Behavior of Surfactants in the Suspension of Coal Components

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The roles and behaviors of an anionic surfactant, such as naphthalenesulfonate-formaldehyde condensate (NSF) and poly(styrenesulfonate) (PSS) in the high-loaded suspensions of the Celejon coal with low mineral content (1.2%), carbon black, kaolinite, and montmorillonite were studied. It was found that it is necessary to prepare a slurry of low-viscosity Celejon coal, carbon black and kaolinite in such a way that the surfactant is present as saturatedly adsorbed on the particles as well as being free in water. In the presence of a surfactant, high-loaded suspensions exhibited non-Newtonian fluidity without yield values in their shear-rate and shear stress relation. In contrast, neither NSF nor PSS showed any adsorption on the bentonite particles. Its suspension exhibited a non-Newtonian fluidity with the yield value, even if its concentration was low. The roles of the bentonite were confirmed by adding bentonite to the CWM of Celejon. The CWM of Taiheiyo coal which carried 4.81% montmorillonite suffered a limited coal concentration due to because of a large yield value. Sodium polycarbonate was found to be effective to reduce the yield value, allowing a high coal concentration in CWM.

A commercially feasible coal water slurry (CWM), as the most economical fluid fuel, must satisfy a high achievable coal concentration, low apparent viscosity, appropriate yield value for its cost, as well as handy transportation, and storage stability.[1] The selection of a surfactant as well as coal is very important in preparing such a CWM.[2—4] Coal basically consists of organic and inorganic portions, the content of the latter portion generally ranging from 10 to 20%./THEYear to play their respective roles in CWM under the presence of a surfactant, as was suggested in a previous paper[5] in relation to the surfactant adsorption on both particles, thus influencing the apparent viscosity and achievable coal concentration of CWM, according to their interfacial properties.

We studied the behaviors of organic and inorganic particles in coal were studied in separate slurries in order to clarify their roles by defining the above properties of CWM, particularly the yield value, which has been found to be lack in some coals.

In the first part of this paper Celejon coal with the least mineral content (1.2%) and carbon black free from minerals are compared in their respective water slurries in order to define their properties with surfactants, and to clarify their common as well as contrasting features according to their interfacial natures such as the surface area and surface functional groups.

The second part of this paper describes the slurry properties of kaolinite and montmorillonite in the presence of a surfactant. Both kaolinite and montmorillonite are known as hydrophobic colloidal particles,[6] and their aqueous suspensions exhibit Bingham fluidity.[7,8] Their interaction with surfactants was also studied, since they adsorb water layers on their surfaces and tend to flocculated upon the addition of an electrolyte.

The third part of the paper deals with the CWM of Taiheiyo coal with a high mineral content (15.9%). Too much mineral may bring about a problem involving a large yield value. Some solutions were searched for by modifying the surface properties of the minerals with polar additives.

Such a series of studies suggests how such representative particles in coal contribute to the above-described properties of CWM, and helps to prepare water slurries of sufficient storage stability at higher achievable concentrations from Celejon coal with a minimum mineral content and from Taiheiyo coal with more minerals, respectively.

Experimental

Test Samples. Celejon coal from Colombia (1.2% mineral matter) and Taiheiyo coal from Japan (15.9% mineral matter) were selected for the present study. Their analytical data are summarized in Table 1. These coals were pulverized using a dry ball mill to pass through a 150 μm screen. The mean diameters and amounts of portions smaller than 1 μm were 26 μm, 7.6% for Celejon coal and 28 μm, 6.0% for Taiheiyo coal, respectively. The mineral matter in the coal was analyzed after low-temperature ashing (LTA), according to Miller.[9] Both X-ray diffraction and Fourier-transform infrared spectroscopy were used for the analyses. The analytical data concerning the LTAs from coals are listed in Table 2.

