

EFFECTS OF INITIAL HYDRATION REACTIVITY OF CEMENT ON THE DISPERSING PERFORMANCE OF POLYCARBOXYLATE SUPERPLASTICIZER

(Translation from Concrete Research and Technology, Vol. 11, No. 2, May 2000)



Kazuo Yamada



Shunsuke Hanehara



Kenichi Honma

The effects of cement's initial hydration reactivity on the dispersing performance of a polycarboxylate superplasticizer (PC) are investigated using normal Portland cement (NPC) and belite-rich low-heat Portland cement (LHC). Initial hydration reactivities are controlled for both NPC and LHC by exposing them to a condition of 80%RH and 20°C. Regardless of differences in cement type and initial hydration reactivity of cement, the fluidity of paste containing PC is found to be positively correlated to the PC adsorption per BET specific surface area of the solid phase of the paste, $Ad_{PC/BET}$. This means that the dispersing force of the PC is determined by the amount of PC adsorbed onto a unit surface area of the solid phase. In both NPC and LHC cases, $Ad_{PC/BET}$ corresponds to the variation in BET specific surface area of the solid phase of the paste, SSA_{PC} . The variation in SSA_{PC} is caused by the variation in cement initial hydration reactivity. Despite SSA_{PC} , experimental results indicate that $Ad_{PC/BET}$ is also affected by the sulfate ion concentration in the aqueous phase of the paste, because sulfate ions act as competitive adsorbates. The value of $Ad_{PC/BET}$ for LHC is larger than that of NPC at the same SSA_{PC} level because of the lower alkaline sulfate content in LHC.

Key Words: *Polycarboxylate superplasticizer, hydration reactivity, fluidity, BET specific surface area, sulfate ion*

Kazuo Yamada is a research scientist in the Cement Chemistry Group of the Central Research & Development Center of Taiheiyo Cement Corporation, Sakura, Japan. He obtained his Doctor of Engineering degree from Tokyo Institute of Technology in 2000. His research activities relate to the chemistry of cement, cement dispersants, expansive additives for concrete, and the durability of concrete. He is a member of the JSCE and JCI.

Shunsuke Hanehara is a manager in the Technology Management Group of the Central Research & Development Center of Taiheiyo Cement Corporation, Sakura, Japan. He obtained his Doctor of Engineering degree from the Keio University in 1986. His research activities relate to the chemistry of cement, the microstructure of concrete, and the durability of concrete. He is a member of the JSCE and JCI.

Kenichi Honma is a research assistant in the Cement Technology Group of the Central Research & Development Center of Taiheiyo Cement Corporation, Sakura, Japan. His research activities relate to the chemistry of cement and the manufacturing of cement. He is a member of the JCI.

1. INTRODUCTION

The fluidity of concrete containing a superplasticizer is known to vary unexpectedly with various factors including the type of cement, differences among manufacturing plant, factories and others [1]. In various attempts to control these variations in fluidity, the mechanism of interaction between cement and superplasticizer has been studied and the relationship between the characteristics of cement and the dispersing performance of the superplasticizer has been described [2], [3], [4], [5], [6]. In particular, various experiments have been carried out on the fluidity of cement pastes made with cement of various characteristics and with superplasticizers of different types: polycarboxylate (PC), naphthalene sulfonate (NS), and melamine sulfonate (MS). Based on these experimental results, two parameters have been proposed for the description of superplasticizer performance: critical dosage and dispersing ability, as shown in Fig. 1 [7].

The effects of adding a superplasticizer on the fluidity of a cement paste can be classified as follows [7]. Up to a certain dosage, the fluidity does not increase. Once this critical dosage is reached, fluidity increases in proportion to the dosage. In this effective region of superplasticizer addition, the rise in fluidity per increment in superplasticizer dosage is defined as the dispersing ability. At a certain superplasticizer dosage, fluidity tends to saturate. In the most common form of superplasticizer usage in concrete, the superplasticizer is used within the range of dosage in which the fluidity can be adjusted by the dosage. In Fig. 1, this range corresponds to the linear part of the relationship. It is the mechanism of superplasticizer operation in this range that will be discussed in this study.

In a correlation analysis of cement characteristics, the critical dosage indicates a positive relationship with initial hydration reactivity of the cement for each type of superplasticizer, as shown in Fig. 2. On the other hand, the dispersing ability shows a negative relationship with the alkaline sulfate content of the cement, as shown in Fig. 3 for each type of superplasticizer.

