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INFLUENCE OF CALCIUM SULFATE IN BELITE-RICH CEMENT ON THE CHANGE IN FLUIDITY OF MORTAR WITH TIME

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ABSTRACT

The fluidity of mortar containing a polycarboxylate-based high-range water-reducing AE agent was studied with respect to the change in fluidity with time after the mixing, and the influence of the kind and amount of calcium sulfate in the belite-rich cement with a low interstitial phases was discussed. The flow of belite-rich cement mortar immediately after the mixing initially increased and then decreased with the increase in the saturation ratio of the liquid phase with respect to $CaSO_4{\cdot}2H_2O$. On the other hand, the flow loss continuously decreased with the increase in the saturation ratio. The saturation ratio of the liquid phase strongly depended on the amount of $CaSO_4{\cdot}0.5H_2O$, and was hardly affected by the other kinds of calcium sulfate. The adsorption of the agent inversely corresponded to the mortar flow immediately after the mixing. However, the flow loss did not coincide with the adsorption tendency. It is suggested that the steric hindrance remains to some degree after the hydrate partially covers the agent adsorbed on the cement particles. *© 1998 Elsevier Science Ltd*

Introduction

Belite-rich cement was developed to have a low heat of hydration and a high strength in later age by an increased belite content as compared with the other kinds of Portland cement (1,2). This type of cement also shows a high fluidity (3,4,5). Therefore, belite-rich cement has been widely recognized to be suitable for high-flowing concrete and high- strength concrete as well as for low-heat concrete. The high fluidity of the belite-rich cement (3,4) is mainly due to the extremely low content of the interstitial phases (C_3A and C_4AF). The fluidity of the belite-rich cement, however, varies with some characteristics of the cement other than the mineral composition of the clinker.

Generally, the characteristics of cement such as burning degree (6), fineness, and particle size distribution (7–9), are important with respect to the fluidity. Moreover, It is also known that the fluidity of the cement paste containing a commercial superplasticizer mainly composed of highly condensed sodium naphthalene sulfonate formaldehyde strongly depends on

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TABLE 1
Character of each cement ground by plant mill.

		AJS			Mineral composition (%)			
Sample name	Blaine (cm^2/g)	15m R (%)	30m R (%)	n value	C_3S	C_2S	C_3A	C_4AF
BC-1	3420	48.0	12.0	1.53	29.4	55.3	2.3	7.3
BC-2	3400	47.0	11.0	1.55	27.6	56.7	2.5	7.0
BC-3	3300	51.0	13.9	1.55	27.1	56.8	2.5	

Note: *n* value, derived from Rosin-Rammlar equations; R_2O, $Na_2O + 0.658\ K_2O$; Gyp, $CaSO_4 \cdot 2H_2O$; Hem, $CaSO_4 \cdot 0.5H_2O$; An, Type II $CaSO_4$; SO_3 (%) from Gyp and Hem, determined by DSC; SO_3 (%) from An, calculated by assuming SO_3 content of clinker as 0.4%.

the kind and amount of calcium sulfate and alkaline sulfate because sulfates depress the adsorption of the superplasticizer onto the interstitial phases (10). However, polycarboxylate-based high-range water-reducing AE agents derived from new technologies such as the steric hindrance of graft copolymer (11) and the continuously developing effect of the cross-linked polymer (12) are major in the recent field of high-flowing concrete and high-strength concrete, and they are characterized by their effect of preventing the slump loss. It has been estimated that the dispersion effect of such an agent mainly depends on steric hindrance rather than electric repulsion (13–17). Recently, Uchikawa et al. (18) first proved the existence of steric repulsive force acting on the surface of chemical admixture adsorbed cement particles experimentally, using atomic force microscope and reliable zeta potential measurement. Therefore, there may be a different mechanism related to the fluidity in the presence of a polycarboxylate-based high-range water-reducing AE agent as compared with the case of the naphthalene sulfonate-based superplasticizer.

In this paper, the fluidity of the belite-rich cement mortar containing a polycarboxylate-based high-range water-reducing AE agent was studied with respect to the change in fluidity with time after the mixing, and the influence of the kind and amount of calcium sulfate was discussed.

