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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. 7
March 1 - May 31, 1994

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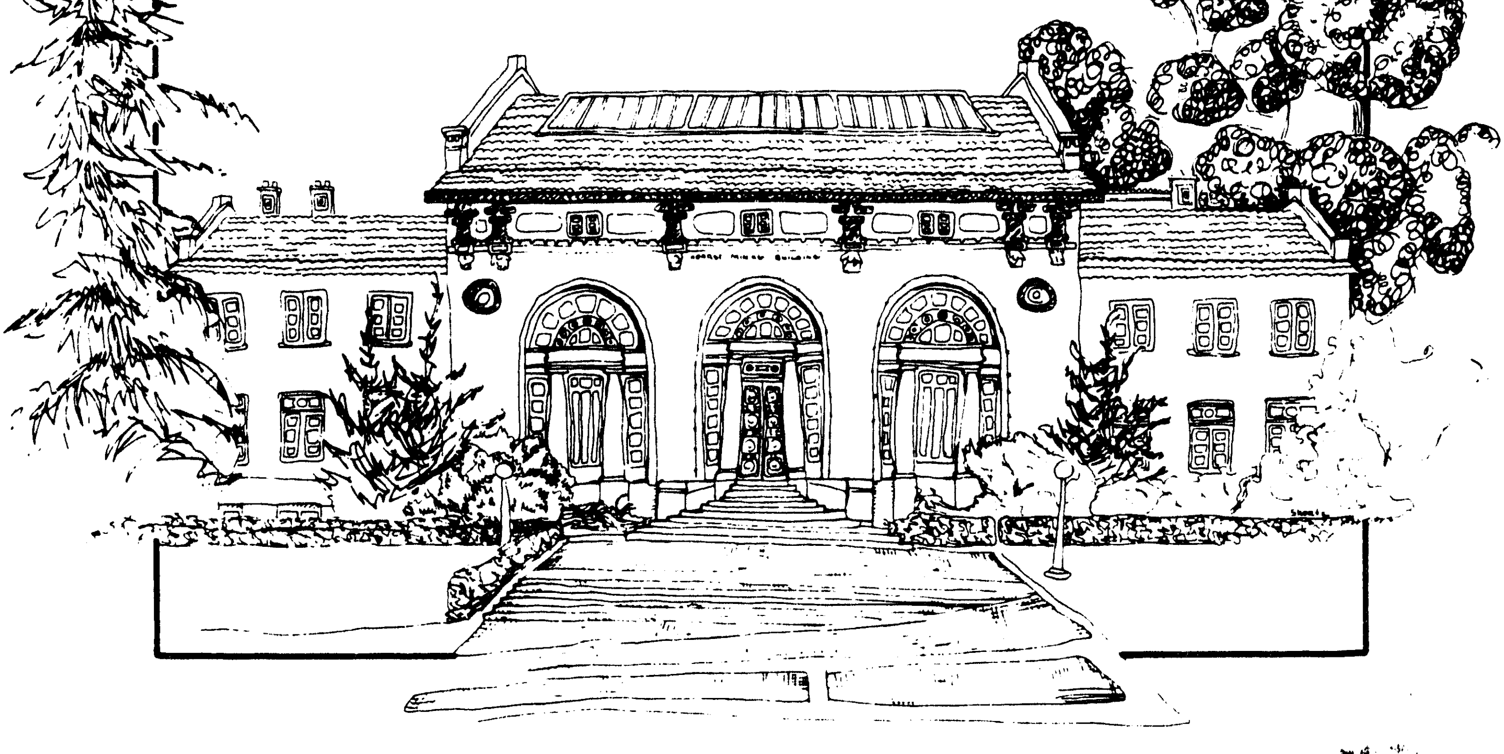

Hearst Mining Building
University of California, Berkeley

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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 and water immobilization on the rheological behavior of coal-water slurries, including the role of different viscometers, such as the Haake Rotovisco RV-12. and Brookfield Synchro-Lectric LVT on the measured results. In Quarterly Report No. 3, we compared the rheological behavior of Pittsburgh No. 8 coal-water slurries using different sensor system. It was found that the Haake-Rotovisco RV-12 with the MV-DIN sensor system performs better than the standard MV-II sensor system at high solids content. Also, Quarterly Report No. 3 summarized the results of studies on the effect of various 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 dosages (0.75-1.0 wt%), with reagents having larger numbers of ethylene oxide groups in their molecular structure being the most effective. In Quarterly Report No. 4, studies on the role of the initial mixing procedure in the preparation of coal-water slurries were summarized. 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 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 of dry coal has little effect on suspension rheology, up to 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 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 systems, 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.

In Quarterly Report No. 6, the effect of nonionic surfactants (Triton X series) on the aggregative stability of coal-water slurries was studied by measuring the relative sedimentation volume and floc size distribution. At low reagent addition, Tritons flocculate the system. However, at higher reagent addition, Tritons disperse the system and lower the viscosity. Grinding of Pittsburgh No. 8 coal in the high-pressure roll mill and deagglomeration of the ground product by stirring in methanol suspensions were also conducted. Even at high energy input, in open circuit the high pressure roll mill could not produce a ground product with more than 30 percent of minus 200-mesh particles, which is much lower than 80 percent minus 200-mesh particles required in the coal water slurries for direct combustion in power plants.

SCOPE OF THE PRESENT INVESTIGATION

When bituminous coal is ground in the high-pressure roll mill the product comes out in the form of an agglomerates or briquetted material, which must be deagglomerated. One way to accomplish this is to regrind the roll mill product in a ball mill. This procedure is termed hybrid grinding. An advantage of hybrid grinding is that the individual coal particles that constituted the briquetted product contain many flaws and microcracks that reduce the overall energy in the ball milling step. The viscosity of slurries prepared with coal by hybrid grinding and ball mill grinding only were compared. The effects of a commonly used dispersant (Coal Master A-23-M from Henkel Corporation, with the active ingredient of 42%), various anionic reagents, and washing the coal to remove dissolved salts on slurry rheology were studied. The effect of aging the slurry on its viscosity and stability was also followed. Preliminary electrokinetic studies at low suspension concentrations were performed in order to understand the behavior of coal water slurries in the presence and absence of Coal Master A-23-M reagent. Coal analyses were performed to determine the moisture, ash content and iron content of prepared samples.

FEED PREPARATION

One of the primary objectives of this research project has been to investigate the rheology of coal-water slurries prepared from coal fines generated by high-pressure roll mill grinding. As already stated, high-pressure roll mill grinding of coal results in briquetted product which has to be deagglomerated and ground further to obtain the required amount of minus 200-mesh coal fines for preparation stable slurries. Ball mill deagglomeration and grinding of the briquetted product has been carried out in open-circuit as well as in closed-circuit configuration. Both the circuits were operated in the batch mode. Figures 1a and 1b present a schematic representation of the open-circuit and closed-circuit grinding configurations, respectively. In an open-circuit grinding experiment, a fixed weight of the high-pressure roll mill product is ground in the ball mill until the coal charge has reached a desired fineness (approximately 95 % minus

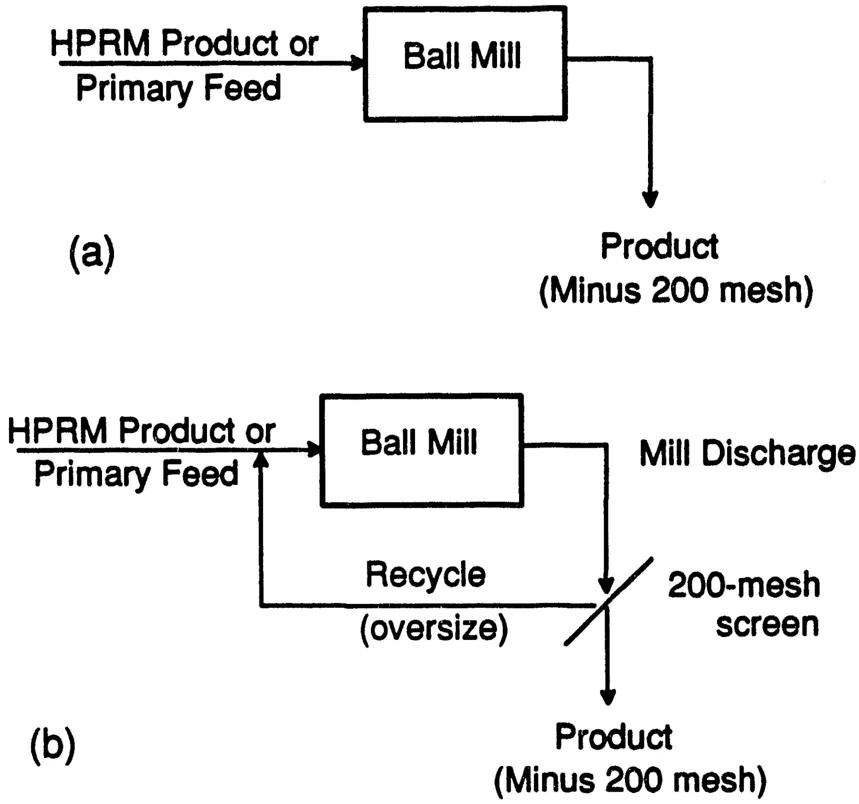


Figure 1. Schematic representation of (a) open-circuit and (b) closed-circuit grinding configuration.

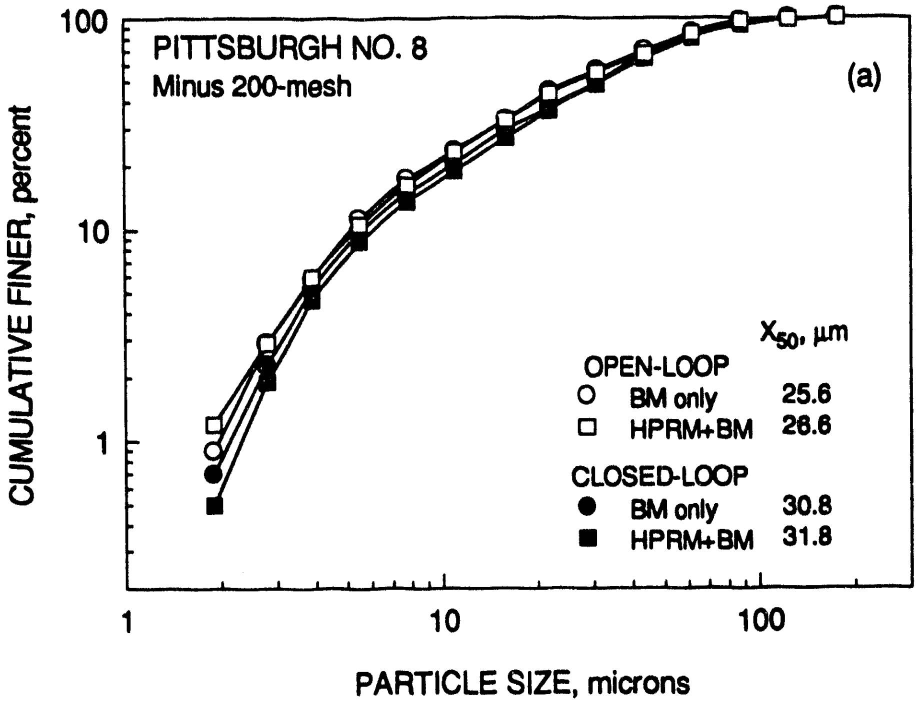
200-mesh). In the closed-circuit grinding mode, a fixed amount of the high-pressure roll mill product is first ground in the ball mill to, say, 40 percent minus 200-mesh. The mill discharge is screened at 200-mesh, with the minus 200-mesh fraction being the desired product. The screen oversize is mixed with fresh high-pressure roll mill product to make up the balance of charge to the ball mill. In these experiments, the ball mill grinds are carried out under batch conditions.

