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# Combined Use of Cation-Masking Agent with Anionic Dispersant for the Preparation of High Performance CWM

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By the combined use of cation-masking agent with anionic dispersant, highly-loaded coal water mixture (CWM) was prepared, and the sedimentation stability and rheological property of CWM were much improved as compared with the case of single use of the anionic dispersant.

Highly-loaded coal water mixtures (CWMs) are the most promising alternative fuel for heavy oil in many industrial applications.[1] The CWMs are required to be loaded by more than 65% coal, and therefore powerful dispersant is essential for the preparation of CWMs in order both to protect the sedimentation of coal particles during their storage and to lower the viscosity during their transportation. Many research efforts are currently devoted to the development of effective and inexpensive dispersants.

It is certain that much metal cationic species elute from coal particles into the aqueous phase of CWM during the storage and conduct adverse effect on the stability and the rheological properties of CWM, however a few and fragmentary pieces of information are hitherto obtained on the effect of cation-masking agent upon the CWM performances above described.[2,3] We report here the combined use of cation-masking agent with anionic dispersant, and prove a remarkable enhancement on the CWM performances.

The coal used in this study was a Saxonvale coal from Australia and its analyses are as follows. Proximate analysis: moisture (3.2%), ash (15.8%), volatile matter (28.9%), fixed carbon (52.1%). Fuel ratio: 1.80. Ultimate Analysis (in dry base): C (74.6%), H (4.2%), N (1.5%), S (0.4%), O (6.5%). As CWM dispersants, a naphthalenesulfonate-formaldehyde condensate ("Koal 100", Kao Corpo-ration, abbreviated as NSF) and a lignin sulfonate ("Pozzolith No.8 IMP", Nisso Master Builders Co., Ltd., abbreviated as LS) were used. Such kind of aromatic sulfonate condensates are known to be effective dispersant for CWM.[4-7]

The coal particle size was adjusted by blending coals under 74 μm and 125 - 74 μm in the weight ratio 80:20 (mean particle size $\bar{\mu}$ = 25 μm). Tap water (170 g) was mixed with a dispersant and a cation-masking agent (5 g, the sum of both agents) for 1 min using a homogenizer and then the mixture was blended with coal powder (325 g) for 10 min by a powerful mixer with four blades (4 000 r.p.m.) to prepare 500 g of CWM. (Composition of CWM: coal (65%, dry coal), water (34%), dispersant and cation-masking agent (1%); pH 7.5 - 8.0). In the case of LS dispersant, an appropriate amount of sodium hydroxide was added to adjust pH 7.5 - 8.0.

The sedimentation stability of CWM was evaluated by the "glass rod penetration test" (penetration ratio (%) and time (s)) in a similar manner to that in the studies on COM as described in our previous papers.[8,9] After the CWM prepared was stored in a glass cylinder (4 cm in diameter; CWM layer 21 cm in height) at room temperature for a definite period, a glass rod (5 mm in diameter , 20 g in weight) was spontaneously dropped down from the CWM surface to the cylinder bottom. The penetration ratio was defined as the percentage of penetration of the glass rod and the penetration time was the time required for the complete penetration (100% penetration ratio). The rheological properties are measured by a rheometer with coaxial rotating cylinder (Haake Rotovisco RV2). The shear history was as follows: shear rate $0 \longrightarrow 150\ s^{-1}$ (3 min), $150\ s^{-1}$ (3 min), $150 \longrightarrow 0\ s^{-1}$ (3 min). Apparent viscosity of CWM was obtained from the shear stress at $20\ s^{-1}$ on the upward curve.

Figure 1a shows the plot of the rod penetration time against the storage time in the case of NSF-CWM. When NSF only was added into the CWM system, the rod penetration ratio was 100%, however the time was considerably long (57 s) after 30 days storage, suggesting that a sedimentation layer of coal particles formed to some extent in the bottom of CWM. The combined use of a cation-masking agent, triphosphate, with anionic dispersant could enhance the CWM stability against the coal sedimentation; the rod penetration time was much shortened and the higher the concentration of cation-masking agent, the better was the stability. In the case of LS-CWM, a similar result was obtained (Fig. 1b). The combined use of cation-masking agent with anionic dispersant was very effective on the stabilization of CWM.