Samples and Experimental Procedures

Samples

Three kinds of belite-rich cements ground in a plant mill by changing the proportion of $CaSO_4 \cdot 2H_2O$ and Type II $CaSO_4$ were mainly used. Table 1 shows the characteristics of the three cements such as fineness, mineral composition, content of each kind of calcium sulfate, and so on. BC-1 was ground using only $CaSO_4 \cdot 2H_2O$ and its SO_3 content was 2.2%. The total SO_3 contents of BC-2 and BC-3, which were ground using $CaSO_4 \cdot 2H_2O$ and Type II $CaSO_4$, were 2.6% and 2.9%, respectively.

Furthermore, five kinds of laboratory-made cements were also used. They were prepared from plant-made cements by the addition of $CaSO_4 \cdot 0.5H_2O$ as shown in Table 2.

TABLE 1
Continued

free CaO (%)	R_2O (%)	Total SO_3 (%)	SO_3 (%) from		
			Gyp	Hem	An
0.4	0.41	2.2	0.5	1.3	0.0
0.4	0.39	2.6	0.3	0.6	1.3
0.6	0.40	2.9	0.1	1.3	1.1

$CaSO_4{\cdot}0.5H_2O$ used for this preparation was obtained from $CaSO_4{\cdot}2H_2O$ with a Blaine specific surface area of 6700 cm^2/g by a heat treatment at 130°C.

Ogasa pit sand was used as the fine aggregate. Two types of high-range water-reducing AE agents, SP-M and SP-R, were used. SP-M is one of the typical polycarboxylate-based agents, and SP-R is also a polycarboxylate-based agent composed of a complex of polycarboxylic ether and cross-linked polymer.

Experimental Procedures

Change in mortar flow with time after mixing: The mixing proportion of mortar was fixed as a water cement ratio (w/c) = 30 wt.% and a sand cement ratio (s/c) = 147 wt.%, which was equal to that of the mortar part in a typical high-flowing and high-strength concrete with a W/C = 30 wt.%, water content = 165 kg/m^3, and sand aggregate ratio (s/a) = 50 vol.%. The amounts of SP-R and SP-M added to the mortar were 2.0 wt.% of cement in both cases. Two types of deforming agents recommended from each agent maker were also used for minimizing the influence of air on the mortar flow. The amount of a deforming agent added for the case of SP-R was 0.03 wt.% of the cement. For SP-M, the amount was 0.04 wt.% of the cement. The mortar was mixed for 5 min. at 20°C. The mortar flow was measured without the movement of the table at 0, 15, 30, and 60 minutes after the mixing.

Ionic concentration in liquid phase: With 3.0 wt.% SP-M, each cement was suspended in a equal weight of water (w/c = 100 wt.%) for 5 min. at 20°C. After that, the liquid phase of the suspension was obtained by filtration. The concentration of OH^- in the liquid phase was titrated and Ca^{2+}, SO_4^{2-}, Na^+ and K^+ were measured by ICP. Following Kondo et al. (19),

TABLE 2
Samples prepared in laboratory from plant-made cements.

Sample name	BC-2a	BC-2b	BC-2c	BC-3a	BC-3b
Base cement	BC-2	BC-2	BC-2	BC-3	BC-3
Hem added (SO_3 %)	0.1	0.2	0.3	0.1	0.2
Total SO_3 (%)	2.7	2.8	2.9	3.0	3.1

Note: Hem, $CaSO_4{\cdot}0.5H_2O$.