The minus 200-mesh feed used for studying the effect of dry storage on the rheology of the slurries were prepared by grinding minus 1/4-inch coal samples, dried at 40^{0} C for 15 hours in a convection oven, in our laboratory-size high-pressure roll mill, with an energy expenditure of 2.0 kWh/ton of coal feed. The high-pressure roll mill product was subsequently ground in a stainless steel ball mill, 11 inches long and 10 inches in inner diameter, charged with grinding media charge comprised of 30 kg of 1-inch diameter steel balls that occupied about 50% of the mill volume at rest. The mill was run at 54 rpm, which is 60% of the critical speed. In each experiment, the coal charge was 1.5 kg and the grinding time was 4 minutes, which corresponds to an energy expenditure of 3.16 kWh/ton of coal ground. The ball mill discharge was dry-sieved on a 200-mesh screen in a Ro-Tap machine for 20 minutes. The minus 200-mesh product was stored in sealed plastic bags. The ball mill was charged with the screen oversize along with fresh high-pressure roll mill product, as make-up charge, for the next grinding cycle.

Fresh samples of minus 200-mesh coal fines were prepared as follows. Plus 1/4-inch coal sample was first equilibrated under atmospheric conditions to allow the moisture content of the coal to reach its equilibrium value. Plus 1/4-inch particles were then crushed in a laboratory jaw-crusher followed by multi-stage crushing in an ordinary roll crusher until the entire sample was finer than 8-mesh. The minus 8-mesh feed was subsequently ground in the high-pressure roll mill, with an energy expenditure of 2.0 kWh/ton of feed. The high-pressure roll mill product was then ground in a stainless steel ball mill, 10 inch long and 8 inch in internal diameter. The grinding media consisted of 8.62 kg of 1-inch diameter steel balls, 5.18 kg of 0.75-inch steel balls and 2.85 kg of 0.5-inch steel balls (the total weight being 16.65 kg and occupying about 45% of the mill volume at rest). The mill was run at 56 rpm, which is 60% of the critical speed, with the coal charge being 500 grams. Grinding for 20 minutes resulted in the production of fines with 95% passing 200-mesh.

In addition, in each case, primary coal samples were ground directly in the ball mill for the production of minus 200-mesh fines. The rheological characteristics of the slurries prepared from this material provide the baseline against which behavior of the slurries prepared from fines produced by the high-pressure roll mill grinding of coal could be compared.

The size distributions of the various minus 200-mesh samples were determined using the L&N Microtrac Particle-Size Analyzer. Figure 2a shows the size distributions of the various feeds used for making the coal-water slurries, and in Figure 2b the size distributions are



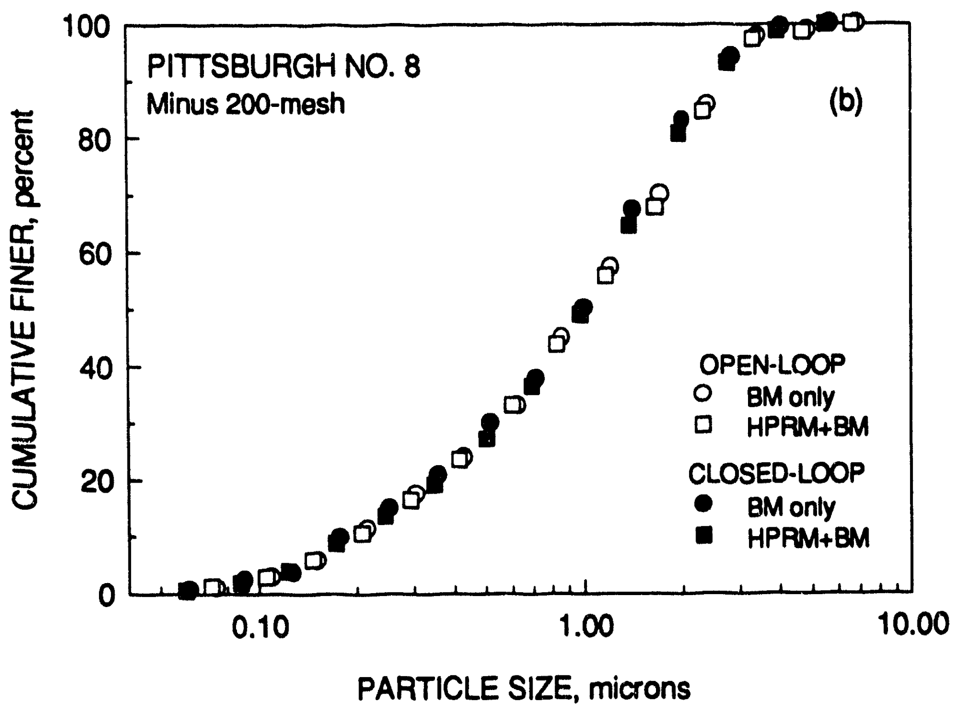


Figure 2. (a) size distributions of the minus 200-mesh products obtained with the different modes of grinding, and (b) the same distributions rescaled in terms of dimensionless size.

replotted in dimensionless size, that is, with size rescaled by the median size. The collapse of the distributions on to a single curve indicates that both open- and closed-circuit grinding configurations result in similar particle size distributions.

The washed coal samples used to study the effect of removing soluble iron on the rheology of the coal-water slurries were prepared by stirring 125 grams of minus 200-mesh coal with distilled water in a 2-liter cell, with and without an anionic iron-complexing reagent (0.1 wt% of sulfosalicylic acid) for 10 minutes at 1200 rpm. The coal suspension was filtered and dried at 40^{0} C for 15 hours in a convection oven before further experimentation.

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

As can be seen by the plots given in Figure 3, the addition of Triton X-405 decreases the apparent viscosity (at 100 sec^{-1}) of slurries made from Pittsburgh No. 8 coal. Unfortunately, for an acceptable coal-water slurry at 65 percent by weight solids concentration, the maximum viscosity for reasonable, cost effective pumping should be lower than 1000 mPa/s at 100 sec^{-1}. Since the addition of Triton reagents did not decrease viscosity of the systems below the acceptable value, another reagent had to be tried at this stage of the project. A commercially available additive, Henkel Coal Master A-23-M reagent, was chosen because it is cheap and performs exceptionally well with clean coals [1].

Figure 4 shows the effect of Coal Master A-23-M addition (1.0 wt%) on the apparent viscosity at 100 sec^{-1} of coal-water slurries made from Pittsburgh No 8 coal by both ball mill (BM) grinding and hybrid high pressure roll mill/ball mill grinding (HPRM/BM). The addition of reagent decreased the viscosity of 65 wt% slurry to almost an acceptable value (around 1000 mPa at 100 sec^{-1}). There is no noticeable difference in the rheological behavior of slurries produced by BM and hybrid HPRM/BM grinding.

Figure 5b presents flow curve behavior of the slurries produced from BM-ground coal in the absence of Coal Master A-23-M reagent. Figure 5a shows the apparent viscosity of the same

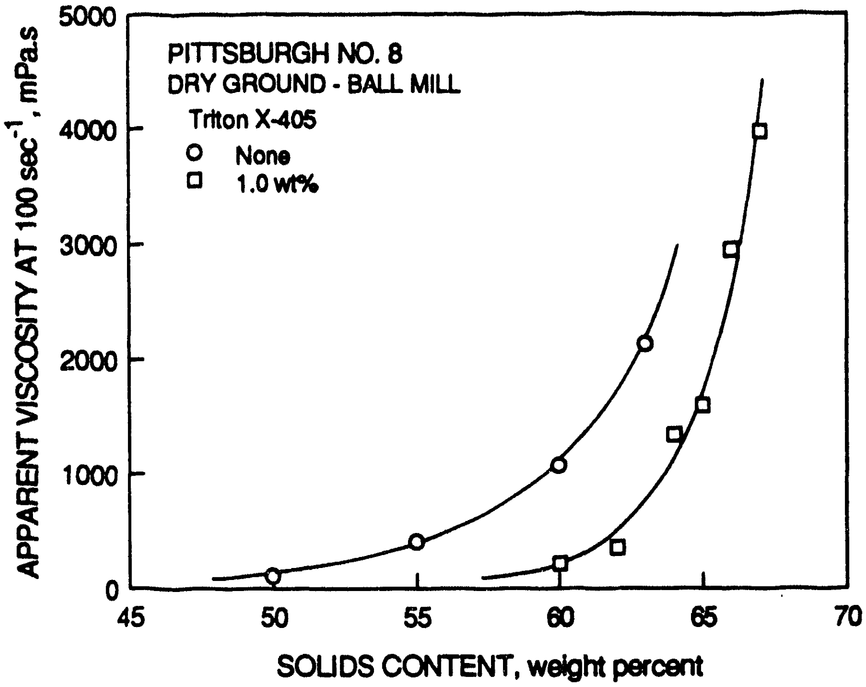


Figure 3. The viscosity of ball mill - ground Pittsburgh No. 8 coal-water slurries as a function of solids content with and without the addition of 1 wt% TX-405.

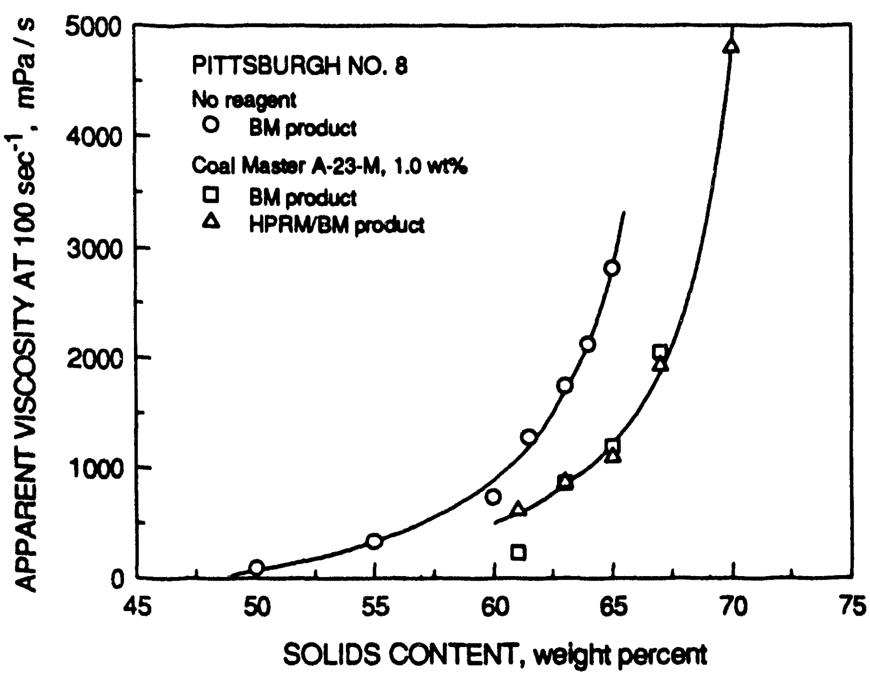


Figure 4. The viscosity of HPRM/BM and BM-ground Pittsburgh No. 8 coal-water slurries as a function of solids content with and without 1.0 wt% Coal Master A-23-M.

