DOE/PC/92526--T12

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. 12
June 1, 1995 - August 31, 1995

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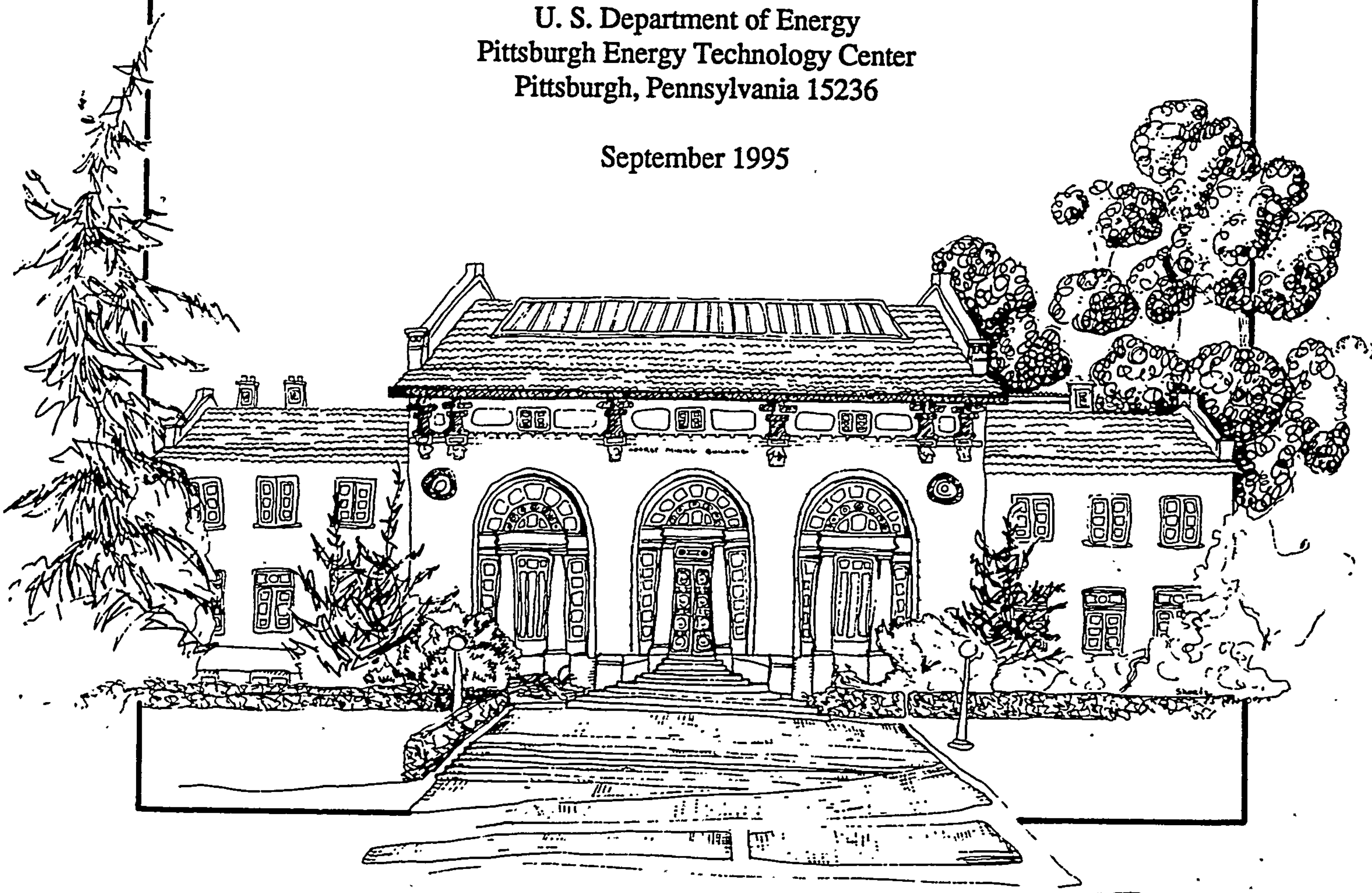
September 1995



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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.