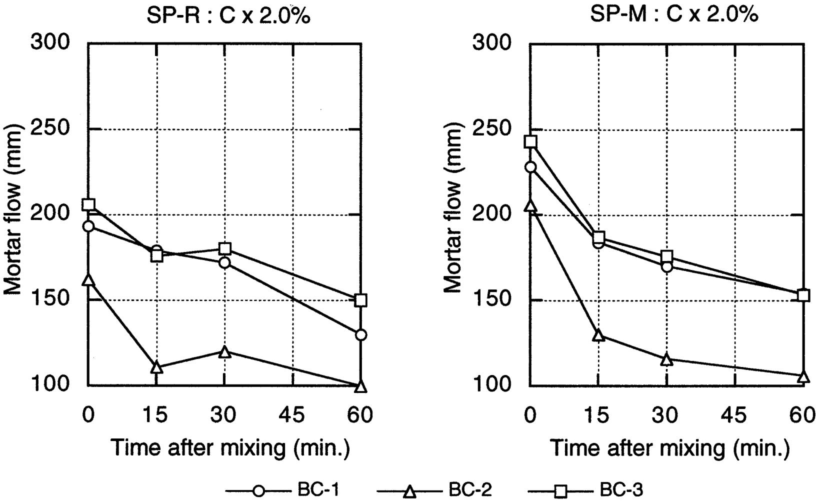


FIG. 1.

Change in mortar flow with time for each plant-made cement.

the saturation ratio of the liquid phase with respect to $CaSO_4{\cdot}2H_2O$ was calculated from the concentration of each ion taking into account the ionic strength. Though the measured concentration of Ca^{2+} ion may contain the combined Ca with SP-M in liquid phase, this factor was not taken into account in the process to calculate the saturation ratio for simplifying the measurment and discussion.

Adsorbed amount of high-range water-reducing AE agent: The concentration of high-range water-reducing AE agent remaining in the liquid phase, which was obtained by the same procedure as mentioned above, was measured using a total organic carbon analyzer and the amount of high range water reducing AE agent adsorbed on the cement particles was calculated.

Results

Fluidity of Plant-Made Cement

The results of the change in mortar flow with time are shown in Figure 1 for the three plant-made cements. Immediately after mixing, the mortar flow of BC-2 ground by using $CaSO_4{\cdot}2H_2O$ and Type II $CaSO_4$ was lower than that of BC-1 ground by using only $CaSO_4{\cdot}2H_2O$. Moreover, the mortar flow of BC-2 rapidly decreased with time, especially in the period from 0 to 15 min. after the mixing. On the other hand, the mortar flow of BC-3, which was also ground using $CaSO_4{\cdot}2H_2O$ and Type II $CaSO_4$, was almost the same as BC-1. In these cases, the decrease in mortar flow with time was relatively gradual until the end of the measurement.

There are no remarkable differences in the characteristics such as mineral composition, free CaO content, alkali content, fineness, and particle size distribution among the three

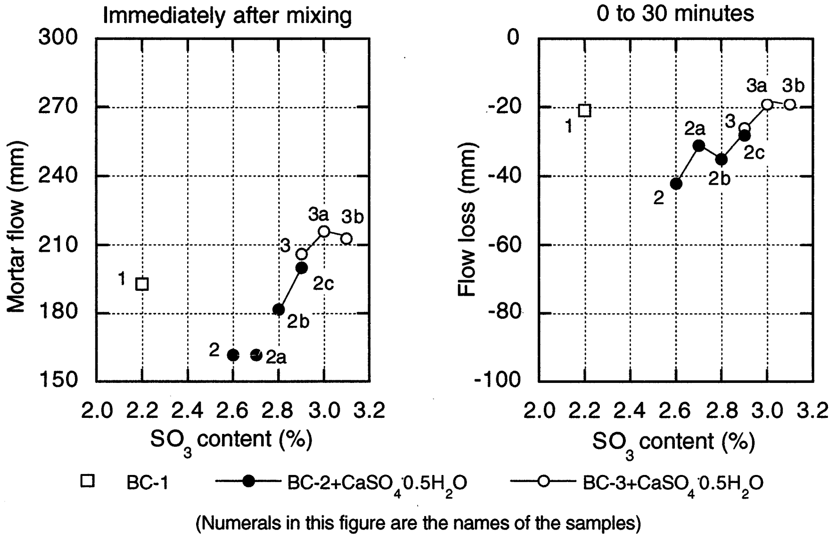


FIG. 2.
Relationship between SO_3 content of cement and fluidity (SP-R: C × 2.0%).

plant-made cements. These cements, however, contain different kinds of calcium sulfate in different proportions. The total SO_3 content of BC-1 is lower than the others, but it contains a relatively large amount of $CaSO_4{\cdot}0.5H_2O$ formed by the dehydration of $CaSO_4{\cdot}2H_2O$ during the grinding process. Concerning the cements ground using both $CaSO_4{\cdot}2H_2O$ and Type II $CaSO_4$, it should be noted that the $CaSO_4{\cdot}0.5H_2O$ content of BC-2 is extremely small. On the contrary, the $CaSO_4{\cdot}0.5H_2O$ content of BC-3 is almost the same as that of BC-1.