Carbon black (MA 100) produced by Mitsubishi Chemical Co. was selected as a model for the organic portion of coal

Table 1. Analyses of Coal

Analytical item	Celejon coal	Taiheiyo coal
Carbon content/%	83.8	78.2
Oxygen content/%	7.8	14.0
Inherent moisture/%	5.8	5.8
Fixed carbon/%	54.5	35.1
Ash content/%	1.2	15.9

Table 2. Analytical Data of Mineral Matter from Coal

Coal	Ash (%)	Mineral matter (%/coal)				Clay (%/coal)	
		Quartz	Carbonate	Sulfonate	Clay	Kaolinite	Montmorillonite
Celejon	1.2	0.44	0.04	0.18	0.54	0.22	0.32
Taiheiyo	15.9	2.23	0.95	0.80	8.75	3.94	4.81

particles in CWM. According to the manufacturer's analyses, its diameter by SEM, surface area by the BET method with N_2 and density are 22 nm, 134 $m^2 g^{-1}$ and 1.841, respectively. In the carbon-back water slurry, the conditions which showed good fluidity, a median-size diameter and a diameter of 90% which could pass through of the dispersed carbon black particles were 0.26 μm and 0.57 μm, respectively.

Purified "Georgia" kaolin and sodium bentonite prepared by Nihon-Bentonite Kogyo Co. were used as representative components of mineral matter in coals according to Sudo.[10] The available kaolin was crushed and pulverized with an agate mortar and pestle before being passed through a screen of 20 μm. Sodium bentonite is a mixture of montmorillonite (as the main component) and silicate, carbonate, and sulfate (as impurities). In order to obtain a purified montmorillonite, the available bentonite was mixed with a large quantity of water, with its pH value being adjusted from 9 to 10 prepare a 3% solution. After storage for 3 d the supernatant solution was collected and concentrated to 20% by vacuum distillation. Analytical values of kaolinite and montmorillonite are summarized in Table 3.

Two types of anionic surfactants, which had been selected in previous studies,[5] were used. One was naphthalenesulfonate-formaldehyde condensate (NSF, mean molecular weight by HPLC of 3700); the other is poly(styrenesulfonate) (PSS, mean molecular weight of 10000). The other chemicals used were a special grade reagent and distilled water was used to prepare the slurry and to conduct the analysis.

Slurry Preparation. Carbon black (30—105 g) was gradually added into water (270—190 ml) containing a surfactant (in the range of 0.25% to 14%/solid); in a 800-ml steel beaker. The total amount of solid powder was added over a period of 20 min while stirring was continued (with blades of the double-helical ribbon type) at 225 rpm. High-velocity mixing was applied by a TK-Homomixer at 4000 rpm during the last period. The solid concentration in the slurry was in the 10 to 35% range. 30% carbon black and 6% surfactant were defined as the standard concentration. Coal and kaolinite water slurries were prepared following the same procedure described above. A montmorillonite water slurry having the required amount of surfactant was diluted to the intended solid concentration with water. After adjusting the concentration of the solids, the slurry was vigorously stirred with the TK-Homomixer at 4000 rpm. According to the pH of the practical CWM, every slurry in this study was adjusted to be within a range of pH 7.0 to 9.0 with a 1 equiv-NaOH solution.

Table 3. Analysis of Clay

Clay	SiO_2	Al_2O_3	Si/Al
Kaolinite	68.1	13.1	4.4
Montmorillonite	48.9	27.0	1.5

Properties of the Slurry. The viscosity of the slurry was measured at 25 °C within a shear rate of 0 to 150 s^{-1} using a double-cylinder type rotary viscometer of Haake (rotor MV-1P, measuring head MK-50 and MK-500). The viscosity at 100 s^{-1} with a decreasing shear rate was adopted as the apparent viscosity of the slurry.

The solid concentration in the slurry was calculated by subtracting the amount of surfactant used from the solid amount obtained after drying prepared slurry at 110 °C.

Prepared slurries were stored in sealed polymer bottles under the mixing condition for 24 h; the solids and solution were then separated by filtration using a millipore filter of 0.45 μm after centrifuging. The concentration of the surfactant in the filtrate was measured with by gelpermeation chromatography; the amounts of the surfactnat adsorbed on the solid particles were calculated as the difference between the amounts of the surfactants added and that in the water.

