Effect of Polyelectrolytes on Coal-Water Mixture in Dispersed/Coagulated States

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The Dispersion mechanism of highly loaded coal-water mixture (CWM) in the presence of a polyelectrolyte additive was investigated. Two important factors have been found : the ability of the additive to apply a sufficient electric repulsive force to the coal particles, and an appropriate affinity of the additive to the coal surface.

This letter concerns an investigation on the dispersion mechanism of an additive for CWM. CWM, a dispersive system of pulverized coal particles in an aqueous additive solution, is a new liquid fuel.[1] As the selection of additives is one of the most important factors that determine the quality of a CWM, many investigations on the dispersion mechanism of additives have been conducted. However, most of these studies were carried out in diluted states.[2] This is simply because in the past there was no suitable method to analyze the properties of a concentrated suspension directly. Since the equilibrium of additive adsorption is thought to be dependent on the diluting condition, it is doubtful if accurate data can be extracted from experiments conducted in a diluted state. We applied a newly developed acoustic method to a CWM, which enabled us to measure the charge and particle size distributions of a CWM in concentrated states.[3] To our knowledge, we are the first to apply this method to a CWM. In this report, we analyzed the influence of molecular weight and the degree of sulfonation of sodium polystyrene sulfonate (PSS) on the rheological behavior of CWM. Note that PSS is the additive employed by Japan COM CO., LTD for their commercial manufacturing of CWM with a production rate of 500 thousand tons per year.

We prepared various PSS samples in our laboratory. The sample coal chosen was bituminous coal and the CWM was prepared by wet grinding using a ball mill. The amount of PSS was 0.4 wt%/CWM where the coal concentration was 59.4 vol%. We measured the viscosity of CWM using a Haake Model RV 20 with an MV Ⅱ P rotor and an M5 profiled sensor. The shear rate was varied from 0 to 150 s^{-1} at 25°C. We calculated the apparent viscosity of CWM from the stress at 100 s^{-1} on the down curve. For measurement of the ζ-potential and the particle size distribution of CWM, we used the AcoustoSizer developed by MATEC Applied Sciences INC. This is the first system of its kind sold in Japan. In this measurement we diluted the original CWM with a KCℓ solution down to 30 vol% (the upper calibration-limit of the AcoustoSizer), keeping the conductivity unchanged.[4] Previously we reported that the effect of this dilution is small enough to assume the electrokinetic behavior of the original CWM to be unchanged.[4]

Firstly, we investigated the influence of the molecular weight of PSS on the viscosity and the ζ-potential of CWM. For all the CWM's examined, the supernatants obtained by centrifugal separation showed the same viscosity as pure water. This indicates that the measurement of ζ-potential was not affected by the viscosity of the dispersed medium. As shown in Figure 1, there was a molecular weight (M_o) that minimized the apparent viscosity. The absolute value of ζ-potential, on the other hand, was found to take its maximum value at this molecular weight. While the absolute value of ζ-potential decreased as the molecular weight either increased or decreased from M_o, the correlation between the apparent viscosity and the ζ-potential was stronger in the low molecular weight region ($M < M_o$). It is known that as the molecular weight decreases its adsorption to the coal surface decreases because the solubility to water increases.[5] From this we can conclude that in the low molecular weight region, electrostatic interaction is predominant, and in addition, that if the molecular weight is not sufficiently large in this region the PSS can not provide the coal particles with an electric repulsive force large enough to peptize aggregates well, and this results in an increase in the apparent viscosity.

In the high molecular weight region ($M > M_o$), on the other hand, while the apparent viscosity increased with an increase in the molecular weight, the change in the ζ-potential was less apparent than in the low molecular weight region. This indicates that in the high molecular weight region, the rheological behavior cannot be explained solely by electrostatic interaction. We suspected that two other effects could increase the apparent viscosity in the high molecular weight region: (1) the viscosity of the medium was increased by non-adsorbed PSS, and (2) aggregates were formed by bridging adsorption across coal particles. Both effects are thought to be enhanced as the molecular weight is increased. In order to investigate which of

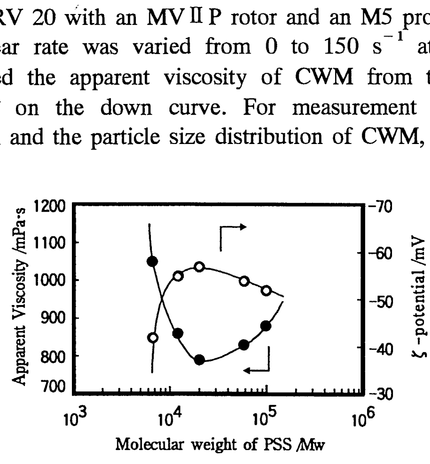

Figure 1. Apparent viscosity and ζ-potential as a function of molecular weight of PSS. PSS addition : 0.4wt%/CWM, ϕ = 59.4vol%.