This result suggests that the fluidity of the mortar containing the polycarboxylate-based high range water reducing AE agent strongly depends on the kinds and amount of calcium sulfate in the cement. It is also clarified that the influence of calcium sulfate on the change in fluidity with time is also large.

Fluidity of Laboratory-Made Cement

The mortar flow and the flow loss of laboratory-made cements, as well as that of plant-made cements, are shown in Figure 2 and Figure 3 as a function of total SO_3 content.

Only the data of BC-1 was plotted in different areas from the other cements. On the other hand, the total SO_3 contents of the others were apparently related to the fluidity. It is confirmed again that the total SO_3 content is not sufficient to estimate the fluidity, though this value is commonly used for quality control in a cement plant.

Comparing the cements, BC-2a, 2b and 2c, prepared from BC-2, the mortar flow immediately after the mixing increased with the increase in SO_3 content in the presence of SP-R. The increase in SO_3 was also accompanied with the decrease in flow loss. Almost the same trends of mortar flow and the flow loss were recognized in the case of SP-M, though the

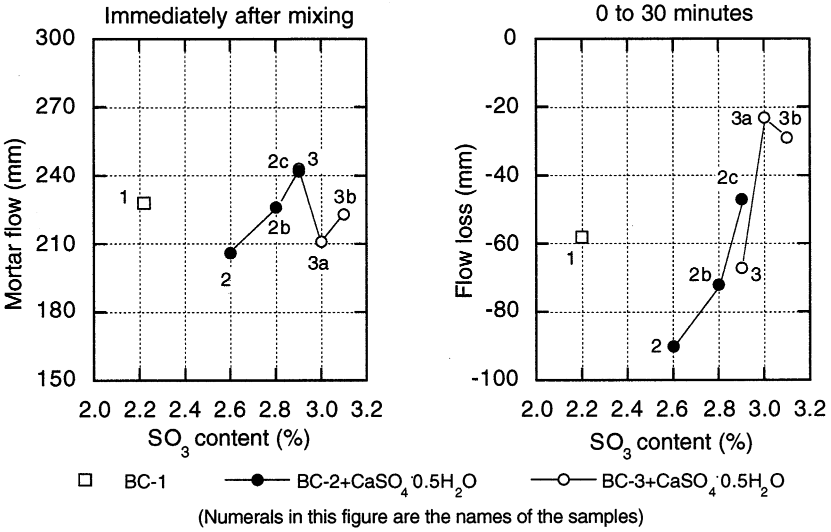


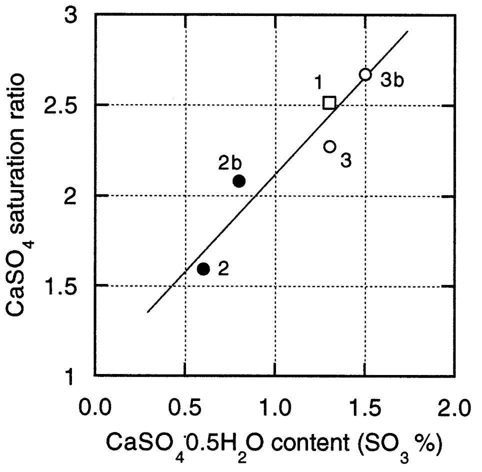
FIG. 3.
Relationship between SO_3 content of cement and fluidity (SP-M: C × 2.0%).

influence of SO_3 content on the flow loss was greater than that of SP-R. The base cement, BC-2, contains 0.3% SO_3 from $CaSO_4{\cdot}2H_2O$ and 0.6% SO_3 from $CaSO_4{\cdot}0.5H_2O$ as shown in Table 1. The rate of dissolution of each calcium sulfate is in the order, $CaSO_4{\cdot}0.5H_2O > CaSO_4{\cdot}2H_2O >$ Type II $CaSO_4$. The hydration of BC-2 is considered to proceed at a low concentration of SO_4^{2-} ion in the liquid phase because of the small $CaSO_4{\cdot}0.5H_2O$ content. Therefore, the improvement in fluidity by the addition of $CaSO_4{\cdot}0.5H_2O$ may suggests that the dispersion effect of the polycarboxylate-based high range water reducing AE agent is closely related to the concentration of SO_4^{2-} ion in liquid phase.