Results

Interactions between the Surfactant and the Organic Portion. The relations between the adsorbed amounts onto Celejon coal and the surfactant concentrations in water are summarized in Fig. 1. The adsorbed amount increased with its increasing concentration in water, reaching a maximum to stay constant in the range of the NSF concentration in water at 1.5 to 5 mmol dm^{-3} and 0.5 to 3 mmol dm^{-3} of PSS. From these values, the saturated adsorbed amounts of the surfactant to Celejon coal particles were estimated to be 4 mg g^{-1} for NSF and 2 mg g^{-1} for PSS.

The adsorption behaviors of the surfactants onto carbon black are summarized in Fig. 2. The constant adsorption values with NSF and PSS were 63 mg g^{-1} over the range of 1.5 to 8 mmol dm^{-3} and 62 mg g^{-1} from 2 to 10 mmol dm^{-3} respectively. The profiles of surfactant adsorption on these organic particles were very

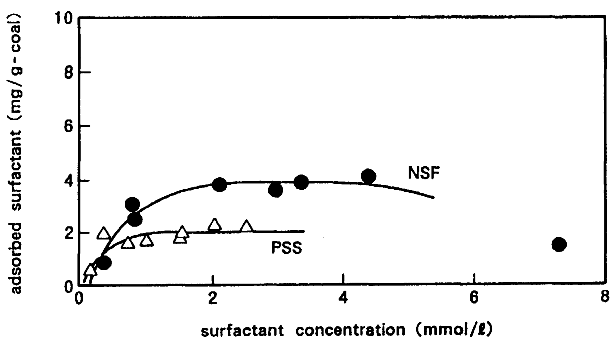

Fig. 1. Adsorption behavior of NSF and PSS on Celejon coal.

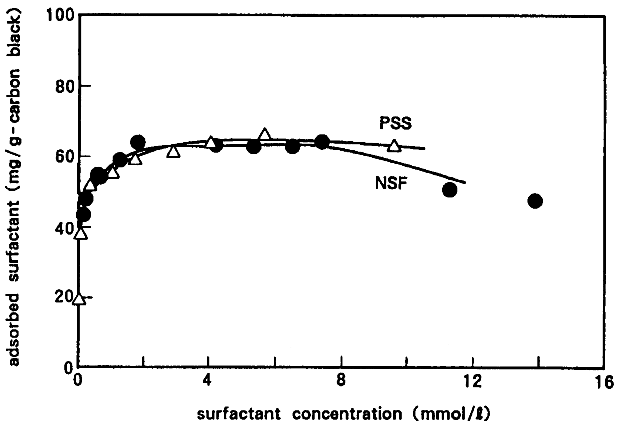

Fig. 2. Adsorption behavior of NSF and PSS on carbon black.

similar, though their different adsorption amounts appear to reflect their particle-size distributions.

The relations between the amount of adsorbed surfactant on the carbon-black particles and the cationic concentrations are illustrated in Fig. 3. The adsorbed amounts of each surfactant increased with an increase in the cation concentration, as observed in a previous paper.[11] The calcium ion allowed more adsorption than did the sodium ion.

The apparent viscosity and surfactant concentration in water of 60% loaded Celejon coal and 30% loaded carbon-black slurries were measured by varying the usage of NSF. As illustrated in Fig. 4, the apparent viscosity decreased at first with an increase in the usage of NSF, reaching constant points with NSF of more than 0.5% with Celejon coal and 6% with carbon black, respectively. NSF began to appear in water when the use of NSF went beyond these values. A greater concentration of NSF than 3% increased the apparent viscosities of both Celejon coal and the carbon-black slurries.