In accordance with this objective, in the first stage of this project, considerable work was conducted to standardize experimental procedures for sample preparation, coal grinding, and rheological measurements to assure reproducibility of the experimental results. Since a Haake RV-12 viscometer with an MV-DIN sensor system was found to give the most reproducible results for measurement of slurry viscosities, it has subsequently been used for all of our rheological measurements. Methods were developed for applying the acoustophoresis technique for studying the electrokinetic behavior of concentrated coal-water suspensions. These measurements were carried out using this technique to identify the potential of chemical additives for functioning as reagents for effective dispersion. Detailed investigations of the effect of solids content and chemical additives on the rheology of coal-water slurries, prepared with fines produced by the ball milling of Pittsburgh No. 8 coal, were conducted during the first phase of our research program. These experiments were to provide a baseline against which the rheological behavior of slurries prepared with fines produced by high-pressure roll milling or hybrid high-pressure roll mill/ball mill grinding could be compared.

Detailed investigation of the effect of high-pressure roll milling on the energetics of fine grinding and the rheology of coal-water slurries prepared with such fines was carried out in the second stage of the project. Our experimental results indicated that a given degree of size reduction could be achieved by hybrid high-pressure roll mill / ball mill grinding with significantly lower energy expenditure as compared to that required for grinding in a ball mill alone. Viscosity measurements showed that the rheological properties of slurries prepared with fine particles produced by the hybrid grinding of coal are similar to or better than slurries prepared with fines produced by grinding coal in a ball mill only. A commercially available popular reagent used to prepare the slurries, Coal Master A-23-M from Henkel Corporation, proved to be a very efficient dispersant. Studies on the effect of grinding environment in the ball mill on the rheology of slurries showed that wet grinding with dispersants results in improved rheological properties.

We also presented a relationship between the packing characteristics of fine particles and the rheology of their slurries. Optimum particle packing corresponding to a minimum in the viscosity was achieved by mixing distributions with different median sizes.

Study of the aging behavior of slurries showed a non-linear increase in their apparent viscosity over time. This increase was found to be partly due to iron released through the oxidation of pyrite contained in the coal. This was confirmed through spectroscopic studies and chemical analysis. Removal of iron by washing coal with iron-complexing reagents significantly lowered the apparent viscosity of freshly prepared coal-water slurries and slowed down the degradation of the rheological properties of the slurries, but only temporarily. Physical cleaning of coal, prior to the preparation of slurries, further improved the long-term rheological behavior of the slurries.

The rheological property of slurries is a manifestation of the particle-particle interaction and the particle-fluid interaction in the slurry. Improvement in the rheology of slurries could be brought about by suitably altering these interactions. The research during this quarter was, therefore, directed towards investigation of the effect co-addition of reagents, which could modify these interactions, on the rheology of coal-water slurries. More specifically, the influence of co-addition of sodium hexametaphosphate and vacuum oil, with CoalMaster as the primary dispersant, on the rheology of coal-water slurries was investigated in detail.

THE EFFECT OF CHEMICAL ADDITIVES ON THE RHEOLOGY OF COAL-WATER SLURRIES

The rest structure of a suspension is probably one of the most significant factors in determining its rheology (Beazley, 1979). The rest structure of suspensions depends on the balance of interparticle forces which can be modified by addition of suitable chemicals to the suspension (Beazley, 1979). There are three kinds of rest structures for concentrated suspensions: weakly flocculated, stable, and ordered stable (Pugh and Bergstrom, 1994). Weakly flocculated slurries usually have very high viscosity at low shear rate, mainly because of their three-dimensional flocculated structure, and exhibit shear thinning with increased shear rates due to the breakage of such structures. Slurries with ordered rest structure exhibit a low viscosity and may undergo shear thickening at high shear rates due to an order-disorder transformation.

