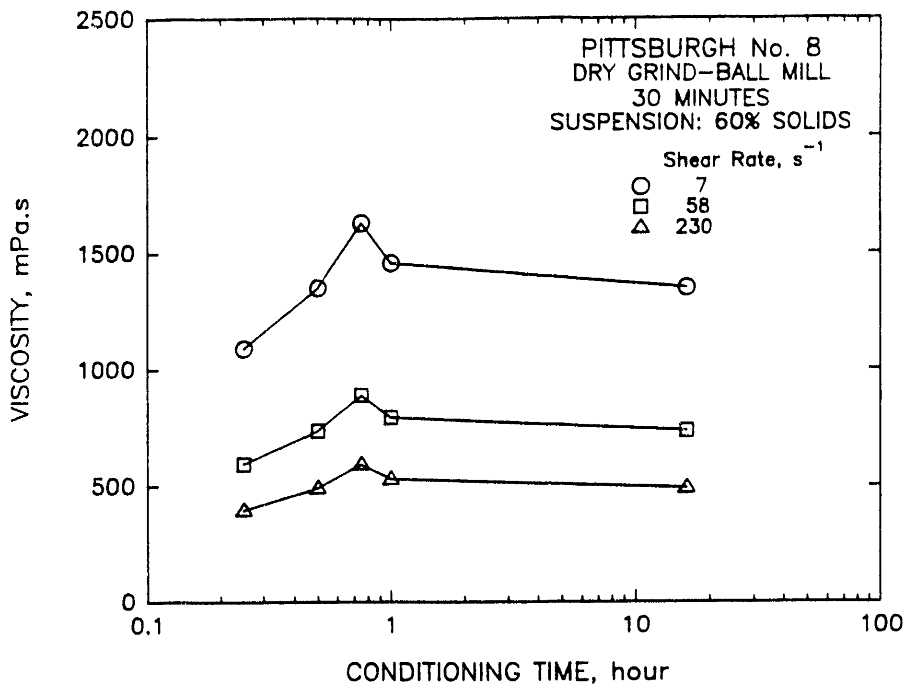

Figure 7. Effect of conditioning time on the viscosity for Pittsburgh No. 8 coal for three different shear rates at 20°C.

Figure 7 presents the viscosity as a function of conditioning time at three different shear rates. As can be seen from these results, which are the average of measurements of three samples, the viscosity of the slurries increases when the conditioning time increases from 0.25 to 0.75 hour and then decreases with further conditioning. Because more and more water may penetrate into the pores of the coal particles as the conditioning time is increased, less external water will be available for the particles to flow. This could cause the increase in the viscosity in the initial stages of conditioning. In addition, water molecules may be also immobilized by hydrophilic interactions with the oxygen functional groups on the coal surface, which may lead to the formation of a hydration layer on the surface of the coal particles. Because the hydration layer increases the effective volume of the coal particles, the viscosity of the slurries will also increase (7). On the other hand, when the conditioning time is extended, the hydration layer and the electrical double layer on coal surface may be developed further. A fully developed hydration layer on coal surface will decrease the hydrophobic attraction between coal particles and a fully developed electrical double layer will increase the electrical repulsion force between coal particles. Both of these factors would lead to reduced viscosity of the slurry.

SUMMARY

The rheological behavior of coal-water slurries made with Pittsburgh No. 8 coal at four solids contents was investigated with the Haake viscometer after conditioning for 16 hours at 20°C. The results show that the viscosity of the slurries increases as the solids content is increased. Slurries at high solid-liquid ratios not only exhibit significant yield stresses but also viscosities which decrease with increasing in the shear rate.

It was found that the empirical Heschel-Buckley equation fits the measured shear stress of slurries at different shear rates quite well. The standard deviation of the shear stress of coal-water slurries measured with the Haake viscometer was found to be less than 10%. The apparent viscosities measured with the Brookfield Synchro-Lectric LVT viscometer were comparable with values obtained with the Haake Rotovisco RV12 viscometer for slurries having solids contents of 50 and 55 wt%.

In studying the effect of conditioning time on the measured viscosity of coal-water slurries (at 60 wt% solids content), it was observed that the viscosity of a slurry increases when the conditioning time is increased from 0.25 to 0.75 hour and then decreases when the conditioning time is increased further. The initial increase in viscosity with conditioning time is probably related to the penetration of water into the pores of the coal, and the decrease in the viscosity at longer conditioning times over 0.75 hour may be due to the development of a hydration layer and the electrical double layer on coal surfaces.

RESEARCH WORK PLAN FOR NEXT QUARTER

During the third quarter, investigation of the effect of chemical additives on the viscosity, sedimentation rate and sedimentation volume of coal-water slurries will be initiated and study of experimental factors involved in slurry rheology measurements will be continued.

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