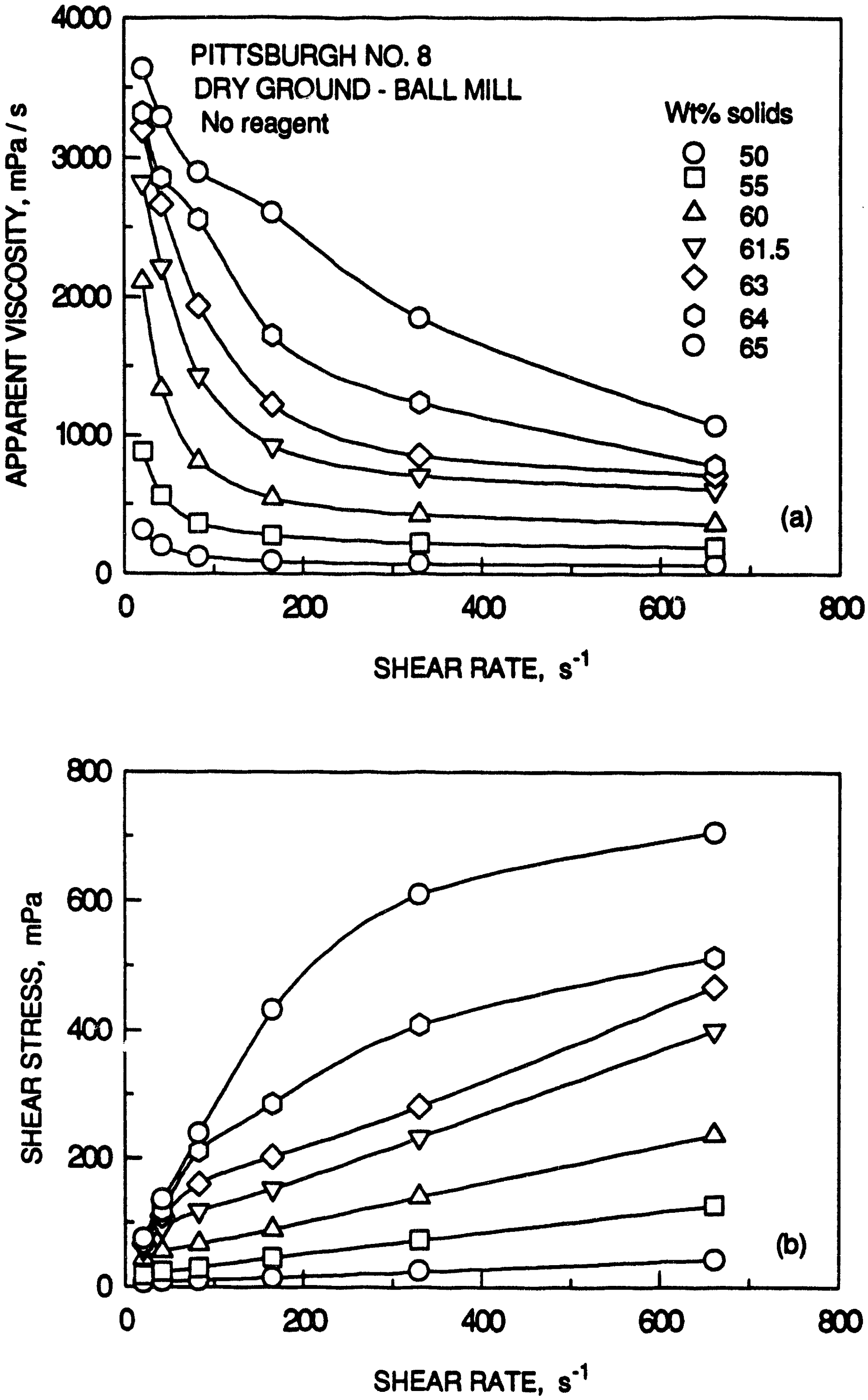


Figure 5. (a) The viscosity and (b) flow curves (rheograms) of BM-ground Pittsburgh No. 8 coal-water slurries as a function of shear rate, with no reagent added.

systems. Those slurries have very high viscosity, low sedimentation stability and some yield stress. The systems obey non-Newtonian behavior, are pseudoplastic, and change with time irreversibly (Figure 6) (shear degradation). Note that thixotropy and rheopexy are reversible phenomena and shear degradation should not be confused with them. Figures 7 and 8 present flow curves for the similar systems in the presence of 1.0 wt% Coal Master A-23-M. Those slurries do not exhibit any yield stress and are almost Newtonian systems, with shear stress being linearly dependent on the shear rate. In the presence of Coal Master A-23- reagent, it is possible to prepare 70 wt% slurries and even measure their viscosity.

These preliminary results suggest that the viscosity of coal-water slurries (CWS) prepared by BM and hybrid HPRM/BM grinding is almost identical. During preparation of the slurries, much higher impeller torques were experienced with the BM slurries. It is our observation that the easier it is to prepare a slurry (the lower impeller torque is) the better are its flow properties. After initial stirring at 1000 rpm, the slurries were equilibrated at 200 rpm for 18 additional hours. It was suspected that some kind of reaction occurs during the equilibration time producing a situation that increases the viscosity of HPRM slurries. Since it is necessary to determine the long-term viscosity and stability behavior of coal-water slurries (CWS), preliminary studies of the effect of wet and dry coal storage on the slurry behavior were performed during this quarter.

As already shown in Report No. 4, a short-term storage (up to four weeks) of dry ground coal does not influence the viscosity of slurries prepared from that material. Coal samples used to prepare the slurries whose behavior is illustrated in Figures 3 to 8 were stored dry (-200 mesh) for approximately nine months. To check how long-term dry storage of coal influences slurry behavior, we prepared slurries from BM and HPRM/BM freshly ground coal and measured their viscosity. The results are presented in Figures 9 to 11. Figure 9 shows the effect of solids loading, ranging from 61 to 67 wt%, on the apparent viscosity at 100 sec^{-1}. The viscosity measured at 61 wt% was identical for BM and HPRM/BM slurries. As the solids load was increased above 61 wt%, however, the HPRM/BM slurries became less viscous than those

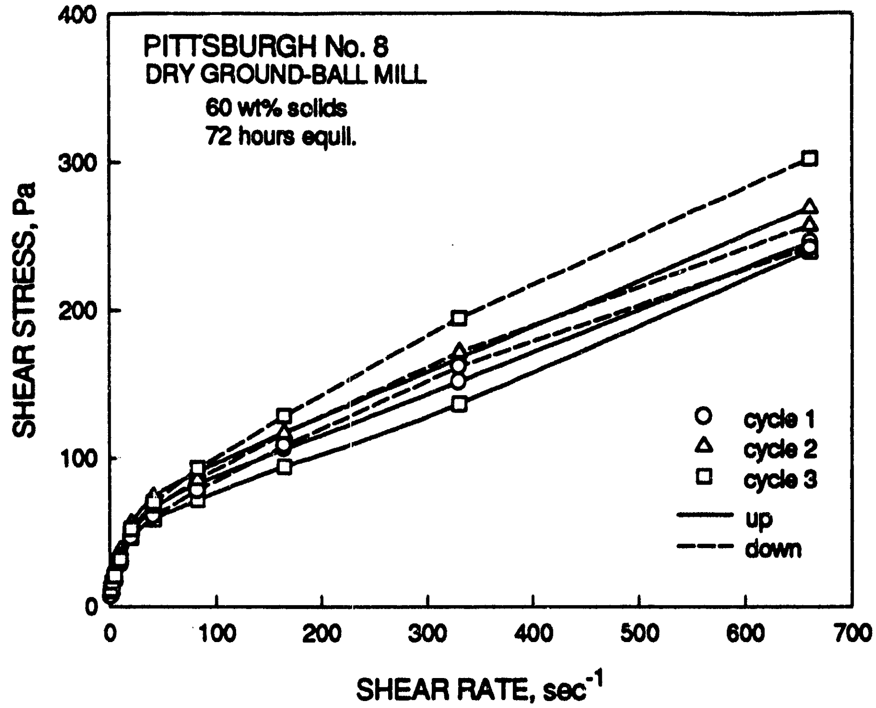


Figure 6. Up and down flow curves for Pittsburgh No. 8 coal-water slurry of 60 wt% content with no reagent added.

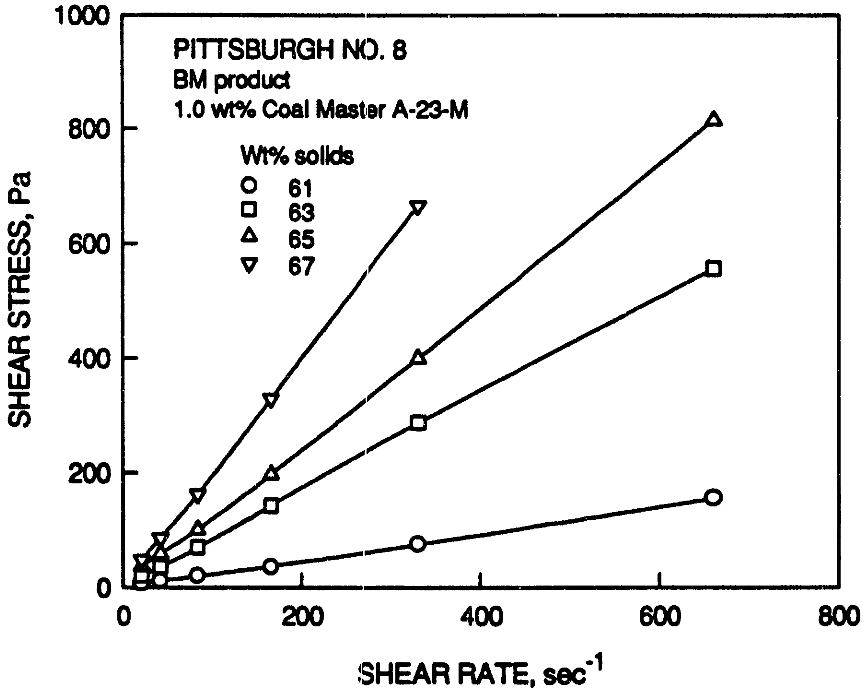


Figure 7. Effect of solids content on the rheology (flow curves) of coal-water slurries prepared using the ball - mill (BM) product and 1.0 wt% Coal Master A-23-M.