The rest structure of coal-water slurries is primarily determined by the surface charge of the particles and the hydrophobic interaction between the coal particles. The formation of a water film on the coal particles is governed by their hydrophobicity. The water film reduces direct particle-particle interaction during shearing, thus contributing to lower viscosity of the slurries. Increased thickness of the film, however, could reduce the amount of free water, resulting in an effective increase of the particulate volume fraction and hence the viscosity of the slurries. The formation of a sufficiently thin water film, while keeping the hydrophobic interaction between the particles to a minimum, can be achieved by suitably modifying the hydrophobicity of the coal surface. The effect of addition of vacuum oil, which is comprised of hydrocarbons with molecular weight of several hundreds, in conjunction with CoalMaster on the rheology of coal-water slurries was therefore investigated in detail.

At 67 percent solids content, coal-water slurries prepared with 1 wt% CoalMaster as dispersant have a weakly flocculated rest structure. While this is primarily a consequence of the balance between the hydrophobic and the electrical interactions, the surface charge of the mineral matter in coal could potentially lead to flocculation through heterocoagulation. Sodium hexametaphosphate [$(NaPO_3)_6$] is a commonly used dispersant in the flotation and selective flocculation of minerals. The adsorption of charged $(PO_3)_6^{6-}$ species on the surfaces of partially-locked as well as liberated mineral matter makes those surfaces highly negatively charged, that is similarly charged to coal particles with adsorbed CoalMaster. The effect of co-addition of sodium hexametaphosphate on the rheological behavior of coal-water slurry has also been studied during this quarter.

Effect of Co-addition of Sodium hexametaphosphate

Preliminary studies showed that addition of sodium hexametaphosphate (SHMP) alone as the dispersant does not improve the rheology of coal-water slurries, presumably because of its poor adsorption on coal. Experiments were therefore performed where different dosages of SHMP were added to the coal-water slurry in conjunction with 1 wt. percent CoalMaster. The shear stress of these slurries as a function of the shear rate are shown in Figure 1. While all the