The mechanism by which alkaline sulfate ions affect dispersing performance has been studied by several researchers [8], [9], [10]. It is assumed that PC is adsorbed onto the surface of the cement and that this adsorption proceeds until equilibrium with the coexisting sulfate ions [11]. In the case of a high sulfate ion concentration, the adsorption equilibrium moves to the desorbed side, as shown in Fig. 4, and the dispersing performance of PC decreases. Similar behavior is exhibited by NS [7]. Here, NS adsorbed onto the cement surface can be removed by increasing the sulfate ion concentration, as shown in Fig. 5. This effect can be demonstrated by an experiment using limestone powder whose surface is expected to be stable in the adsorption experiments, as well as the case of the delayed addition of NS to cement paste. Some researchers have assumed that the loss

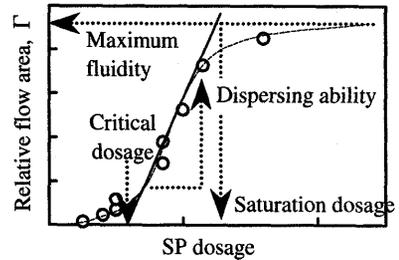


Fig. 1 Critical dosage and dispersing ability [7]

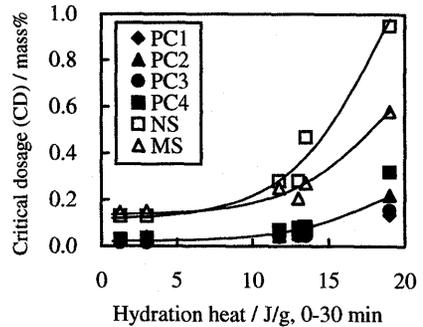


Fig. 2 Initial hydration reactivity and critical dosage [7]

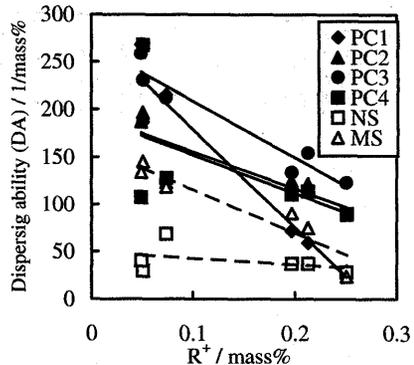


Fig. 3 Soluble alkaline content and dispersing ability [7]

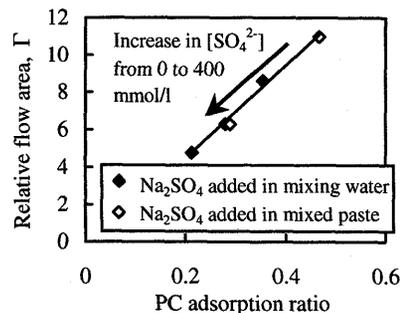


Fig. 4 Relationship between PC adsorption and fluidity [11]

of dispersing performance of NS when the water-cement ratio is low can be attributed to a reduction in the electric double layer, which is set up by the adsorption of NS, because ionic strength rises at low-water cement ratios [12], [13]. However, a recent study suggests an effect of sulfate ions on the competitive adsorption equilibrium of NS with sulfate ions [14].

In the case of NS, one important effect contributes to the adsorption equilibrium; the absorption into initial hydrates. The authors have investigated the mechanism of this absorption from experiments using cements with various hydration reactivities [15] with reference to previous studies [2], [3], [4], [5], [16], [17], [18], [19].

In the case of PC, there have been few studies of the effect of initial hydration on dispersing performance. This study is an investigation of the mechanisms at work using cements with various initial hydration reactivities controlled by exposure to moist conditions in a humid atmosphere.

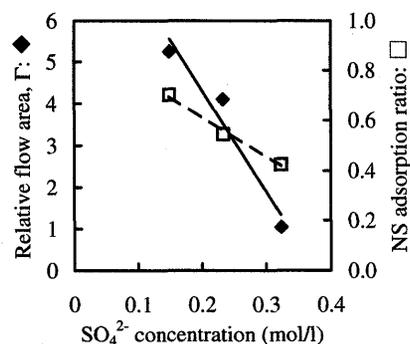


Fig. 5 The effect of sulfate ion concentration on the dispersing performance and adsorption behavior of NS [7]

Table 1 Cement characteristics (mass%) [20]

Chem. comp.	ig.loss: 550°C	ig.loss: 950°C	insol.	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	Na ₂ O	K ₂ O
NPC	0.5	2.0	0.2	20.9	4.5	2.9	64.9	1.2	2.0	0.3	0.5
LHC	0.6	0.7	0.1	25.3	3.0	2.8	63.7	1.5	2.7	0.2	0.4
Mineral comp.	C ₃ S	C ₂ S	C ₃ A	C ₄ AF	Ca(OH) ₂	free-CaO	R ₂ SO ₄ *	CaCO ₃			
NPC	60.5	14.1	7.0	8.8	0.2	0.5	1.0	3.4			
LHC	28.4	51.2	3.2	8.5	0.6	0.5	0.3	0.2			

*) R₂SO₄ represents the soluble alkaline sulfate based on measurement of Na⁺ and K⁺ in a solution extracted by centrifugal separation a cement paste with a water-cement ratio of 40 % immediately after mixing.