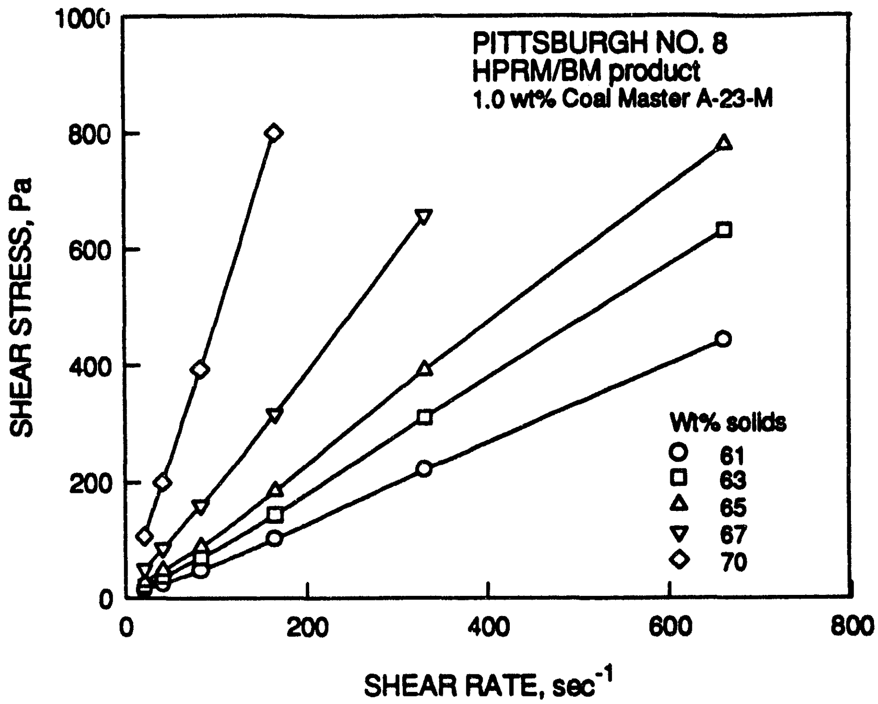


Figure 8. Effect of solids content on the rheology (flow curves) of coal water slurries prepared using the HPRM/BM product and 1.0 wt% Coal Master A-23-M.

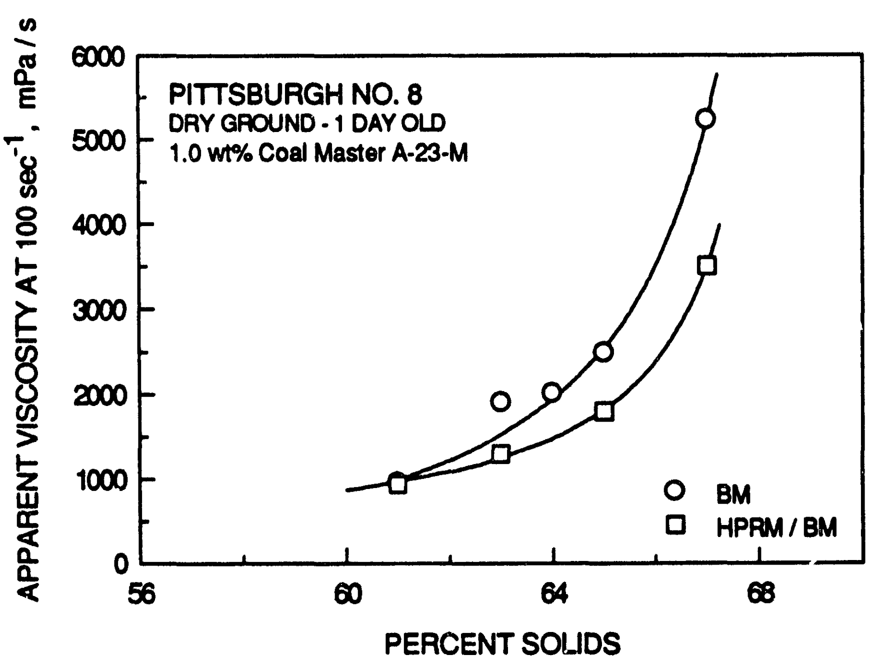


Figure 9. Effect of solids load on the viscosity of coal water slurries prepared using the freshly ground HPRM/BM and BM product and 1.0 wt% Coal-Master

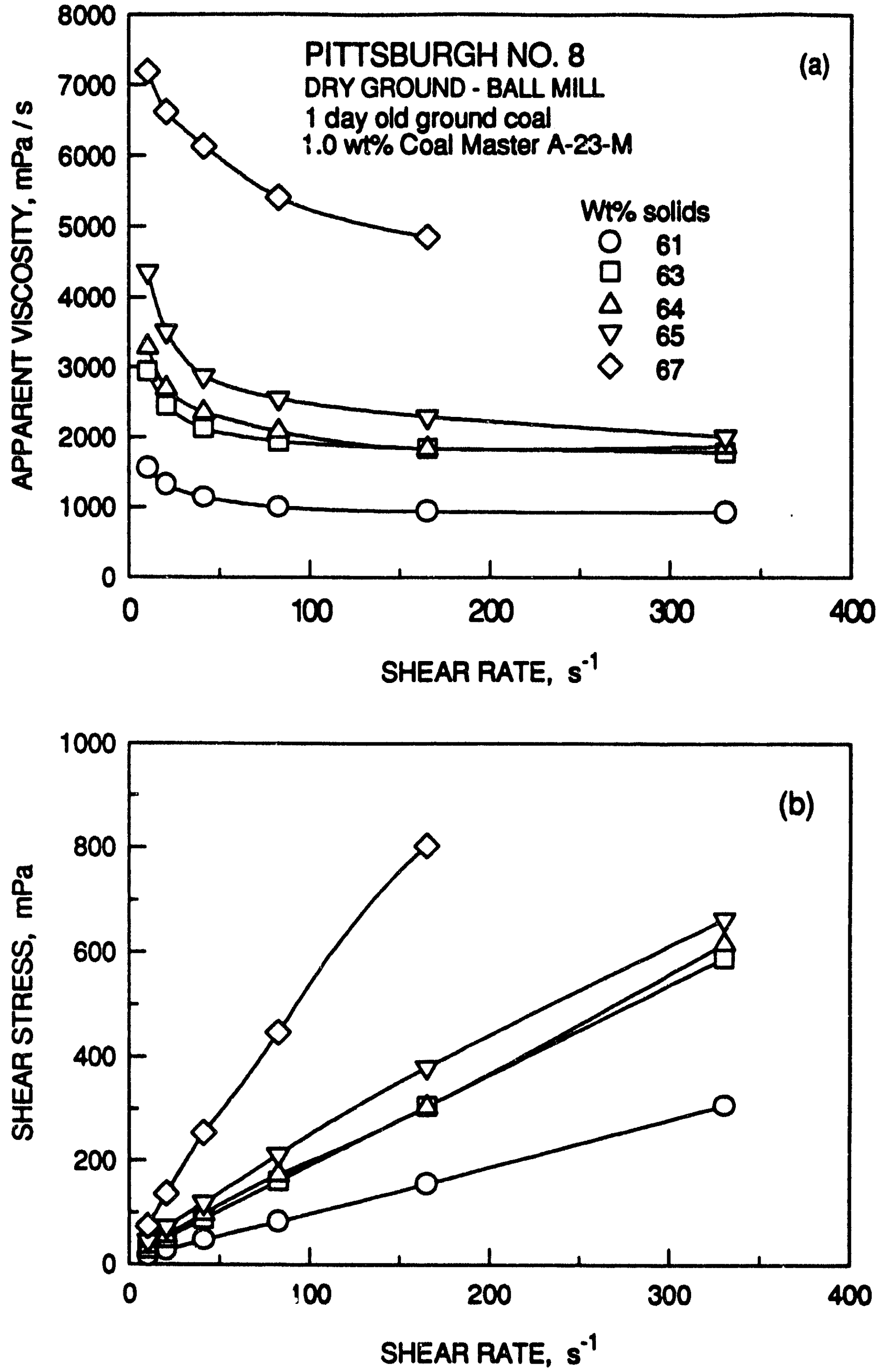


Figure 10. Effect of solids content on (a) the viscosity (b) the flow curves of coal-water slurries prepared using the freshly ground BM product and 1.0 wt% Coal Master A-23-M.