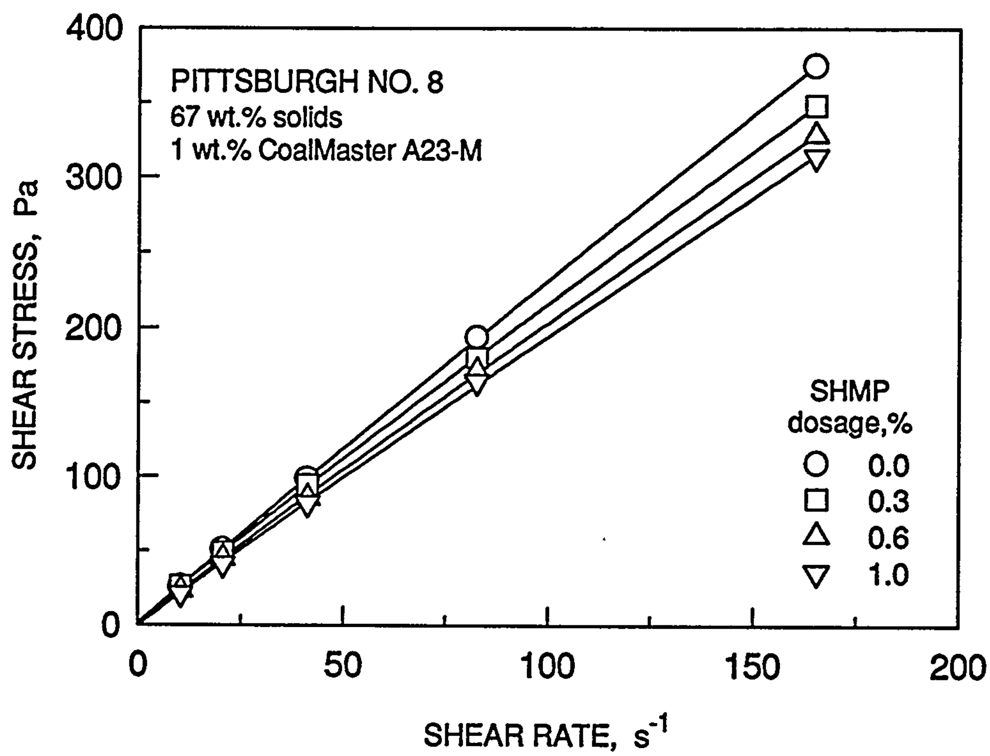

Figure 1. Effect of co-addition of sodium hexametaphosphate on the flow behavior of coal-water slurries.

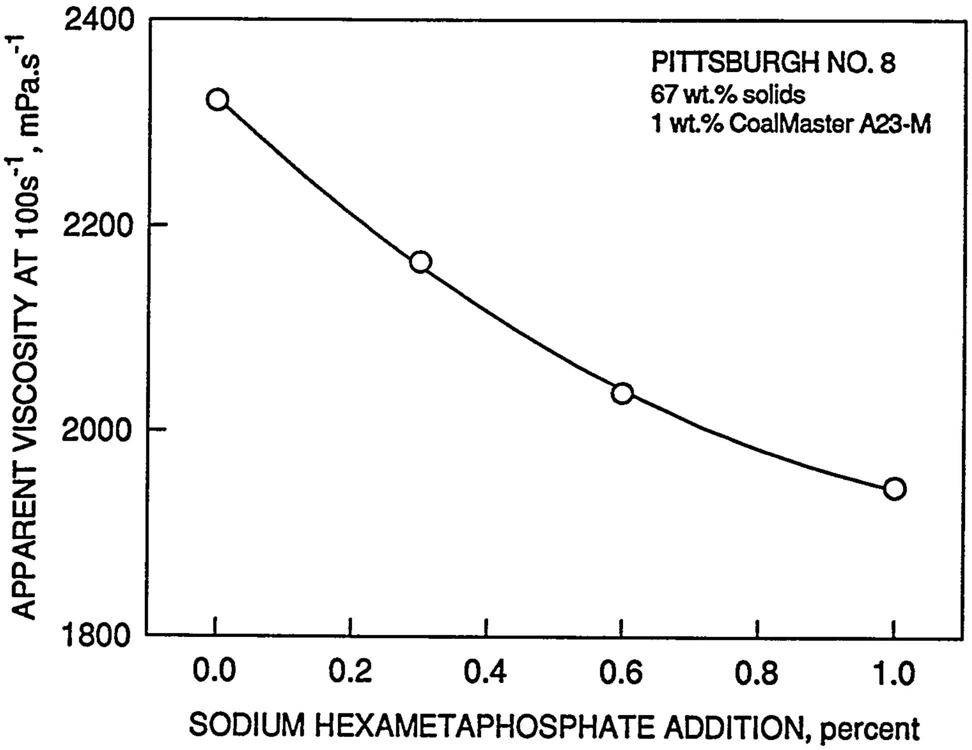

Figure 2. Effect of co-addition of sodium hexametaphosphate on the viscosity of coal-water slurries.

slurries exhibit near-Newtonian behavior, the decreasing slope of the plots with the increase in the SHMP dosage indicates a progressive lowering of the viscosity of the slurries. Figure 2 shows the apparent viscosity at shear rate of $100s^{-1}$ for these slurries as a function of SHMP addition.