2. Samples and experimental method

2.1 Samples

The cements used in the experiment were commercial normal Portland cement (NPC) and high-belite low-heat cement (LHC) as specified by JIS R 5201 and JIS R 5205, respectively. The excellent compatibility of LHC with PC means that it is commonly in concrete with a low water-cement ratio. The reason for this excellent compatibility is thought to be the low alkaline sulfate content as well as the low C₃A content of LHC [21].

The initial hydration reactivity of cement samples was modified by exposing them to moist conditions. To do this, a vessel measuring 7 cm in depth, 25 cm in width, and 35 cm in length was filled with 5 kg of cement and exposed to an atmosphere characterized by 20 °C and 80 %RH for 0.25, 1, 3, and 7 days. The basic characteristics of these cements have been previously reported [20]. Three-day exposure to these conditions corresponds to storage of bagged cement in a warehouses for 8 weeks.

The superplasticizer used was a commercial polycarboxylate superplasticizer with polyether graft chains. Its solid content was 27.1 mass% after drying at 105°C. A chemical analysis was carried out to gain an understanding of the chemical structure of the PC. The graft chain consisted of polyoxyethylene comprising 23 repetitions of ethyleneoxide. The trunk chain was polymerized methacrylate including matharylsulfonate. The molecular weight was 47,000 (mass average) as measured with a gel permeation chromatograph using a column, Shodex OHpak SB806M. Polyoxethylene was used as the standard material. The molar ratio of each component was 66 mol% of methacrylic acid, 21 mol% of grafted methacrylate, and 6 mol% of metharylsulfonate. For reference, a beta-naphthalene sulfonate superplasticizer (NS) was also used.

2.2 Properties of cement paste

The dispersing performance of the superplasticizer was evaluated by measuring the fluidity of a cement paste. The superplasticizers were added to the cement in the form of a premixture with water. Cement paste with a 30% water-cement ratio was mixed in a Hobart mixer for 1 min. at low speed followed by 3 mins. at high speed. The flow (f) of the cement paste was measured just after mixing in accordance with JASS 15 M 103-3.5 using a pipe 50 mm of diameter and 51 mm of height. As an index of cement paste fluidity, the relative flow area was calculated as follows:

$$\Gamma = \frac{f^2 - 50^2}{50^2}$$

2.3 Analysis of aqueous paste phase

The aqueous phase was separated in a centrifugal separator (rotating rate: 13,5000 rpm; rotating radius: 12 cm; and centrifuge time: twice for 1 min.) just after mixing. The sulfate ion concentration in the aqueous phase of the paste was measured using an ion chromatograph. The PC concentration was measured using a total organic carbon analyzer. By comparing the PC concentrations before and after mixing, the change in PC concentrations was obtained and assumed to correspond to the amount adsorbed.

2.4 Analysis of initial hydration reactivity

The initial hydration reactivity of the cement was evaluated by measuring the heat of hydration in a micro calorimeter for 30 min. after mixing with water. The specific surface area of the solid phase of the hydrated cement paste was also measured. First, after mixing the cement paste, it was immersed in plenty of acetone in order to stop hydration. The solid phase was then separated by suction filtration. The separated sample was dried at 20°C and 11%RH for 7 days and the specific surface area was then measured by the one-point BET method using nitrogen gas adsorption.

Table 2 Changes in cement characteristics after exposure to moist conditions [20]

Cement		NPC					LHC				
Exposure (day)		0	0.25	1	3	7	0	0.25	1	3	7
Specific surface area (m ² /g)	Blaine	0.320	0.318	0.318	0.311	0.321	0.365	0.365	0.353	0.364	0.382
	BET	0.79	0.88	0.97	1.07	1.10	1.01	1.02	1.06	1.17	1.31
Hydration heat (J/g, 0-30min)		14.1	12.9	5.0	3.6	2.0	11.5	10.6	7.4	4.9	1.8
ig. loss (mass%, 550°C)		0.53	0.66	0.93	1.54	1.57	0.62	0.68	0.89	1.10	1.11

3. Results and discussions

3.1 Change in cement characteristics after exposure to moist conditions

The changes in cement characteristics after exposure to moist conditions are summarized in Table 2 [20]. Although the Blaine specific surface area did not change, the BET specific surface area increased as the period of exposure increased, rising by 1.4 times from that of untreated cement after 7 days of exposure. Observation with a SEM (scanning electron microscope) revealed that fine hydrate particles measuring less than 1 µm were formed as a result of exposure to moist conditions. These fine particles were identified as probably ettringite and gypsum in XRD (X-ray diffraction analysis).