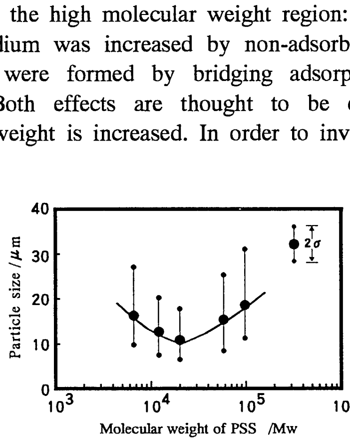

Figure 2. Particle size distribution of coals in CWM as a function of molecular weight of PSS.

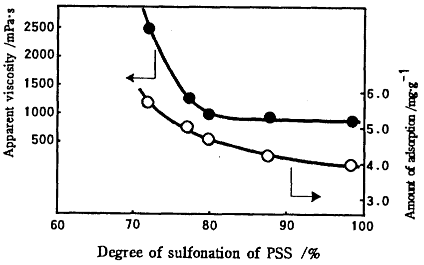

Figure 3. Apparent viscosity and adsorption of PSS as a function of degree of sulfonation of PSS.
PSS addition: 0.4wt%/CWM, $\phi = 59.4$vol%.

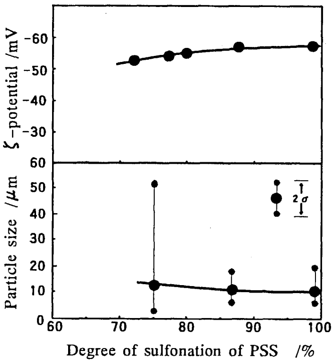

Figure 4. ζ-potential and particle size distribution of coals in CWM as a function of degree of sulfonation of PSS.

these two effects is predominant, we measured the particle size distribution of coal particles in a concentrated state. The result is shown in Figure 2. In this figure, the symbols show the median values of the particle size (m) and the error bar around the symbol denotes the standard deviation (σ) which was calculated assuming a logarithmic normal distribution. The particle size was seen to be at the minimum when the molecular weight was close to M_o, indicating that in this region the coal particles were most stably dispersed. From this we now suspect that bridging adsorption is responsible for the increase in the CWM viscosity in the high molecular weight region. Note that it has been reported that such a weak force as the bridging adsorption can bind particles strongly enough to form a network structure in a dispersive system.[6] The result of the present study supports our previous report that the static stability was increased when PSS with high molecular weight is added.[7]

Next we examined the influence of the degree of sulfonation of PSS. Figure 3 shows the CWM viscosity and the PSS adsorption as a function of the degree sulfonation. When the degree of sulfonation became lower than 80 %, the apparent viscosity was seen to increase rapidly. Similarly, the adsorption of PSS increased with a decrease in the degree of sulfonation. However, as the upper part of Figure 4 indicates, the ζ-potential did not change appreciably when the degree of sulfonation varied. This weak correlation between the apparent viscosity and the ζ-potential indicates that there should be a mechanism, other than electrostatic interaction, that causes the formation of aggregates when the degree of sulfonation is decreased. Based on this speculation, we measured the particle size distribution of coal particles as a function of the degree of sulfonation. As shown in the lower part of Figure 4, as the degree of sulfonation decreased, the size of aggregates definitely increased. Since PSS became more hydrophobic as the degree of sulfonation decreased, it can be said that as the adsorption of PSS increases with a decrease in the degree of sulfonation, the coal surface was transformed to be more hydrophobic. Consequently, large aggregates are formed more easily. On the other hand, when the degree of sulfonation was higher than 80 %, it was seen that an increase in the degree of sulfonation caused a slight increase in the ζ-potential in spite of a decrease in the adsorption of PSS, and that the increase in the ζ-potential contributed to the decrease in the apparent viscosity. This result suggests that in this region dispersion stability of CWM is due to the electrostatic effect and not to the steric repulsive effect.

From the results presented above, we have reached the following conclusion: (1) the viscosity of CWM decreases through the peptization of aggregates mainly due to the electric repulsive force induced by the adsorption of PSS; (2) however, PSS having high affinity to coal particles can increase the viscosity of CWM; (3) accordingly, in the selection of additives, it is important to note that not only must the additive be capable of providing a high electric repulsive force but also that its affinity to coal particles is low enough to avoid the formation of aggregates. In addition, it has been proved that the new acoustic method is very powerful for investigating the dispersion behavior of a concentrated suspension unlike the conventional method.

References and Notes

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