Effect of Co-addition of Vacuum Oil

As anticipated, the addition of vacuum oil alone significantly increased the yield stress as well as the viscosity of the slurry. This was due to increased hydrophobic attraction between the coal particles due to oil addition. Addition of sodium hexametaphosphate, however, restored the balance between the hydrophobic and electrostatic interactions. Increasing the dosage of SHMP transformed the slurry structure from a flocculated one to a well dispersed one. As the amount of oil is increased, the tendency to agglomerate the coal particles through coalescence of the oil on adjacent particles may also increase. The addition of highly charged hexametaphosphate ions could prevent this coalescence through charge repulsion. The transition of the slurry structure

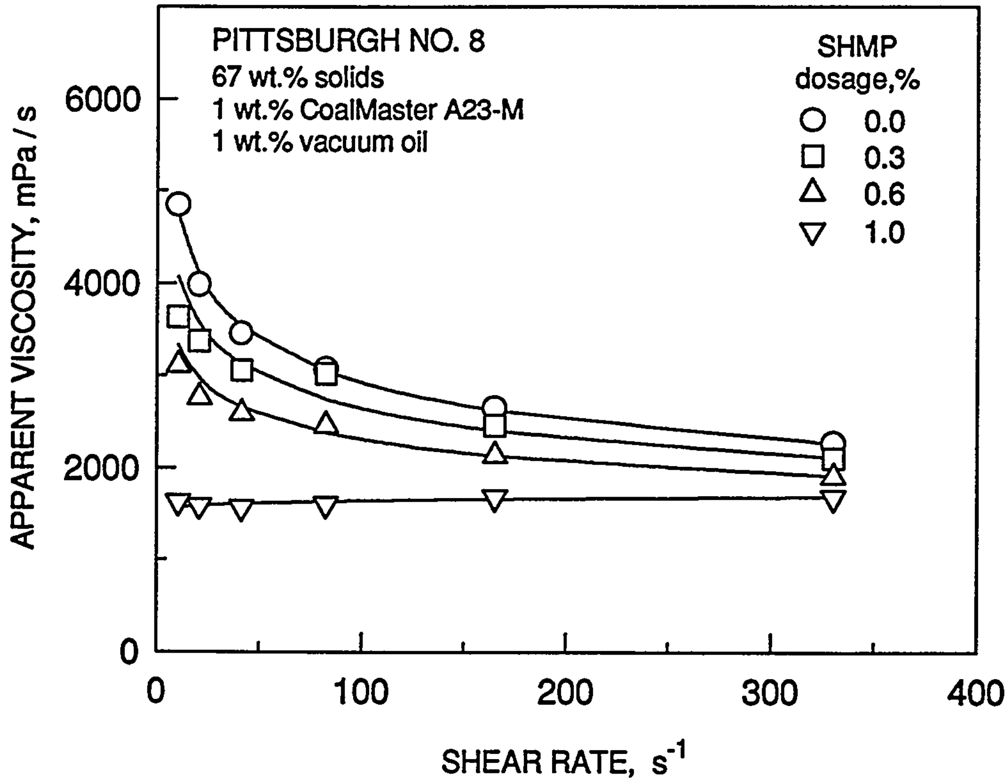

Figure 3. Effect of sodium hexametaphosphate addition on the structure (viscosity) of coal-water slurries prepared with CoalMaster and vacuum oil as viscosity modifiers.

from a flocculated one to a well dispersed one is clearly demonstrated in Figure 3 which shows the apparent viscosity of slurries, prepared with the addition of 1 wt% each of vacuum oil and CoalMaster and various dosages of SHMP, as a function of the shear rate. The apparent viscosities of these slurries at shear rate of $100 s^{-1}$ are plotted in Figure 4 as a function of sodium hexametaphosphate dosage. Further investigations to delineate the influence of oil addition on the rheology of coal-water slurries were carried out with slurries containing 1 wt% each of CoalMaster and SHMP as co-added dispersants.

Figure 5 shows the effect of oil dosage on the rheology of coal-water slurries. It is apparent from the figure that there is an optimum dosage of oil addition which results in a minimum viscosity of the slurry for a given dosage of dispersants. Unfortunately, the addition of oil does not significantly lower the viscosity.