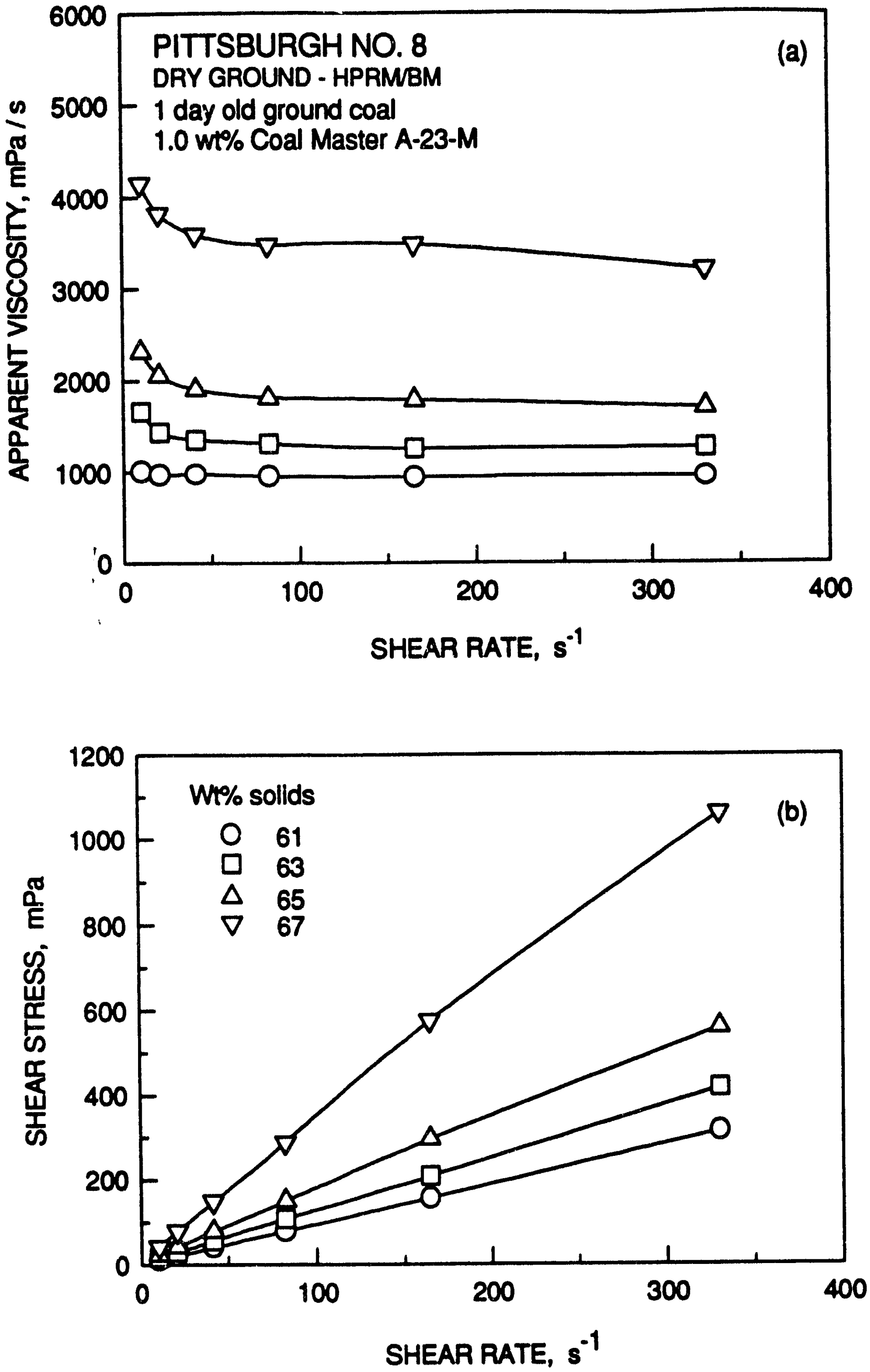


Figure 11. Effect of solids content on (a) the viscosity and (b) the flow curves of coal-water slurries prepared using the freshly ground HPRM product and 1.0 wt% Coal-Master A-23-M.

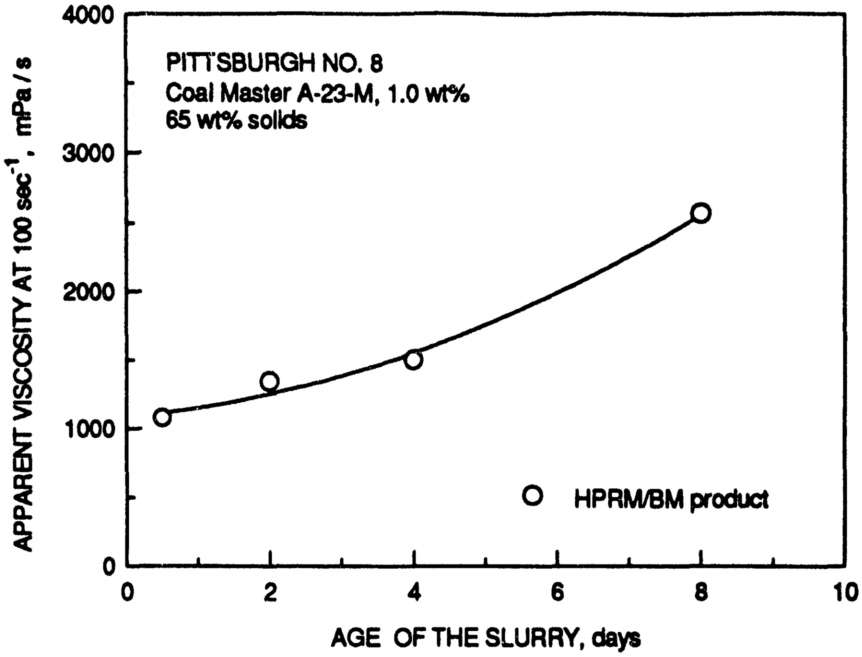


Figure 12. Effect of slurry aging on the viscosity of coal-water slurries prepared using the HPRM/BM product and 1.0 wt% Coal Master A-23-M.

prepared from BM-ground coal. Figure 10a shows the effect of shear rate on the apparent viscosity of BM-ground slurries with solids load from 61 to 67 wt% (freshly ground coal). Slurries made with BM-ground coal are pseudoplastic (that is, their viscosity decreases with increasing shear). The apparent viscosities measured were high (several thousand mPa/s). This viscosities are higher than expected because the particle size distribution and the pH had not been optimized and the coal had not been beneficiated. Flow curves (Figure 10b) for the same systems illustrate almost linear shear rate - shear stress dependence with no yield stress. Figures 11a and b present similar results for HPRM/BM slurries (freshly ground coal). At all shear rates and solids loading, HPRM/BM slurries exhibited lower apparent viscosity than BM.

Figure 12 illustrates the effects of slurry aging on the apparent viscosity. The slurry viscosity was acceptable one day after preparation but started to increase afterwards. Eight days after preparation, the apparent viscosity of the sample at 100 sec^{-1} doubled its value to 2000 mPa/s. Figure 13a, which presents the apparent viscosity of the same slurry as a function of

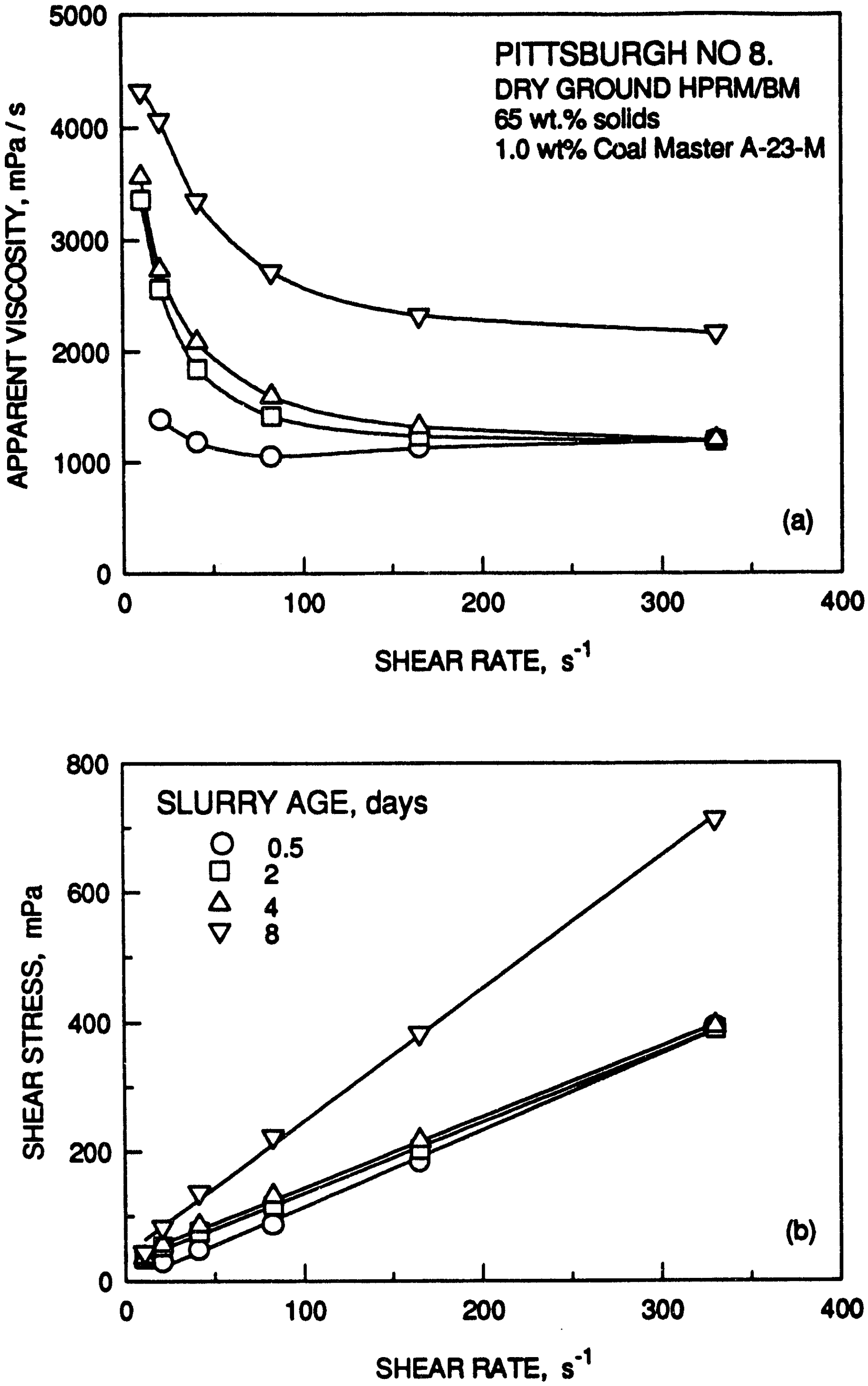


Figure 13. Effect of slurry aging on (a) the viscosity (measured at different shear rates) and (b) the flow curves of coal -water slurries prepared using the HPRM/BM product and 1.0 wt% Coal Master A-23-M.

shear rate, shows that the slurry is pseudoplastic and its apparent viscosity increases with time at all shear rates. A flow curve (Figure 13b) indicates almost linear dependence of shear rate and shear stress and the absence of any significant yield stress.

All samples described above exhibited shear thinning (pseudoplastic) behavior, which is desirable in industry. Our preliminary experiments indicated that some coal samples change flow behavior after cleaning (washing). Figure 14a presents the apparent viscosity of "as received," water washed, and sulfosalicylic acid (anionic reagent) washed HPRM/BM samples as a function of shear rate. The "as received" coal sample shows shear thinning behavior but washed coal - water slurries are characterized by increasing apparent viscosity with increasing shear rate. Such "dilatant" flow behavior is undesirable industrially because any increase in pump shear rate might cause unpredictable slurry viscosities. More work remains to be done to indicate the nature of physicochemical processes that induce change in the rheology of these particular slurries. As can be observed from the plots given in Figure 14b, after washing, the linearity in the shear rate-shear stress plots is lost and the shape of flow curves becomes typical of dilatant systems.

In all of the foregoing experiments, the dispersant concentration was held constant at 1.0 wt% and other parameters such as solids loading or equilibration time were varied. Additional experiments were performed to delineate the effect of additive concentration, and the results are plotted in Figure 15. At constant solids loading (67 wt%), the dispersant level was varied from 1.0 to 6.25 wt%. The dispersant dosage is specified as weight percent of added Coal Master A-23-M on a dry coal basis. Minimum viscosity was observed at 3.12 wt% of dispersant. Further minimization of reagent usage is expected to be possible after the pH and particle size distribution are optimized. Figure 16a shows the apparent viscosity as a function of shear rate at different reagent dosages and indicates pseudoplastic behavior. Shear rate shear stress plots (flow curves) are almost linear at all reagent dosages, as can be seen from the plots given in Figure 16b.