During the storage, the aqueous phase of CWM contained 300 - 400 ppm alkaline earth metal ions ($Ca^{2+}$ and $Mg^{2+}$) and trace of $Al^{3+}$ and $Fe^{3+}$ which were eluting from the coal particles. It is considered that in the CWM using anionic dispersants, the coal particles are dispersed in the water due to the electrostatic repulsion by the anionic charges of dispersants adsorbed on the coal surface. Those multi-valent metal ions are concentrated on the coal surface possessing anionic charges, so that the charges are neutralized to result in the lowering in the electrostatic repulsion force and consequently in the sedimentation of coal particles. Cation-masking agents such as triphosphate can successfully mask those metal cations and hence eliminate such an adverse effect of the metal ions on the CWM stabilization.

Figures 2a and 2b indicate the plot of the apparent viscosity against the storage time in the case of NSF-CWM and LS-CWM, respectively. When the cation-masking agent were added into the CWM system, the apparent viscosity was greatly lowered leading to the realization of high performance CWM. This may be attributed to a similar reason mentioned above in the sedimentation stability. Thus the electrostatic repulsion between coal particles acts as a lubricant in the flowing CWM, and the cation-masking agent can prevent the neutralization of anionic charge on the coal surface by metal cations.

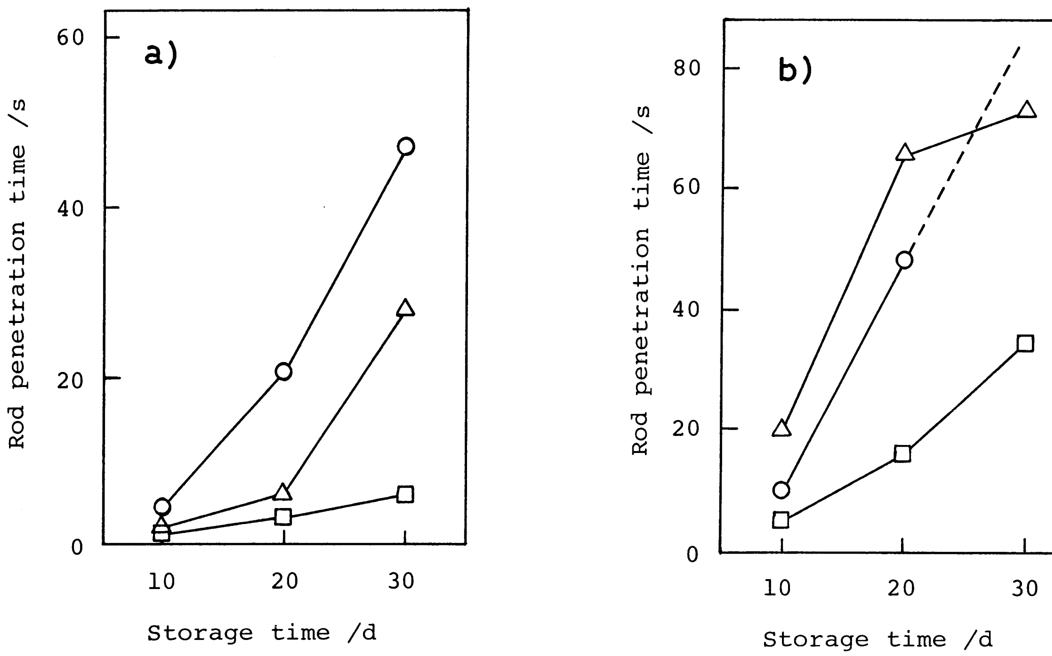

Fig. 1. Plots of rod penetration time vs. storage time. a) NSF-CWM, b) LS-CWM. The amounts of anionic dispersant and cation-masking agent (sodium triphosphate) added into the CWM system were as follows: ( ○ ) 1.0% and 0%, ( △ ) 0.75% and 0.25%, ( □ ) 0.5% and 0.5%, respectively. The rod penetration ratio was 100% in all cases except for the LS-CWM without the masking agent after 30 days storage (74%).