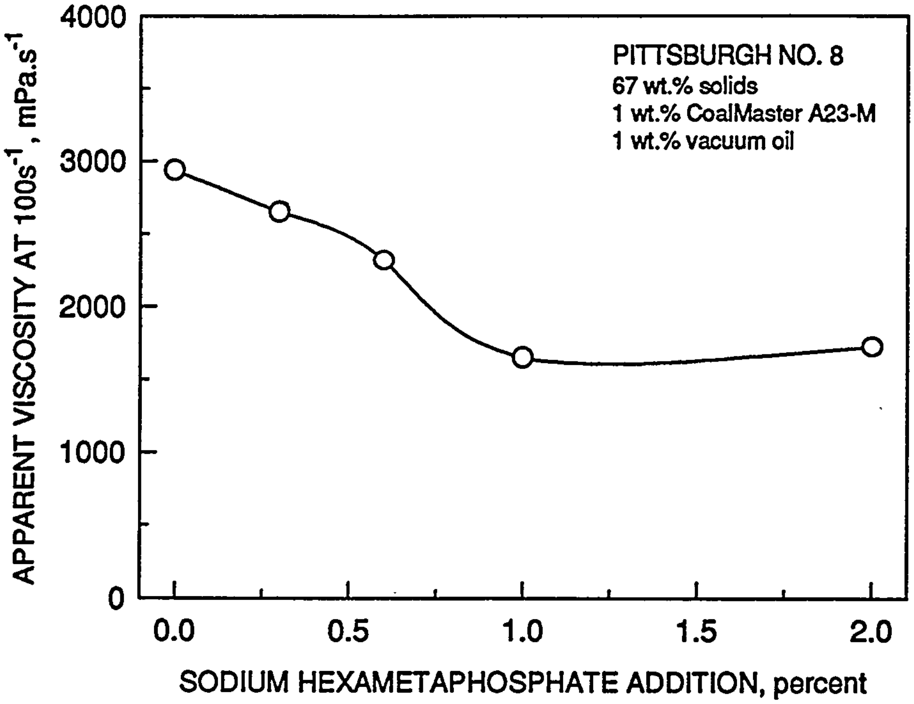

Figure 4. Effect of sodium hexametaphosphate dosage on the viscosity of coal-water slurries prepared with CoalMaster and vacuum oil as viscosity modifiers.