Rheograms of carbon-black slurries with 4.5 to 8% NSF use are summarized in Fig. 5. NSF of 4.5% provided pseudo-plastic behaviors with a large hysteresis loop, thus indicating the presence of strongly agglom-

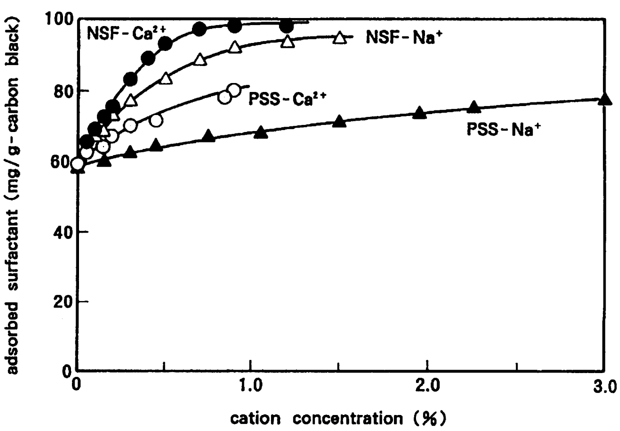

Fig. 3. Effects of cations on the surfactant's adsorption.

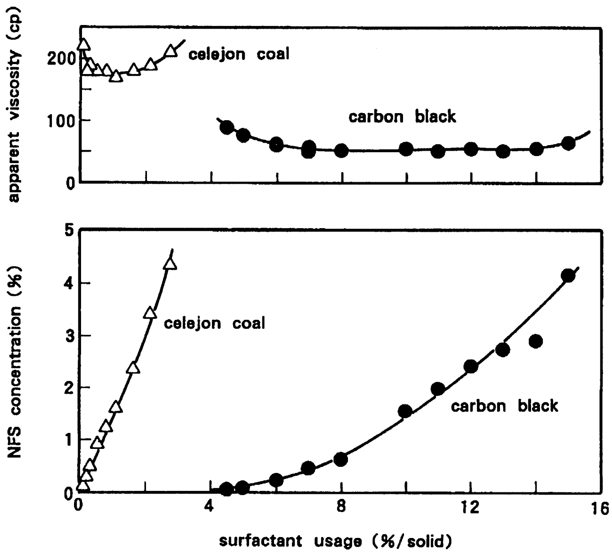

Fig. 4. Apparent viscosity and NSF concentration in water vs. NSF usage.

erated particles in the slurry, due to an insufficient amount of surfactant. A particular rheogram with a large yield value was observed with 5% NSF of the slurry. It is very interesting that the amount of the surfactant is still slightly insufficient, allowing a weak agglomeration. The slurry showed an apparent yield value. A sufficient dispersion of the carbon black was achieved by using NSF in the 6 to 8% range to give a pseudo-plastic flow with a small hysteresis loop and a lower viscosity. It should be notes that a highly concentrated carbon black slurry did not show a yield, even when a sufficient surfactant was added in order to prohibit an agglomeration of its particles.

Interaction between the Surfactant and the Inorganic Portion. The amounts of surfactant adsorbed to kaolinite particles (52 to 63% in water) are summarized in Fig. 6. The equilibrium adsorption amounts on the kaolinite were 5 mg g^{-1} with NSF and 3 mg g^{-1} with PSS. These values are almost the same as those on coal particles in CWM, but one tenth of those on carbon black.

The apparent viscosity and yield values vs. the use of a surfactant in kaolinite slurries are plotted in Fig. 7. Both NSF and PSS decreased the apparent viscosity and the yield value of the slurry with an increase in surfactant use to level off by adding 1.0% surfactant to give a 0.1% concentration in water.

In contrast, neither NSF nor PSS showed any adsorption on montmorillonite particles. The apparent viscosities of 5% montmorillonite slurries with surfactant were in the 40 to 90 cP range (1 cp$=10^{-3}$ Pa s) with NSF and 70 to 110 cP with PSS, respectively, and showing a typical Bingham-type fluid behavior.