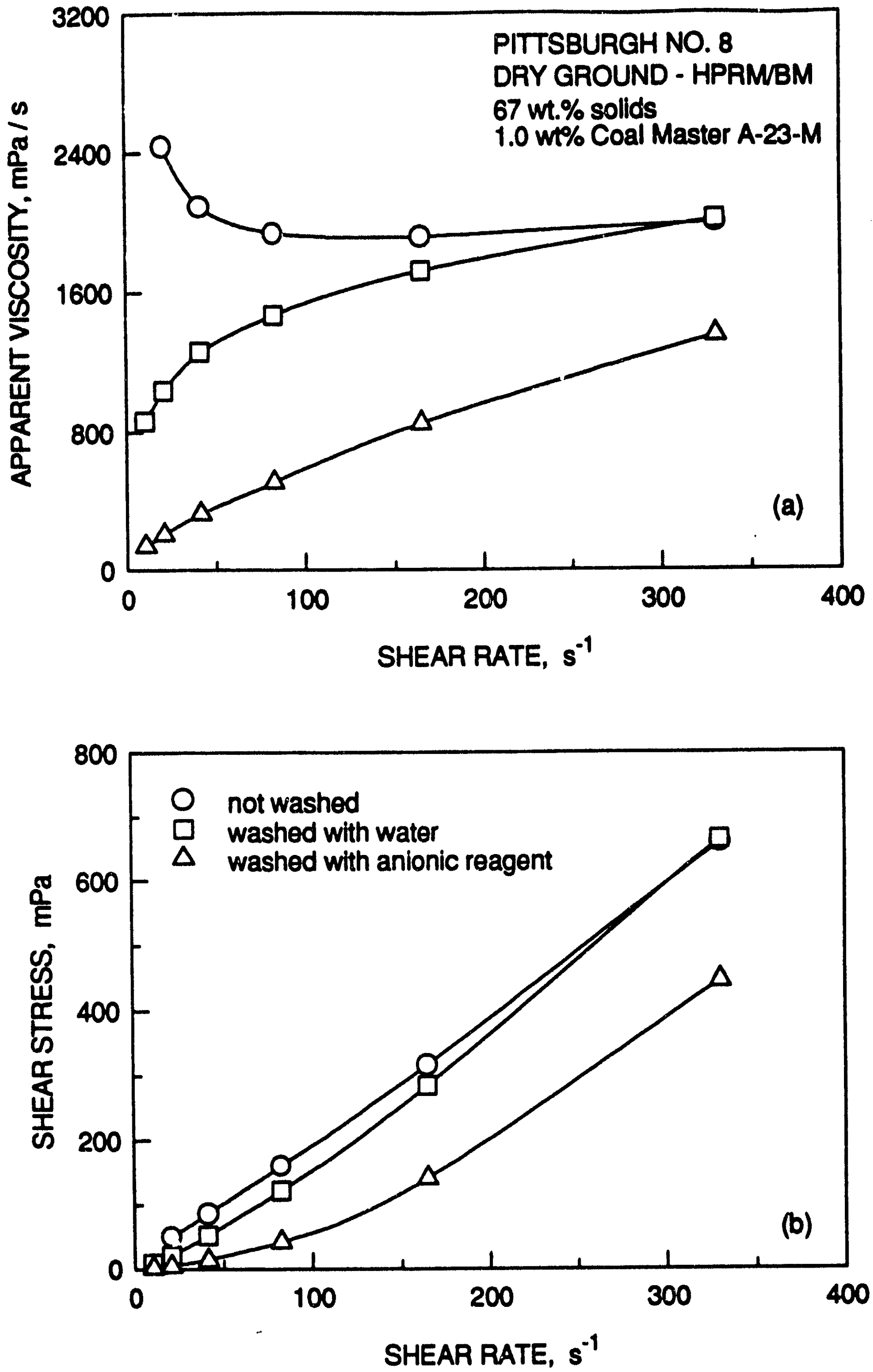


Figure 14. (a) The viscosity and (b) flow curves for unwashed, water washed and sulfosalicylic acid washed Pittsburgh No. 8 coal-water slurries prepared using the HPRM/BM product and 1.0 wt% Coal Master A-23-M as a function of shear rate.

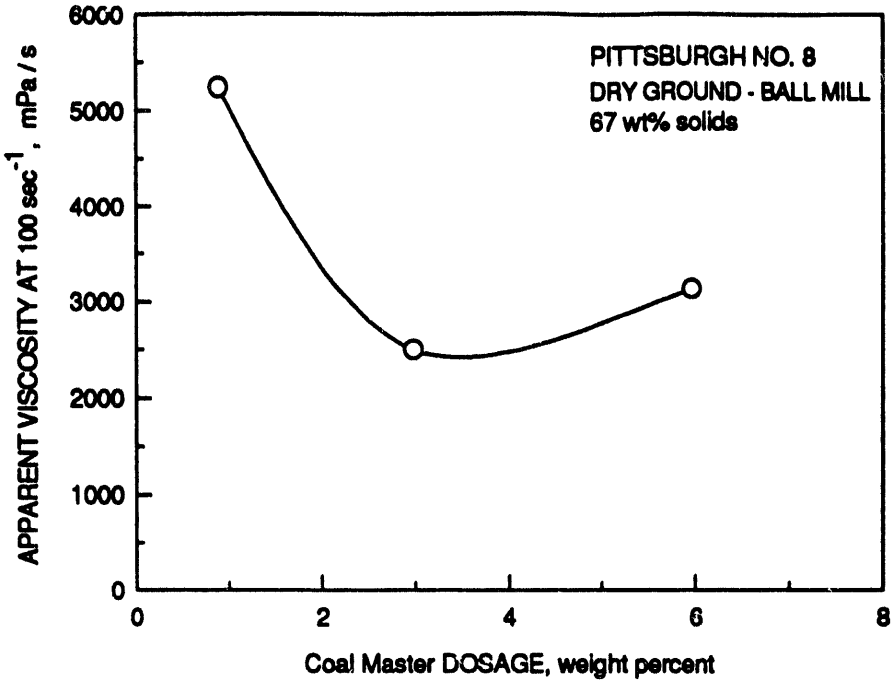


Figure 15. Viscosity for 67 wt% Pittsburgh No. 8 coal-water slurry prepared using the HPRM/BM product as a function of Coal Master A-23 -M dosage.

ELECTROKINETIC BEHAVIOR OF COAL-WATER SLURRIES

The electrokinetic behavior of coal particles in dilute and concentrated slurries might provide information on coal surface properties and on interaction between coal particles suspended in liquid. As shown by Fuerstenau and coworkers [2], such information might be extremely important in explaining coal-water slurry behavior. Depending on the rank of the coal, the degree of oxidation (of both coal and pyrite) and mineral matter content, the electrokinetic behavior of coal will vary significantly. In this study, the stability and viscosity of coal-water slurries will be correlated with the electrokinetic behavior in dilute and concentrated slurries.

Traditional electrophoretic mobility measurements require samples of low solids concentration, which necessitates dilution of the original slurry (up to 10000 times). The measurements were conducted with a ZetaMeter 3.0 manufactured by ZetaMeter. Inc. New York. The voltage applied was normally 100 volts, and the mobility of the sample was taken as

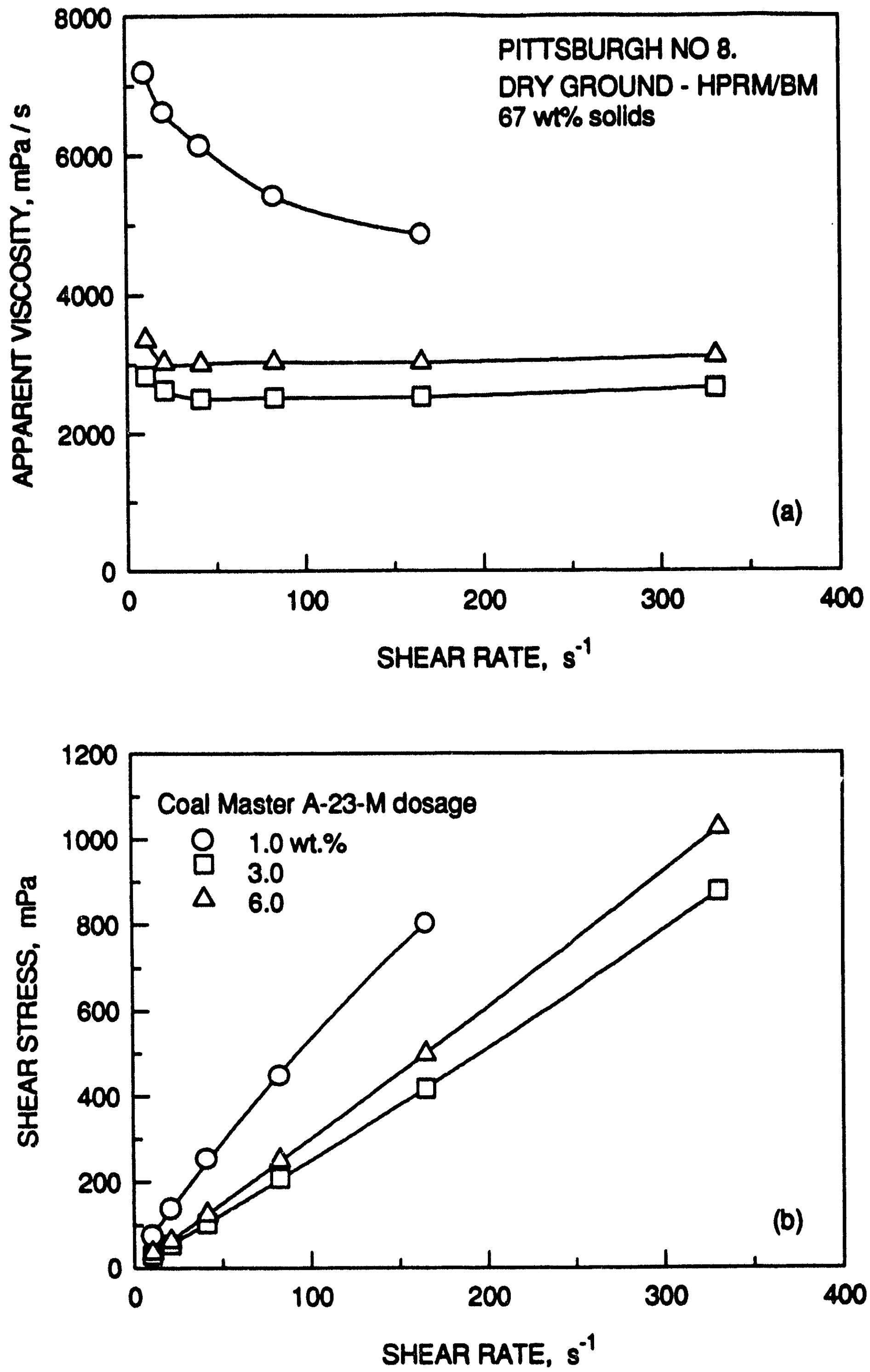


Figure 16. (a) The viscosity as a function of shear rate and (b) flow curves (rheograms) for 67 wt% Pittsburgh No. 8 coal-water slurry prepared using the HPRM/BM product and various dosages of Coal Master A-23-M.

the average of twenty measurements. The mass concentration of suspensions used in the actual measurements was 0.01g/100 ml, and the ionic strength was adjusted with 0.001 M $NaNO_3$.