As for the initial hydration reactivity, the heat released in the 30 min. after mixing with water decreased from 14.1 J/g for unexposed NPC to 2.0 J/g after 7 days of exposure. It decreased from 11.5 J/g for unexposed LHC to 1.8 J/g after the same period of exposure. The heat release in this period is thought to be attributable to the hydration reaction of interstitial phases such as C₃A to ettringite. Comparing the release of hydration heat by LHC and NPC, the amount of C₃A in LHC is half that in NPC, as shown in Table 2, whereas the amount of hydration heat only 18 % less. This result indicates that the release of hydration heat is not directly related to the

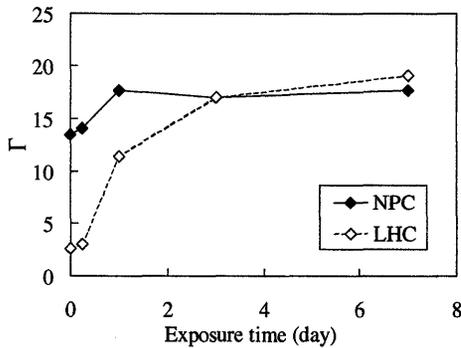


Fig. 6 Effect of exposure on fluidity (NS)

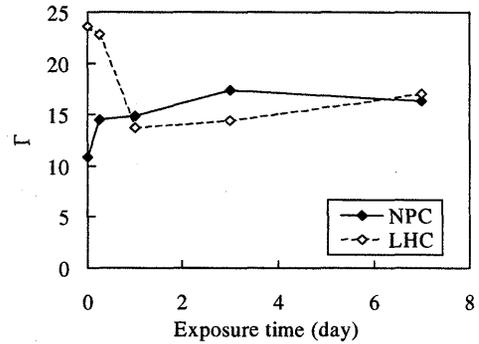


Fig. 7 Effects of exposure on fluidity (PC)

amount of C_3A . Thus it is necessary to evaluate the amount of C_3A that takes parts in reaction.

Exposure to moist conditions is shown to successfully control the initial hydration reactivity, and this effect will be discussed in the next section.

3.2 Change in fluidity of paste by exposure of cement to moist conditions

The changes in fluidity of cement paste containing superplasticizers due to exposure to moist conditions are shown in Figs. 6 and 7 for NS and PC, respectively. The superplasticizer dosages were 1.2 and 0.8 mass% per kg of cement as the received forms of commercial liquid for NS and PC, respectively.

When unexposed, NS indicated a fluidity of $\Gamma=13$ for NPC and $\Gamma=3$ for LHC. The fluidity of paste with NS increased for both NPC and LHC to the same value of $\Gamma=18$ after exposure to moist conditions; this took one day in the case of NPC and more than three days in the case of LHC.

Further, the fluidity of NPC paste with PC showed a similar tendency to the NS case, with the fluidity increasing after exposure to moist conditions up to $\Gamma=15\sim 18$ after more than 0.25 days. In contrast, the fluidity of LHC paste showed a different tendency. Although the fluidity was high in the unexposed state ($\Gamma=24$), it decreased to $\Gamma=14$ after one day of exposure to moist conditions. The fluidity then remained constant with longer exposure to moist conditions.

For the case of LHC, which showed significant change in fluidity with exposure to moist conditions and behavior dependent on the type of superplasticizer, the relationship between dosage and fluidity was examined. Relationships for unexposed and 7-day exposed LHC in the case of mixing with NS and PC are shown in Figs. 8 and 9, respectively.

In the case of NS, the critical dosage decreased by half and dispersing ability increased with exposure to moist conditions. As a result, for a constant dosage of NS, the fluidity of paste with NS can be expected to increase with exposure to moist conditions. In the case of PC, the critical dosage changed little with exposure to moist conditions because the critical dosage was not very significant even in the unexposed case. Dispersing ability decreased with exposure to moist conditions. As a result, in the case of constant dosage of PC, the fluidity of PC-dosed paste can be expected to decrease with exposure to moist conditions.