Effects of Mineral Matter on the Rheology of CWM. The CWM of Celejon coal showed an achievable coal concentraion of 63% upon using 0.6% PSS. It

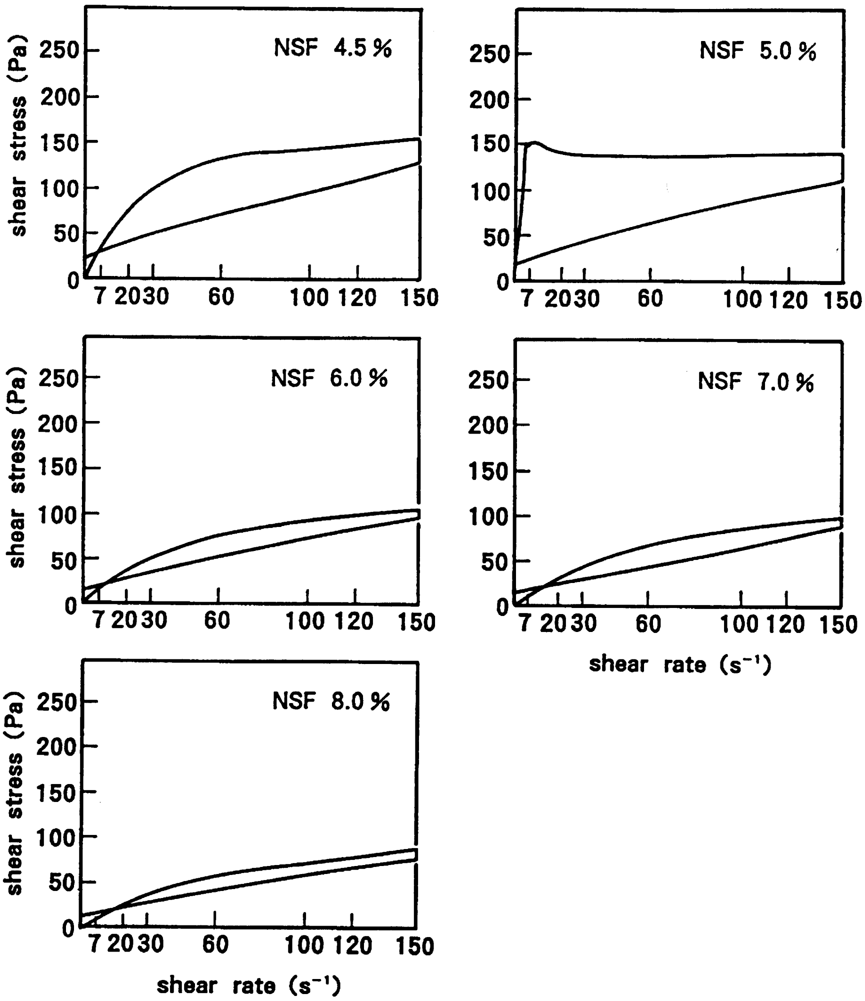

Fig. 5. Rheograms of carbon-black slurries prepared with various usage of NSF.

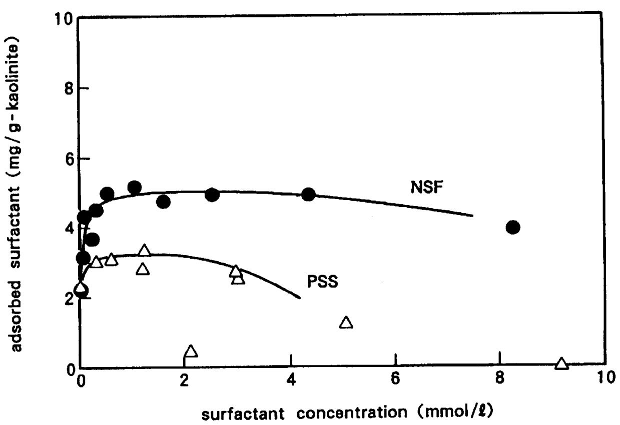

Fig. 6. Adsorption behavior on kaolinite particles.

was classified as a non-Newtonian fluid with no yield value, being very similar to that of a carbon-black water slurry. Sediments were often detected during measurements of its viscosity, thus indicating its insufficient stability.

The addition of bentonite to CWM of Celejon coal gave the yield value as shown in Fig. 8 and provided storage stability to the suspension. However, its addition increased the apparent viscosity according to its amount over in the range of 3000 to 10000 ppm (Fig. 9).