In the cases of BC-3a and 3b prepared from BC-3, the flow loss decreased with the increase in SO_3 content, which is similar to the cases of BC-2a to 2c. However, the mortar flow immediately after the mixing was not improved by the addition of $CaSO_4{\cdot}0.5H_2O$. Especially in the presence of SP-M, the mortar flow decreased with the increase in SO_3 content. The base cement, BC-3, contains a relatively large amount of $CaSO_4{\cdot}0.5H_2O$. It may be considered that the supply of SO_4^{2-} ion from BC-3 to the liquid phase is at a high level and the influence of SO_4^{2-} ion at this level is different from that at a lower level, which will be further discussed below.

Saturation Ratio of Liquid Phase with Respect to $CaSO_4{\cdot}2H_2O$

The ionic activity product relevant to the $CaSO_4{\cdot}2H_2O$ in the saturated solution varies with the ionic strength (20). It is better to consider the influence of ionic strength for estimating the degree of supersaturation of the liquid phase. Therefore, the saturation ratio (19) was calculated from the concentration of each ion determined after the 5-min. suspension of



(Numerals in this figure are the names of the samples)

FIG. 4.
Relationship between $CaSO_4 \cdot 0.5H_2O$ content of cement and $CaSO_4 \cdot 2H_2O$ saturation ratio of liquid phase.

cement in the presence of SP-M. Figure 4 shows the relationship between the $CaSO_4 \cdot 0.5H_2O$ content of each cement and the saturation ratio of the liquid phase.

The $CaSO_4 \cdot 2H_2O$ saturation ratio of BC-2 was significantly lower than that of BC-1 and 3. It is clear that the saturation ratio during the initial stage of hydration strongly depends on the $CaSO_4 \cdot 0.5H_2O$ content of the cement, though some degree of deviation is recognized. It is considered that the influence of other kinds of calcium sulfate such as $CaSO_4 \cdot 2H_2O$ and Type II $CaSO_4$ is relatively small.

A certain amount of Type III $CaSO_4$ can be formed in the plant-made cement by the dehydration of $CaSO_4 \cdot 0.5H_2O$ according to the temperature during the grinding process. Type III $CaSO_4$ should be treated as being just as important as $CaSO_4 \cdot 0.5H_2O$ because they have a similar rate of dissolution. Alkaline sulfate in the clinker is also important because of its high dissolution rate. There should be a large influence of the Type III $CaSO_4$ and alkaline sulfates if their contents significantly vary. However, such an influence was hardly recognized, and the saturation ratio well coincided with $CaSO_4 \cdot 0.5H_2O$ in this study. The clinker used in this study was produced by one plant in a short period and the analyzed values of SO_3 in the clinker samples were stable (0.4 to 0.5%) during that period. Therefore, the degree of the influence of alkaline sulfate is considered to be almost the same in each cement. On the other hand, it is difficult to quantitatively estimate the Type III $CaSO_4$ content because DSC can not detect calcium sulfate without the combined water. However, it can be pointed out that the sum of the SO_3 values from the clinker and the measured calcium sulfates are in good agreement with the total SO_3 content in the case of BC-1. It is considered that Type III $CaSO_4$ does not exist in the cements used in this study.