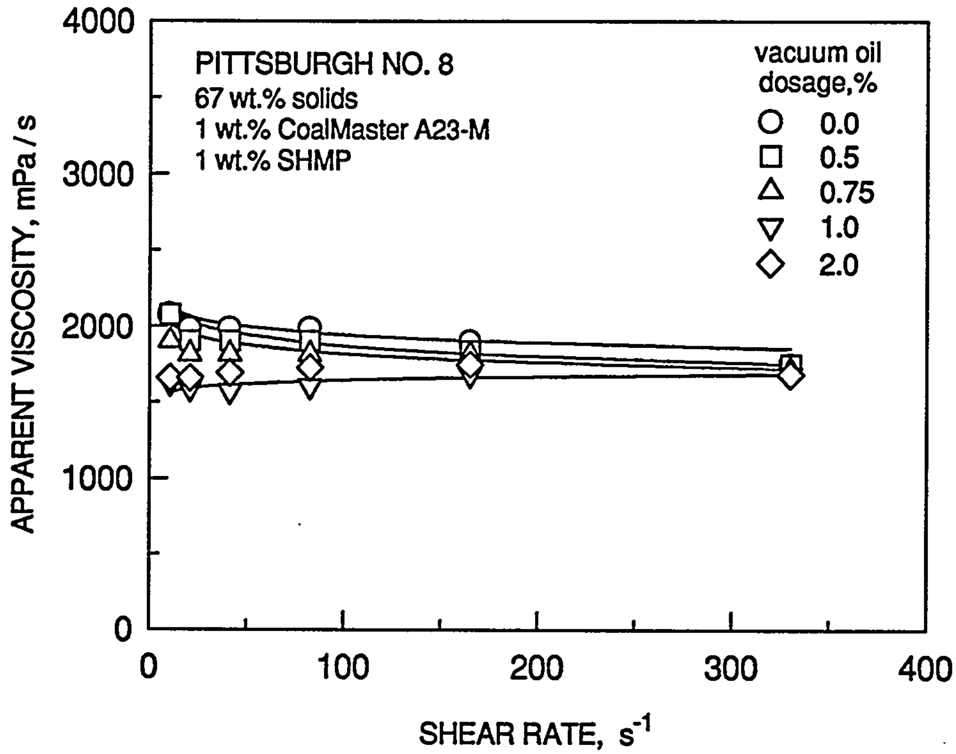

Figure 5. Effect of vacuum oil dosage on the viscosity of coal-water slurries prepared with CoalMaster and SHMP as dispersants.

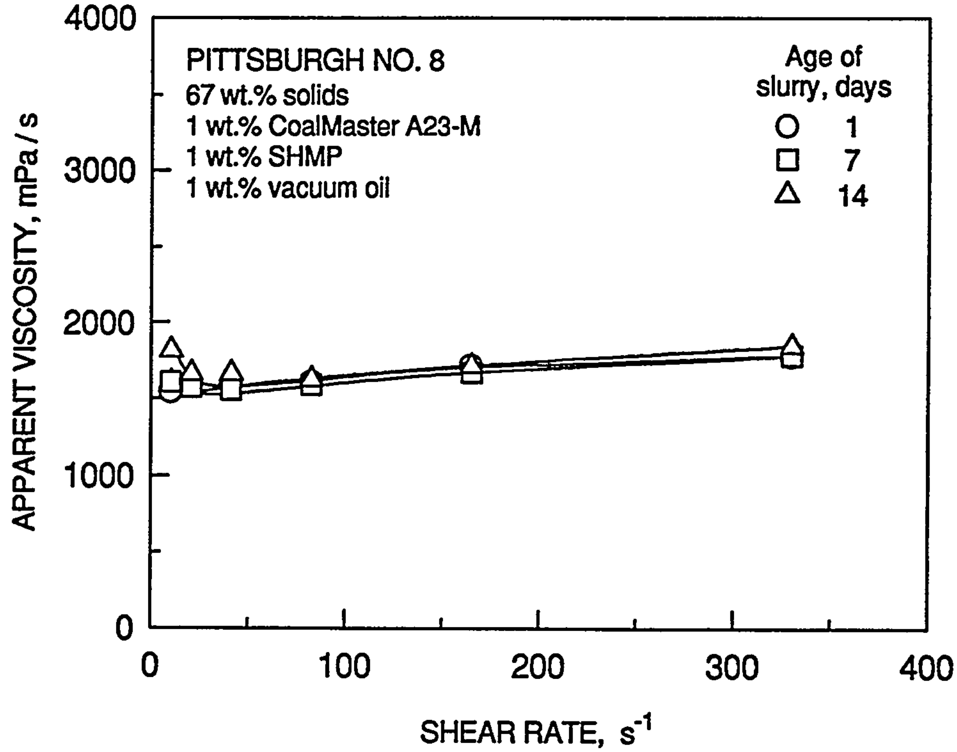

Figure 6. Effect of vacuum oil addition on the aging behavior of coal-water slurries.

The addition of oil lowers the interaction of water with the coal surface. The degradation of rheological properties of slurries is mainly due to loss of free water through adsorption of water in the pores of coal particles over time and the leaching of iron from pyrite in coal by water and oxygen. Since the addition of oil reduces the coal-water interaction, it was expected that oil additions should have some bearing on the aging behavior of coal-water slurries. Preliminary aging studies indicate that oil addition indeed improves the long-term aging behavior of coal-water slurries. As shown in Figure 6, there is no discernible change in the rheological properties of slurries containing 1 wt% oil over a period of two weeks.