An important parameter for characterizing the surface charge of coal particles in water is the condition when both the surface charge and the surface potential are zero (point of zero charge, PZC). Another condition of importance is when the Stern layer potential (potential at the first layer of counter ions) is zero. The electrokinetic or zeta potential, which is measured in this study, is the potential at the shear plane where slip must occur when the solid moves relative to the liquid and it is often assumed that it approximates Stern layer potentials. It is important to note that the behavior of the solid particles in liquid under this condition is governed by the charge density at the shear plane, and consequently the zeta potential correlates usually well with stability. Zeta potentials can be changed through adsorption of inorganic or organic ions at the Stern plane. Therefore, cationic or anionic impurities, which are common in coal, can completely control the surface properties and stability of suspensions and slurries. Specific adsorption of cations or anions can change the location of the isoelectric point, or the zeta potential reversal (PZR). Specific adsorption of cations increases the PZR and the absolute value of the measured zeta potential, but the opposite is true for specific adsorption of anions (see Figure 17).

To find the PZR of pure Pittsburgh No. 8, a sample of this coal was ground under an argon atmosphere to prevent oxidation, and thoroughly washed by filtration under high vacuum condition. As illustrated by the results given in Figure 18, the PZR of clean Pittsburgh No. 8 coal was found to occur at pH 4.3, which is not unusual for clean coal [2]. This was a significant decrease in the PZR when compared to "as-received" sample of this coal, studied in the same experiment (PZR at pH 6.6). It is apparent that some specifically adsorbed cation controls the surface properties of "as received" coal sample.

Preliminary analysis of filtrates and supernatants obtained after removal of the coal particles indicates that iron is a major cationic impurity in Pittsburgh No. 8 coal. Iron is

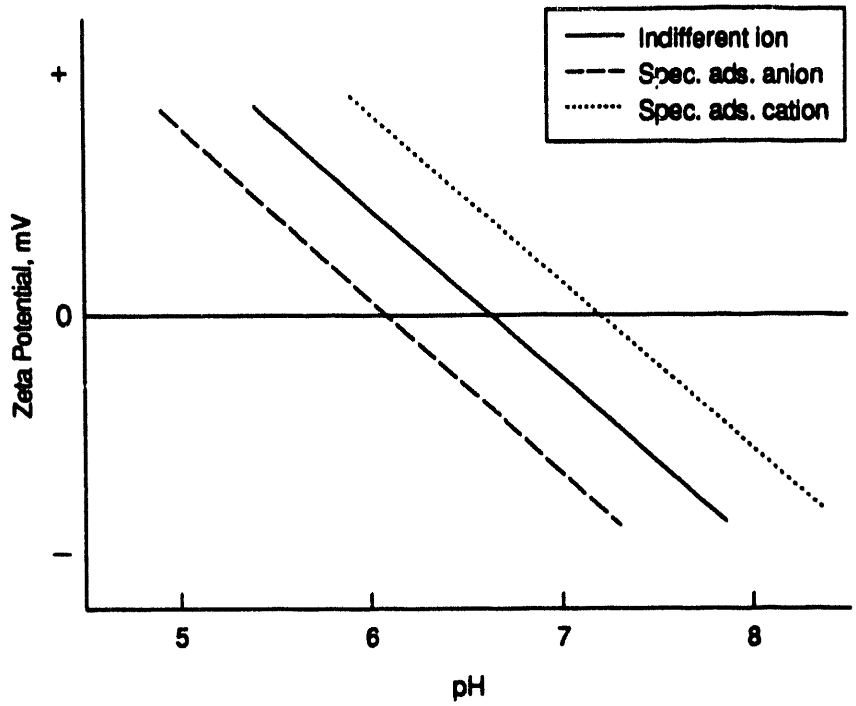


Figure 17. Schematic illustration of the effect of specific adsorption on the mobility and PZR of a colloid suspension.

probably produced by pyrite oxidation during storage of the coal for prolonged time (or under oxidizing conditions in contact with air). This dissolved iron specifically adsorbs on coal particles, increasing the pH of the PZR and absolute values of zeta potentials. Rheology measurements indicated that the stability of slurries decreased and viscosity increased significantly with time. These slurry aging effects would be highly undesirable industrial and is most probably caused by coal impurities. Since it was found that the PZR increases with time, indicating specific adsorption of cations, iron was suspected to be the major "culprit" that caused the observed aging phenomenon.

Numerous procedures for coal beneficiation are described in the literature and applied in practice [3]. In our future work, coal will be beneficiated and the pyrite and ash levels lowered to the acceptable level (< 5 wt% ash and < 1% pyrite). Even with such beneficiated coal, pyrite which remains in coal may still be oxidized and some iron released during several months of slurry storage. Consequently, something has to be done to remove or complex produced iron. It

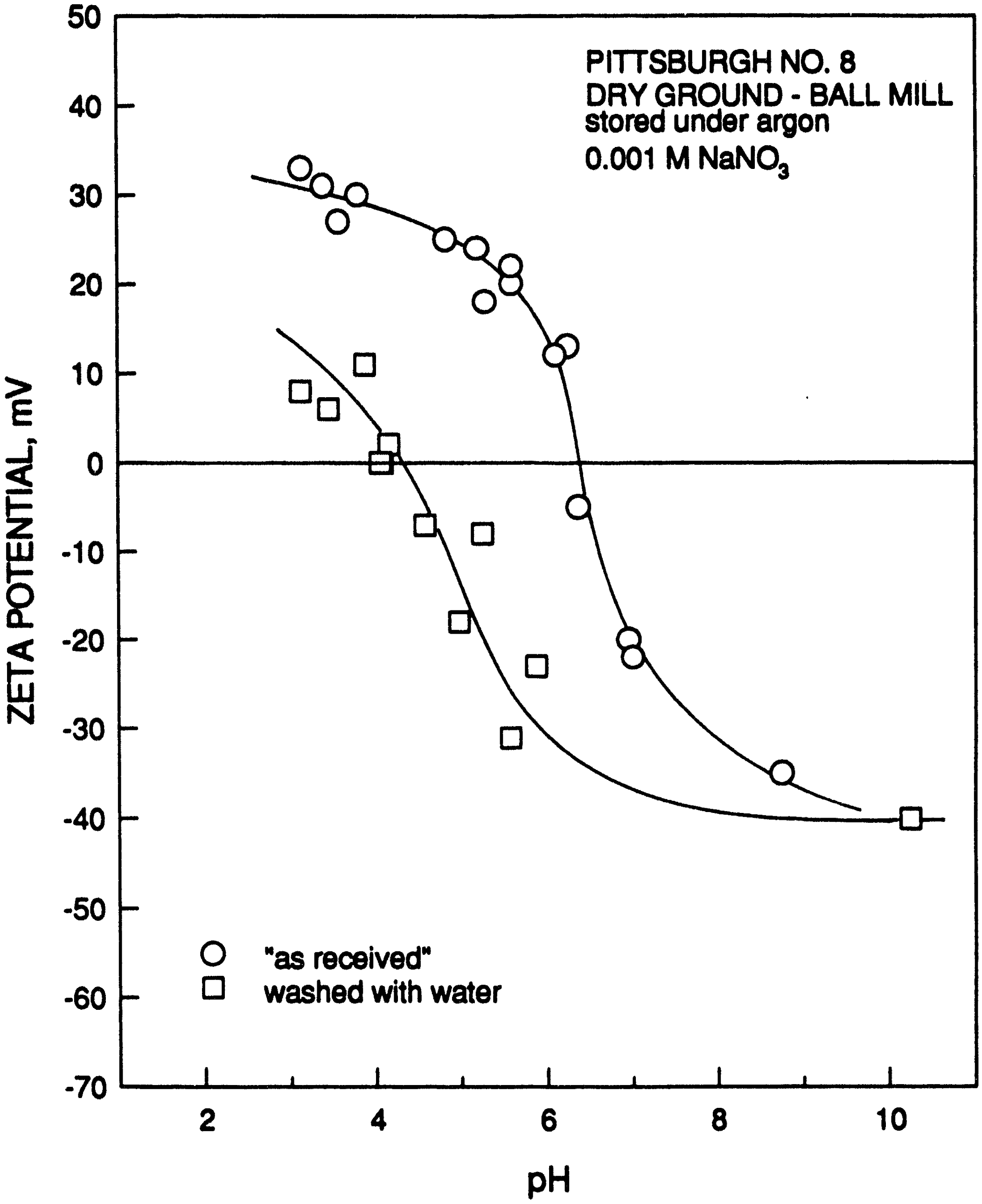


Figure 18. The zeta potential as a function of pH for unwashed and thoroughly washed Pittsburgh No. 8 coal samples prepared by ball milling stored dry under argon.

is quite possible that if iron can be complexed or neutralized in some way, slurries would be stable for several months and aging would not occur.

The effects of coal washing with water and iron complexing reagents on the zeta potential and PZR are illustrated in Figure 19. The PZR of "as-received" Pittsburgh No. 8 coal (HPRM/BM grind) was found to occur at pH 7.1. Washing with water or sulfosalicylic acid (anionic reagent), which is known to complex iron, lowered the pH of the PZR to 4.8. This is still higher than the PZR of thoroughly washed coal (pH 4.3) but any kind of really intense washing in industry may not be economically feasible. More work has to be done on finding the best iron-complexing reagent, which showed not interfere with the dispersants and stabilizers.

In Figure 20, the effect of washing the coal with water and an anionic iron-complexing reagent on the electrokinetic behavior and PZR of Coal Master A-23-M dispersed CWS after one week of aging was presented. Coal that was washed with the anionic reagent (sulfosalicylic acid) was highly negatively charged at pH's between 3 and 10. This coal sample never exhibited a reversal of charge. On the other hand, "as-received" and water-washed coals showed two PZR's, one at pH 6 and another at pH 4. All three slurries were prepared using a HPRM/BM product and 1.0 wt % Coal master A-23-M. The solids load of each slurry was 67 wt % and 10000 times dilution was necessary to perform the electrokinetic studies with traditional methods, which had been used in this study.