Both the yield value and the apparent viscosity upon the addition of the bentonite to CWM increased with a higher concentration of coal in CWM. Hence, the achievable coal concentration in CWM stabilized by bentonite was slightly reduced to maintain the apparent viscosity.

A rheogram of 58% loaded CWM of Taiheiyo, prepared with 0.5% NSF, is illustrated in Fig. 10. This CWM is classified as being a Bingham fluid with a large yield value. This value appears to be responsible for the low achievable coal concentration (59%) as well as the difficulty of handling after long-term storage, since a higher coal concentration further increased the yield value, thus requiring a larger shear to fluidize. Rheograms of a 62% loaded CWM (0.5% NSF) without and with 0.2% sodium polycarbonate (KM-7) are illustrated in Fig. 10. KM-7 definitely decreased the yield value of the slurry. The addition of KM-7 allowed for an increase in the achievable coal concentration from 59 to 62%.

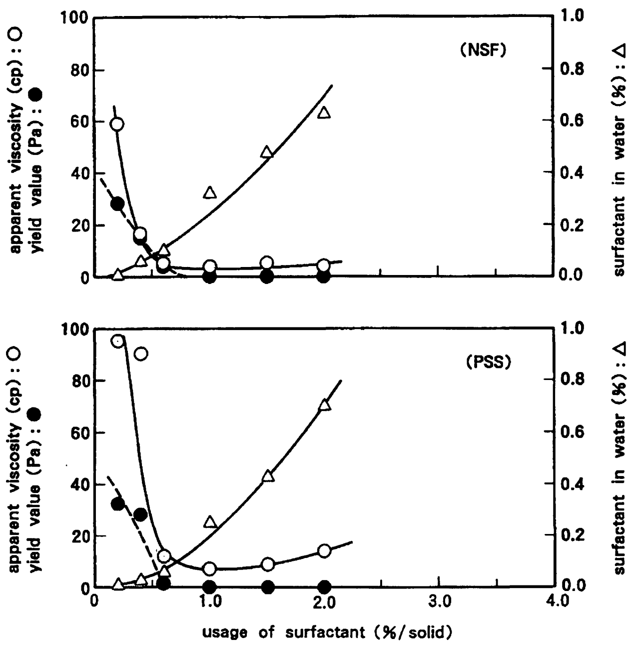

Fig. 7. Apparent viscosity, yield value and surfactant concentration in water vs. surfactant usage.

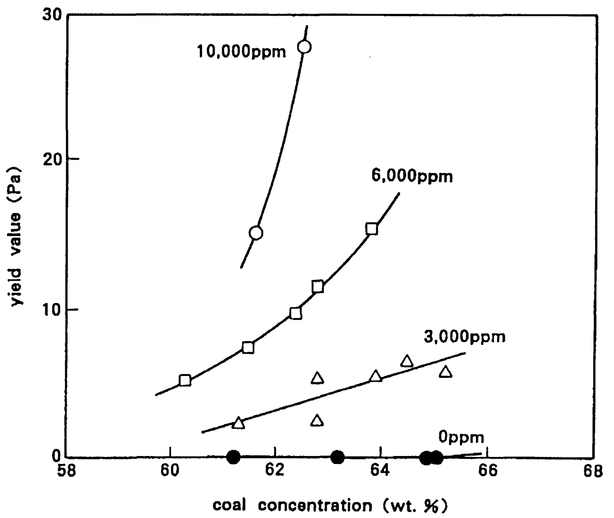

Fig. 8. Effects of bentonite on the yield value of CWM.

Discussion

CWM as a fluid fuel is required to provide a stable and adequate viscosity throughout its handling, such as its transportation, storage and combustion. Hence, CWM should show pseudo-plastic, or Bingham flow regarding in its rheological properties.[10] The CWM of high coal concentrations in water has achieved such properties by the aid of surfactants. However, there is a fundamental question as to whether such properties can be obtained exclusively by organic particles and surfactants, since some coals show very low stability.