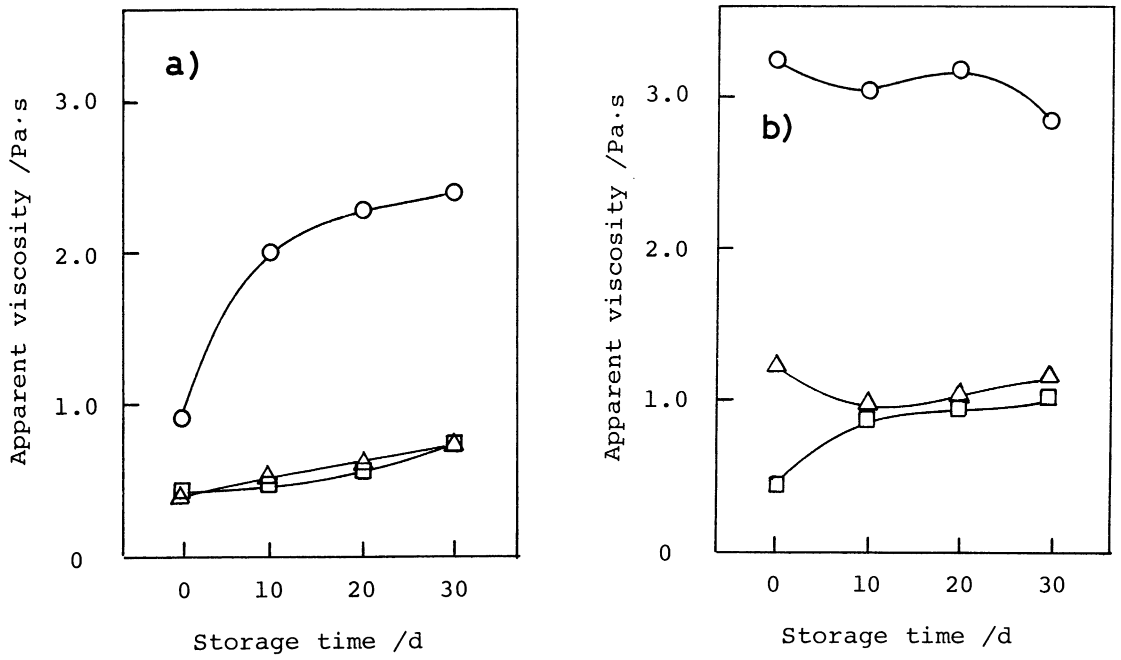

Fig. 2. Plots of apparent viscosity vs. storage time. a) NSF-CWM, b) LS-CWM. The symbols are the same as those in Fig. 1.

The addition of cation-masking agent into the CWM system considerably affected its rheological feature. The LS-CWMs without the cation-masking agent after more than 20 days storage showed a rheopexy to some extent, whereas the CWMs with the agent exhibited a thixotropy which is desirable property in the CWM utilization. The NSF-CWMs showed a thixotropy both in the presence and in the absence of cation-masking agent.

As the cation-masking agent, pyrophosphate was as effective as triphosphate on raising the performances of CWM. Complexon-type agents such as nitrirotriacetic acid and ethylenediaminetetraacetic acid were also efficient. However, in the sedimentation stability as well as in the rheological property, the CWMs using the polyphosphate-type cation-masking agents were superior to those with the complexon-type agents.

In conclusion, the combined use of cation-masking agent with anionic dispersant proved to be very effective on the performances of CWMs using polymer sulfonate type anionic dispersants; such a phenomenon certainly deserves further exploration.

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## References

1) Y. Iwabuchi, Petrotech, 8, 1053 (1985).
2) R. Kaji, Y. Muranaka, H. Miyadera, and Y. Hishinuma, Nenryo Kyokaishi, 66, 842 (1987).
3) Y. Shimizu, M. Nakayama, and M. Sugiyama, Jpn. Kokai Tokkyo Koho, JP 62 72,789 (1987), Chem. Absr., 107, 158103y (1987).
4) Y. Nakabayashi, N. Sato, H. Ito, S. Tatsumi, Y. Kajibara, and S. Takao, Proc. 8th Internat. Symp. Coal Slurry Fuels (1986), p.55.
5) M. A. McLaughlin, J. E. Funk, and D. R. Dinger, Proc. 8th Internat. Symp. Coal Slurry Fuels (1986), p.63.
6) Y. Ogura, Y. Mizuno, N. Uejima, and A. Naka, Proc. 8th Internat. Symp. Coal Slurry Fuels (1986), p.129.
7) Y. Nakamoto, S. Nakagawa, N. Otabe, and H. Ishimatsu, Jpn. Kokai Tokkyo Koho, JP 58 45,287 (1983).
8) T. Takeshita, S. Maeda, M. Imayoshi, and Y. Kitada, Sekiyu Gakkaishi, 25, 136 (1982).
9) S. Maeda, S. Kanamori, M. Imayoshi, and T. Takeshita, Fuel, 65, 1658 (1986).

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