SUMMARY

Comparison have been made for ground coal that had been produced by ball mill grinding only and a ground coal that was first comminuted in the high pressure roll mill and then in a ball mill. The rheological and surface behavior of coal - water slurries prepared by HPRM/BM and BM grinding were compared. It is easier to prepare slurries from HPRM/BM feeds, but after 18 hours of equilibration their viscosities are identical to or higher than those of feeds produced by BM grinding only. The opposite was true for freshly ground coal. A commercially available, popular reagent Coal Master A-23-M from Henkel Corporation, was

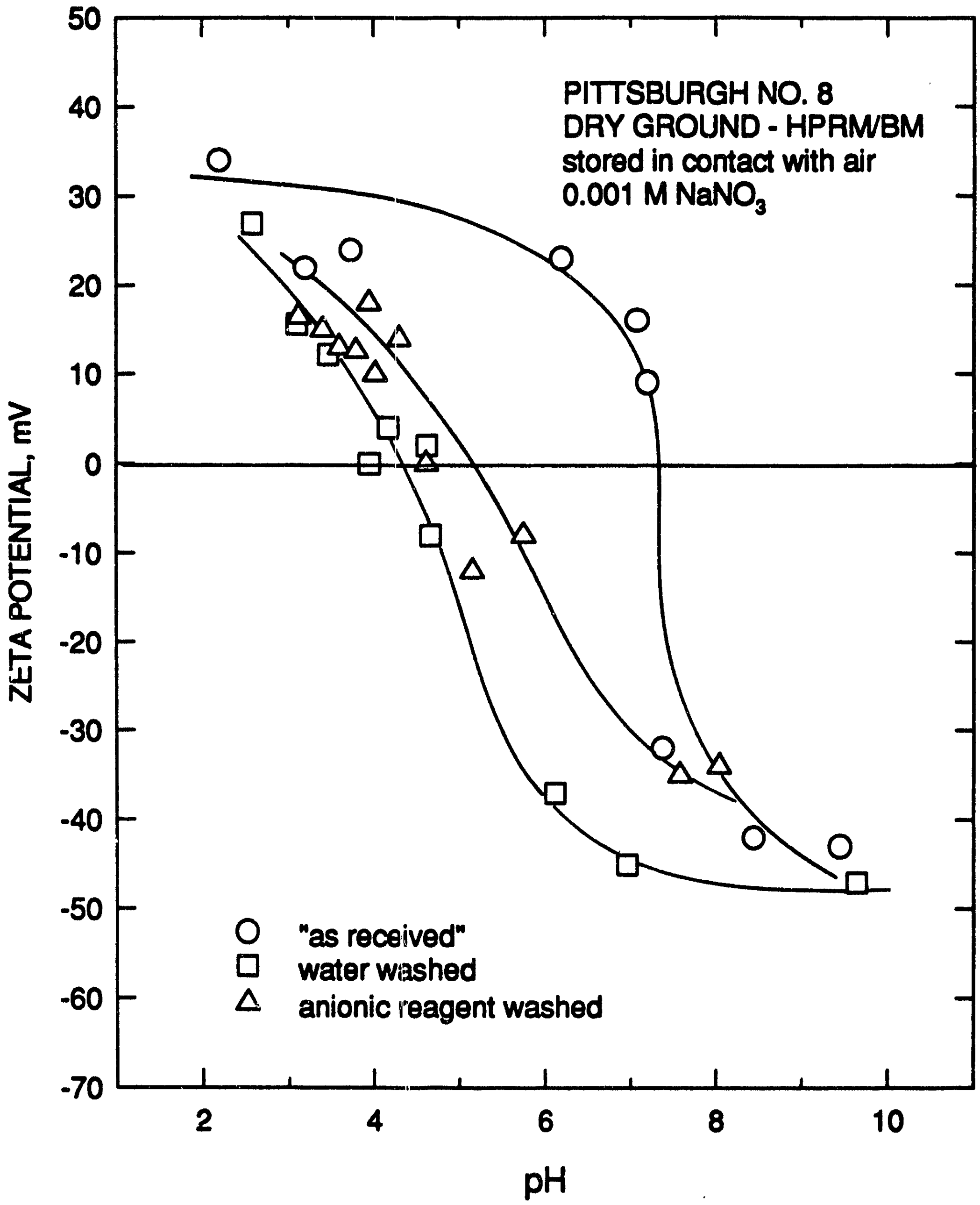


Figure 19. The zeta potential as a function of pH for unwashed, water-washed and sulfosalicylic acid-washed Pittsburgh No. 8 coal samples produced using the HPRM/BM product and stored dry in contact with air for nine months.

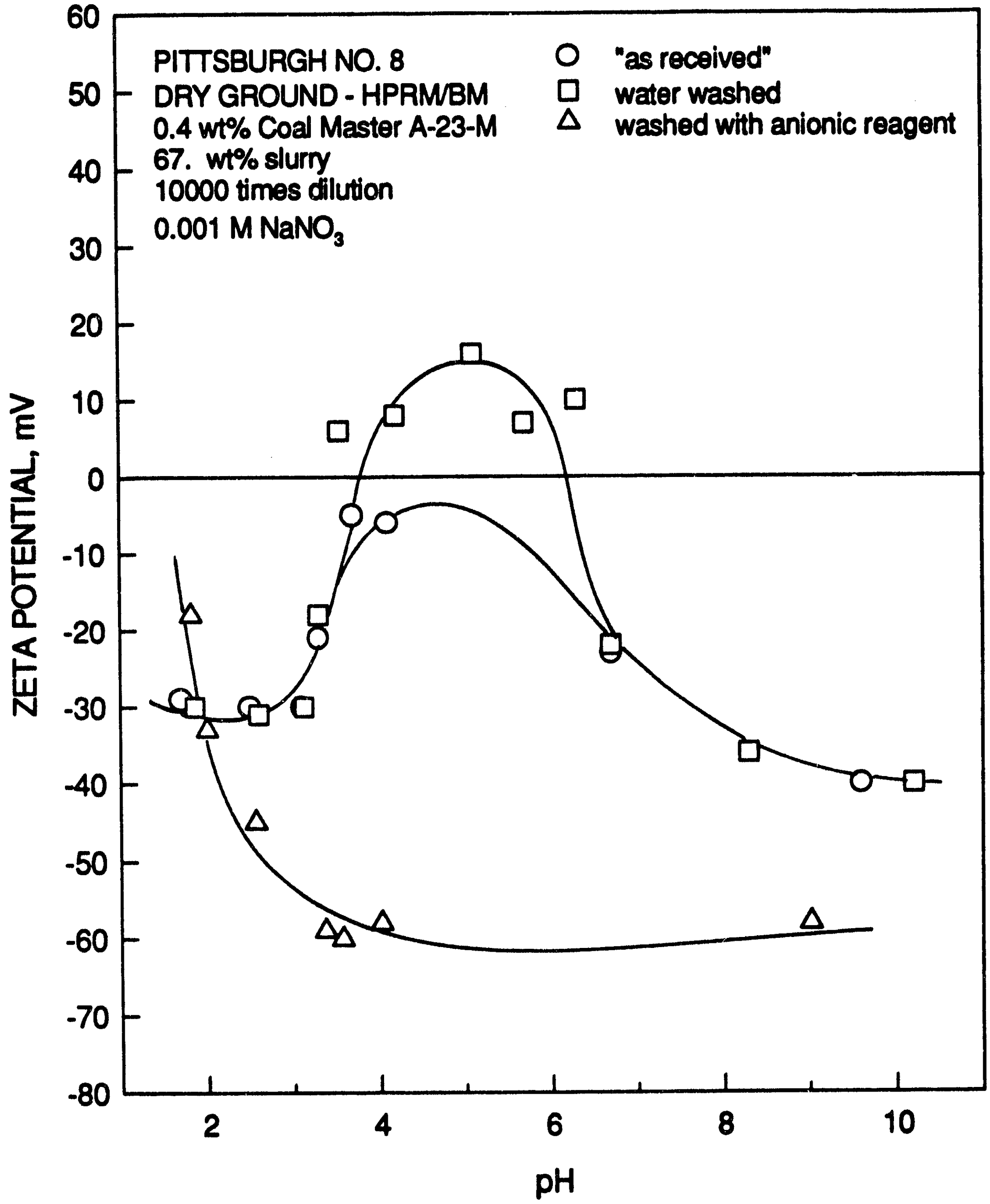


Figure 20. The zeta potential as a function of pH for the 10000 times diluted 67 wt% Pittsburgh No. 8 coal-water slurry prepared using unwashed, water washed and sulfosalicylic acid washed HPRM/BM product and 1.0 wt% Coal Master A-23-M and equilibrated for one week.

used to prepare the slurries. Coal Master A-23-M proved to be a very efficient dispersant (slurries up to 67 wt % with acceptable viscosities were prepared) but aging increased the viscosity and decreased the stability of the slurries

Preliminary electrokinetic studies at low solids loads were performed in order to understand the nature of the behavior of coal-water slurries prepared with Coal Master A-23-M reagent. Comparison of PZR and absolute values of measured zeta potentials of "as-received" and washed coal indicated that specific adsorption of some multivalent cation controls the surface properties of coal. Further analysis indicated that iron is the most probable "culprit" which interferes with the performance of the Coal Master A-23-M dispersant. Washing with water did not successfully solve that problem but anionic iron complexing reagents did much better job. Iron is released by pyrite oxidation and remains in the ferrous (+2) form due to the reducing environment in coal - water slurries. At pH's 9 - 10 (where Coal Master performance is optimal) iron precipitates (reversibly) in the form of iron (+2) hydroxide and (irreversibly) in the form of some orange precipitates of presently unknown nature.

Washing with anionic iron complexing reagent improved the rheological behavior of the slurries, and low viscosities were retained up to a period of one week for a 67 wt% slurry. Optimization of Coal Master A-23-M dosage and pH has been performed, but pH is constantly drifting towards the acidic range, which decreases the dispersant efficiency. Pittsburgh No. 8 coal used in this study, which was not beneficiated, contains up to 2 wt% of pyrite and 10 wt % of ash, which is twice as much as permitted by current regulations for burning coal - water slurries. Coal beneficiation will further improve the efficiency of the Coal Master A-23-M reagent and HPRM/BM grinding.

RESEARCH WORK PLAN FOR NEXT QUARTER

During the 8th quarter, a preliminary flow sheet involving coal beneficiation, hybrid HPRM/BM grinding, iron complexation, and dispersant and stabilizer dosage optimization will be developed. Reagents tested will be optimized to find conditions where they do not interfere with each other. This will require combination of coal beneficiation, electrokinetic studies at high (acoustophoresis) and low solids load, monitoring the iron concentration in slurry filtrates, the rheological behavior and stability of the suspensions, and also preliminary spectroscopy studies (XPS and FTIR) to investigate the nature of iron surface species which coat the coal particles.

REFERENCES

1. J. L. Morrison, B. G. Miller, and A. Scaroni, "Preparing Coal-Water Slurry Fuels from Bituminous Coal Sources," Penn State Energy and Fuels Research Center, report No. 93262.
2. D. W. Fuerstenau, J. M. Rosenbaum, and Y. S. You, "Electrokinetic Behavior of Coal," Energy and Fuels, Vol. 2, pp. 241-245 (1988).
3. D. Huber, J. Hoppe, C. L. Miller, and D. Uthus, "A Status Report on the Clean Coal Technology Demonstration Program," Proceedings of the 18th International Technical Conference on Coal Utilization & Fuel Systems, Clearwater, Florida, USA; April 26-29, (1993), pp. 51-63.

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