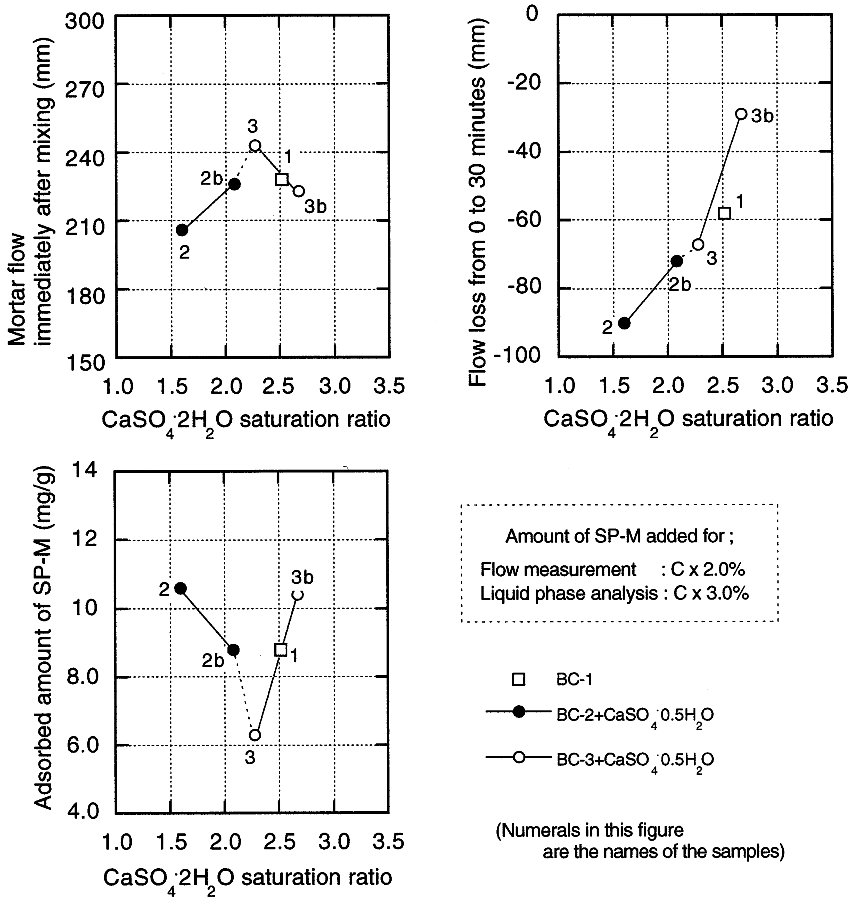
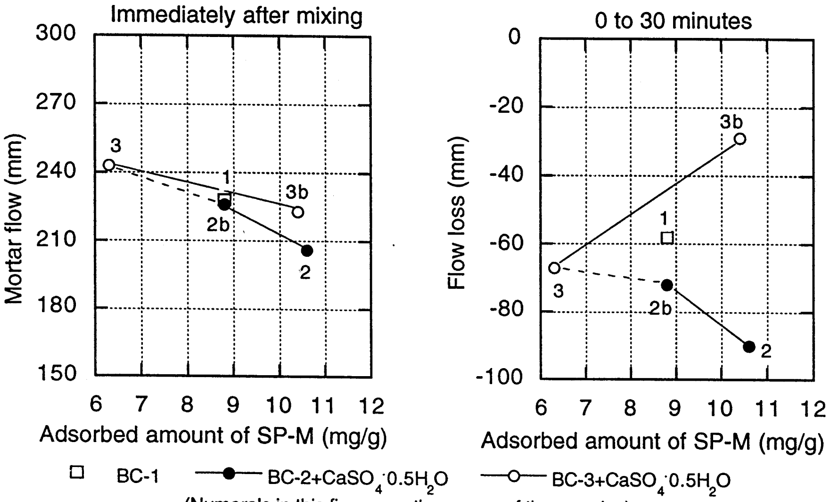


FIG. 5.
Relationships between saturation ratio, adsorption of SP-M and fluidity of mortar.

Influence of Saturation Ratio on the Adsorption of Agent and the Fluidity

The relationships between the saturation ratio, the adsorption of SP-M, and the fluidity of mortar are shown in Figure 5 and Figure 6. The amount of SP-M adsorbed on the cement particles was determined after the 5-min. suspension, as well as the measurement of the saturation ratio.