The organic portion of the coal is basically hydrophobic, although some hydrophilic groups are also

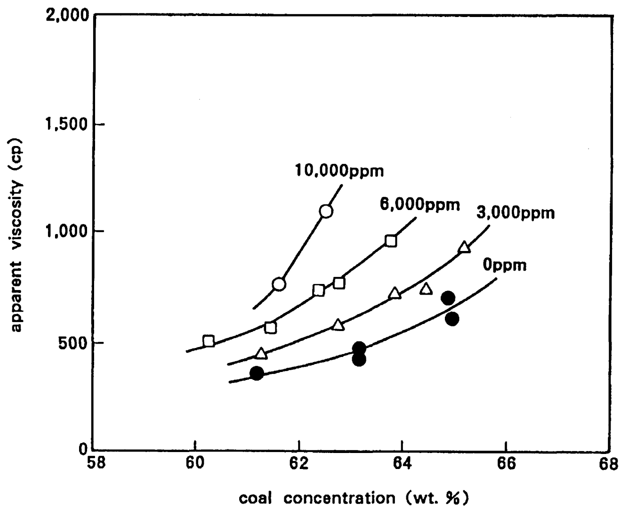

Fig. 9. Effects of bentonite on apparent viscosity of CWM.

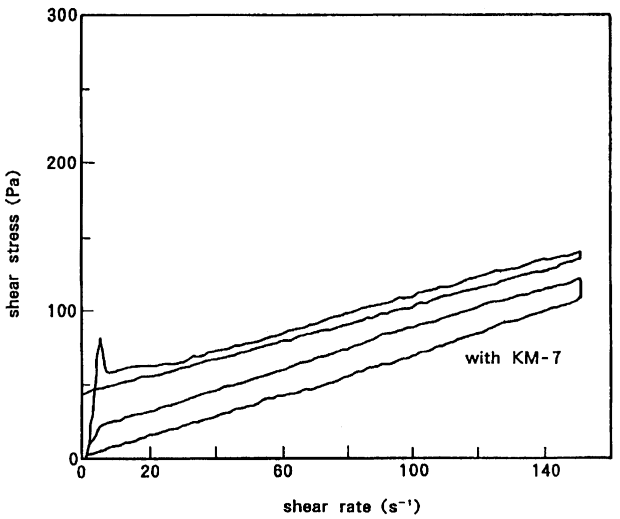

Fig. 10. Rheograms of Taiheiyo coal slurries.

present in minor amounts. Bascially, their properties depend on their coalification and weathering. On the other hand, coals always carry some mineral matter in the 0 to 20% range. The mineral matter comprises a mixture of clay minerals, silicates, sulfates, sulfides, and carbonates, classified as hydrophilic substances. Such substances should also interact with the water and surfactants, thus influencing the fluid properties of the high-loaded CWM. It is thus necessary to clarify their effects on the behavior of a surfactant in CWM.

Celejon coal with a mineral content as low as 1.2% failed to provide a stable slurry, and exhibited sedimentation easily, even during measurements of its viscosity. Although its slurry showed low viscosity and a pseudoplastic fluidity, with the aid of proper amount of surfactant, its rheogram indicates that the instability of the slurry is due to the lack of any yield value. In contrast, Taiheiyo coal with a mineral content of 15.9% showed a very large yield value in its CWM, appearing to lower its achievable coal concentration. Thus, it is evident that mineral matter plays a very important role in CWM.

The behaviors and roles of surfactants are of value when discussing in detail their interactions with organic and inorganic components of coal in order to define the roles of each component in the preparation of high-concentration CWM. The adsorptioon behaviors of NSF and PSS on bituminous coals, regardless of their mineral contents,[11] and on carbon black appear to be very similar, thus strongly influencing the apparent viscosity of the CWM. The effects of cations in water on the adsorptions of NSF and PSS are also similar for coal and carbon black. These effects are very similar to those of sodium alkyl sulfate (AS), sodium α-alkenesulfonates (AOS)[12] and sodium bis (2-ethylhexyl) sulfonatosuccinate (Aerosol OT)[13] onto carbon black. This similarity indicates that these surfactants are adsorbed on the carbon black at their hydrophobic parts.