Optimization of CoalMaster Dosage

Our research has shown that co-addition of sodium hexametaphosphate and vacuum oil along with CoalMaster as viscosity modifiers improves both the short-term and long-term rheological properties of coal-water slurries. In order to minimize the reagent addition,

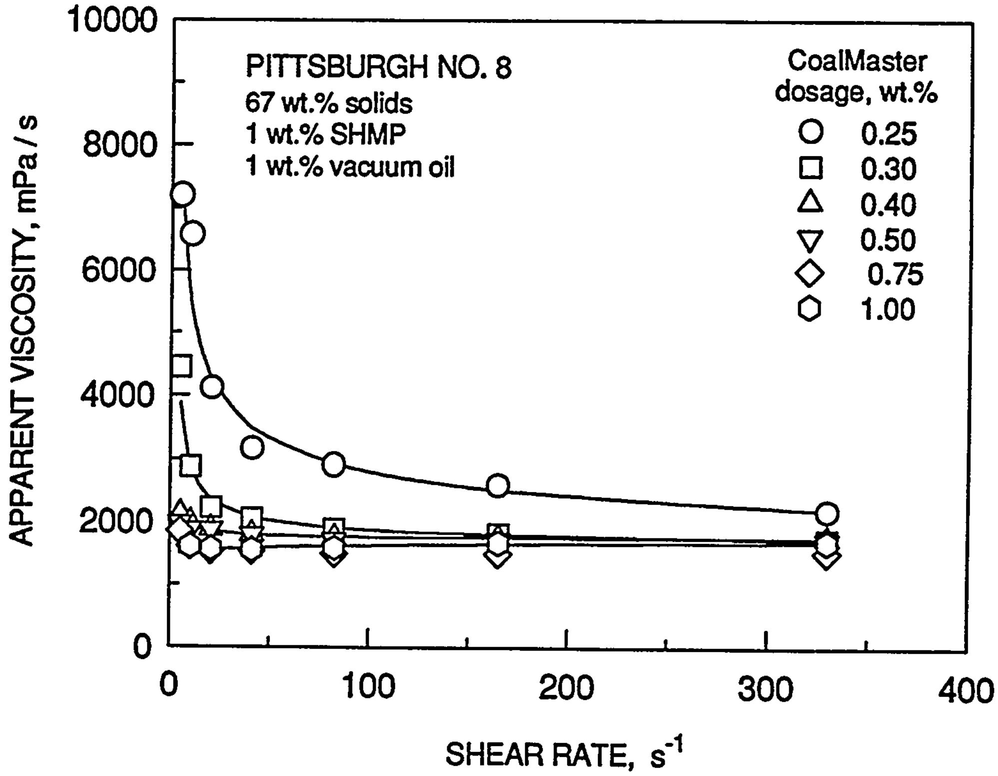

Figure 7. Effect of CoalMaster dosage on the viscosity of coal-water slurries prepared with vacuum oil and SHMP co-added as viscosity modifiers.

experiments were carried out to optimize the CoalMaster addition. The results, presented in Figure 7, indicated that while addition of 0.75 wt% CoalMaster results in the best rheological properties, CoalMaster dosage can be reduced to 0.4 wt% without significantly affecting the rheology of the slurries.

RESEARCH WORK PLAN FOR THE NEXT QUARTER

Our research, so far, has helped delineate the factors that control both the short- and long-term rheological properties of coal-water slurries and identify the reagents for modifying these factors. We have also identified the best operating conditions for the high-pressure roll milling for the production of coal fines for the preparation of slurries. Our research emphasis in the next quarter will be to identify the optimum operating conditions, feed distributions, and reagent additions which will result in maximum solids content of the slurries with acceptable viscosities.

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