Concerning all the cements including BC-1, the $CaSO_4{\cdot}2H_2O$ saturation ratio of the liquid phase was closely related to the fluidity of the mortar. With the increase in the $CaSO_4{\cdot}2H_2O$ saturation ratio of the liquid phase caused by the increase in the $CaSO_4{\cdot}0.5H_2O$ content of the cement, the mortar flow immediately after the mixing initially increased and then decreased. The range of the saturation ratio in which the mortar flow reached its highest level was about 2.0 to 2.5. The tendency of adsorbed amount of SP-M inversely corresponded to the mortar



(Numerals in this figure are the names of the samples)

FIG. 6.
Relationship between adsorption of SP-M and fluidity of mortar.

flow immediately after the mixing. The adsorbed amount of SP-M initially decreased and then increased with the increase in the saturation ratio.

The improvement in the fluidity accompanied by the decrease in the adsorbed amount of organic agent has already been reported with respect to the naphthalene sulfonate-based superplasticizer (21). It was explained in some reports (22,23) that all cement particles mainly composed of calcium silicate are easily dispersed when the adsorption of superplasticizer onto the specified components such as the interstitial phases is small.

On the other hand, the flow loss from 0 to 30 min. decreased with the increase in the $CaSO_4 \cdot 2H_2O$ saturation ratio. There was no specific range for the saturation ratio such as in the case of the mortar flow immediately after the mixing. It should be noted that the flow loss continuously decreased even in the range of a high saturation ratio in which the adsorbed amount of SP-M begun to the increase.

In the case of the naphthalene sulfonate-based superplasticizer, it has been suggested that the hydration of the cement consumes the superplasticizer adsorbed on the cement particles (21,23) and the change in fluidity with time is in good agreement with the concentration of the superplasticizer remaining in the liquid phase (24). It has also been suggested that a large adsorption of the superplasticizer due to the initial hydration of the cement causes a large loss in fluidity with time because of a small supply of superplasticizer from the liquid phase onto the surface of hydrates (23).

The increase in adsorption recognized under a high saturation ratio means a decrease in the polycarboxylate-based high-range water-reducing AE agent in the liquid phase. Though the rate of flocculation also depends on the physical characteristics of cement such as fineness and density (25,26), the physical characteristics of the laboratory-made cements should not be affected by the addition of $CaSO_4 \cdot 0.5H_2O$. Therefore, the decrease in flow loss at a high saturation ratio is difficult to understand from the above mentioned mechanisms for the naphthalene sulfonate-based superplasticizer.

Discussion

The influence of the $CaSO_4 \cdot 2H_2O$ saturation ratio of liquid phase (or $CaSO_4 \cdot 0.5H_2O$ content of cement) on the fluidity can be roughly classified as follows:

1. Decrease in fluidity due to the rapid formation of $CaSO_4 \cdot 2H_2O$ by the hydration of $CaSO_4 \cdot 0.5H_2O$ in the cement
2. Increase in fluidity due to the depressed hydration of interstitial phase at a high saturation ratio of the liquid phase with respect to $CaSO_4 \cdot 2H_2O$
3. Increase in fluidity due to the efficient dispersion of all the cement particles accompanied by the inhibited adsorption of organic agent onto the interstitial phases at a high concentration of SO_4^{2-} ion in the liquid phase

Influence 1 is a well-known phenomenon in commercially ground cements (27). Influence 2 was reported (6) to become significant at a relatively low saturation ratio of liquid phase with respect to $Ca(OH)_2$. Therefore, it is considered that the hydration of the interstitial phase in belite-rich cement obeys this manner. Influence 3 was suggested from the investigation using the naphthalene sulfonate-based superplasticizer (10). From the result at a relatively low saturation ratio, it is considered that the adsorption of the polycarboxylate-based high range water reducing AE agent onto interstitial phases is also in competition with the SO_4^{2-} ion in the liquid phase.