In a carbon-black water slurry, the relationships between the apparent viscosity and the surfactant concentration in water suggest that the saturated adsorption of a surfactant on the solids, and its presence in water, are both required to disperse the fine organic powders in water. Insufficient amounts of surfactant allow the aggregation of dispersed particles, due to their strong hydrophobic natures, even if mechanical mixing is being continued. In contrast, a sufficient surfactant allows for a high dispersion in the slurry, thus producing a pseudoplastic fluid with no yield values. The adsorbed surfactants on the solids act as a coating layer, thus greatly dispersing particles in water.

The highly dispersed organic particles in water, however, never exhibit the yield value, even when a sufficient amount of surfactant is added for the acceptable apparent viscosity. Organic particles in such a slurry without a yield can not be stably suspended in water of low viscosity. Hence, such a slurry of organic particles alone, even with a sufficient amount of surfactants, is not sufficiently stable, and thus suffering sedimentation during its storage.

NSF and PSS show similar adsorption behaviors on kaolinite particles with organic particles. The surfactants decrease the apparent viscosity as well as the yield value with their adsorption. Hence, kaolinite particles may behave in the same way as do organic particles in CWM.

The present study found that the addition of bentonite is very effective to induce an appropriate yield value in CWM with a sufficient amount of surfactants for an appropriate apparent viscosity. Meanwhile, kaolinite failed to do so, although both mineral particles alone without a surfactant in the slurry exhibited yield values. Thus, a particular mineral would apparently be necessary for the stabilization of CWM with a yield value.

The surfactants used in the present study were found to be adsorbed on kaolinite, thus removing the yield value from its slurry in a concentration range of 0.2—3%. Hence, kaolinite is not effective to give a yield value to the CWM. In contrast, no adsorption of the surfactants was observed on bentonite, and a large yield value of its slurry survived under the CWM condition with a sufficient amount of surfactant. Since the organic particles may be sustained, thus indeed, in a Bingham fluid slurry, no sedimentaion takes place during storage.

Bentonite has been reported to adsorb a great variety of low molecular-weight organic species. Nevertheless, it was found in the present study that it does not adsorb a polymeric surfactant. It is inferred that very fine particles of bentonite could not adsorb a large molecular-weight surfactant, such as NSF (3700) and PSS (10000) used in this study. A detail study of the relation between the particle and molecular sizes of a suitable surfactant is very much needed.

Finally the yield value of a mineral matter slurry appears to be proportional to the mineral concentration. Hence, too much bentonite in the slurry may have induced an excessively high yield value, thus requiring too large a shear for the appropriate apparent viscosity of the slurry, as observed with the Taiheiyo coal slurry. Hence, achievable concentration of coal in the slurry is limited by this reason. Surfactants cannot handle this problem, because of no adsorption and no influence on the yield. However, sodium polycarbonate was found to moderate the yield value of a Taiheiyo coal slurry. The polycarbonate increased the achievable coal concentration from 59 to 62%, thus reducing the apparent viscosity. Since polycarbonate is known to be a polymeric flocculant against mineral particles,[14] it may be adsorbed on bentonite to decrease the effect of bentonite on the yield value.

On the basis of the above discussion, the effects of the organic and inorganic portions of coals on the roles and behaviors of the surfactants were clarified in terms of the rheological properties of the suspensions as follows: (1) Celejon coal, carbon black and kaolinite adsorb surfactants over a pH range of 6 to 8 as required for CWM. (2) Both surfactants that adsorbed on solids and were free in water were necessary to prepare a favorable suspension of these solids. These suspensions were non-Newtonian fluids without yield values, thus suffering insufficient storage stability. (3) Neither NSF nor PSS was adsorbed by bentonite particles. The suspension of bentonite was a non-Newtonian fluid with a yield value, even if its concentration was low and a surfactant was present. (4) The addition of bentonite to a Celejon coal–water slurry induced a yield value, thus improving its storage stability to a practically acceptable point. (5) Sodium polycarbonate moderates the yield value due to a large amount of bentonite, thus allowing a higher coal concentration in CWM of Taiheiyo coal.

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