Concerning the $CaSO_4 \cdot 2H_2O$ saturation ratio of the liquid phase (or $CaSO_4 \cdot 0.5H_2O$ content of cement), there are opposite influences on the fluidity. The existence of the best range of the saturation ratio related to the mortar flow immediately after the mixing can be explained as a combination of these influences. For example, it is considered that the small mortar flow value of BC-2 immediately after the mixing is due to an insufficient degree of Influences 2 and 3 accompanied by a small supply of SO_4^{2-} ion from the cement into the liquid phase. For the increase in Influences 2 and 3, it is effective to increase the amount of soluble calcium sulfate such as $CaSO_4 \cdot 0.5H_2O$. This action is considered to promote the decrease in the adsorbed amount of the polycarboxylate-based high- range water-reducing AE agent and the increase in mortar flow. However, the excessive amount of $CaSO_4 \cdot 0.5H_2O$ enhances the Influence 1. It is considered that the rapid and large amount of $CaSO_4 \cdot 2H_2O$ formation from $CaSO_4 \cdot 0.5H_2O$ leads to an increase in the adsorption and the decrease in mortar flow.

On the other hand, the flow loss decreased with the increase in the $CaSO_4 \cdot 2H_2O$ saturation ratio as shown in Figure 5. This result suggests that the formation of $CaSO_4 \cdot 2H_2O$ from $CaSO_4 \cdot 0.5H_2O$ proceeds in a relatively short period and hardly affects the flow loss. It is also suggested that Influence 3 can be obtained for a long period by maintaining a high saturation ratio of the liquid phase with respect to $CaSO_4 \cdot 2H_2O$. It is considered that a cement such as BC-1 or BC-3b which shows a high saturation ratio at the initial age maintains the saturation ratio at a relatively high level at a later age as compared with a cement such as BC-2. Type II $CaSO_4$ gradually dissolves, but its effect on the flow loss was not recognized. It should be difficult for the Type II $CaSO_4$ to supply a sufficient amount of SO_4^{2-} ion into an already supersaturated liquid phase even in the later age.

One more factor can be considered from the decrease in the flow loss and the increase in the adsorption recognized at a high saturation ratio of the liquid phase. It may concern the dispersion mechanism of the polycarboxylate-based high-range water-reducing AE agent. As mentioned above, the naphthalene sulfonate-based superplasticizer adsorbed on the cement particles is easily embedded (or absorbed) in the hydrates and loses the dispersion effect (21,23). It is considered that the consumption of superplasticizer by the initial hydration of a specified component such as the interstitial phase or $CaSO_4 \cdot 0.5H_2O$ is directly related to the increase in flow loss. On the other hand, the polycarboxylate-based high-range water-reducing AE agent generally has a large molecular weight and long graft copolymers (11,12), and the dispersion effect mainly depends on the steric hindrance rather than the electric repulsion (13–17). Therefore, such an agent sterically adsorbed on the surface of cement particles has a difficult time entirely embedding in the hydrates and it is possible to maintain the dispersion effect to some degree even after the hydrates partially covered it. The hydrates of BC-2, for example, are considered to consist mainly of ettringite. On the other hand, the hydration of BC-3b is characterized by the formation of $CaSO_4 \cdot 2H_2O$ rather than ettringite. The degree of remaining steric hindrance that is considered to affect the flow loss may be different in each case because of the difference in the kind, amount, size, and morphology of hydrates.

Conclusion

1. The fluidity of belite-rich cement mortar containing a polycarboxylate-based high-range water-reducing AE agent strongly depended on the saturation ratio of the liquid phase with respect to $CaSO_4 \cdot 2H_2O$. The mortar flow immediately after mixing initially increased and then decreased with the increase in the saturation ratio. On the other hand, the flow loss continuously decreased with the increase in the saturation ratio.
2. The saturation ratio of the liquid phase with respect to $CaSO_4 \cdot 2H_2O$ strongly depended on the amount of $CaSO_4 \cdot 0.5H_2O$ in the belite-rich cement. The saturation ratio was hardly affected by the other kinds of calcium sulfate such as $CaSO_4 \cdot 2H_2O$ and Type II $CaSO_4$.
3. The adsorption of the polycarboxylate-based high-range water-reducing AE agent inversely corresponded to the mortar flow immediately after the mixing. However, the flow loss did not coincide with the adsorption tendency especially at a high saturation ratio. It is suggested that the steric hindrance remains to some degree after the hydrate partially covers the agent adsorbed on the cement particles.

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