3.3 Mechanism of change in fluidity with NS

The mechanism by which the fluidity of paste including NS changes with variations in initial hydration reactivity of the cement is discussed here with reference to a previous paper [20]. Besides adsorption of NS onto cement hydrates, a significant amount of NS is thought to be absorbed into the hydrates in competition with sulfate ions. This absorbed NS does not exhibit a dispersing effect. As shown in Table 2, as the initial hydration reactivity of cement is reduced through exposure to moist conditions, the amount of hydrates produced decreases and NS tends to remain in the aqueous phase. There, it contributes further to dispersion. It is thought to be for this reason that the critical dosage of NS decreases.

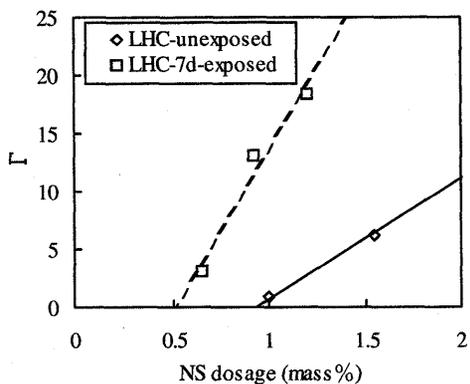


Fig. 8 Effect of exposure on relationship between NS dosage and fluidity

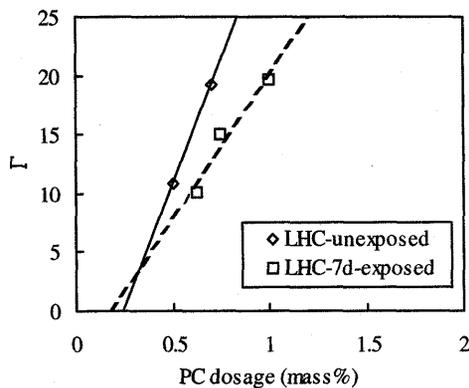


Fig. 9 Effect of exposure on relationship between NS dosage and fluidity

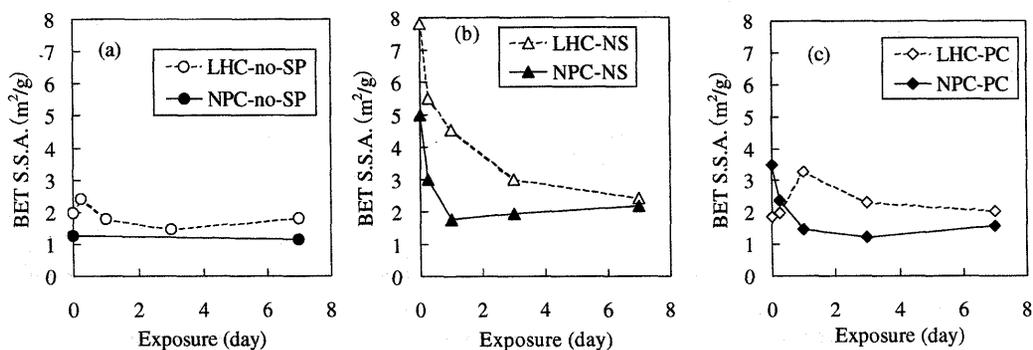


Fig. 10 Effect of exposure on specific surface area (S.S.A.) of initial hydrates

The change in specific surface area of the solid phase of the paste is shown in Fig. 10. The BET specific surface area of the solid phase of paste dosed with NS (abbreviated as SSA_{NS}) increased in the unexposed case as compared to that of paste without the superplasticizer. With exposure to moist conditions, SSA_{NS} decreased irrespective of the kind of cement. In general, a superplasticizer is thought to exhibit a dispersing effect only after adsorption onto particles, and the dispersing performance is proportional to the amount adsorbed per unit surface area. Therefore, for a particular NS dosage, dispersing ability increases because the surface on which the NS is adsorbed decreases; that is, the NS adsorption per unit surface area of the hydrates increases. For a more detailed discussion of this issue, it is necessary to make a distinction between the NS absorbed by hydrates and the NS adsorbed onto hydrates.

3.4 Mechanism of change in fluidity with PC

a) Subject of analysis

The initial hydration reactivity of cement did not affect the critical dosage very much in the case of PC. Consequently, the dispersing ability is discussed here with reference to Fig. 9. Where the critical dosage is constant and independent of exposure to moist conditions, a comparison of Γ at constant PC dosage corresponds to a comparison of dispersing ability. Thus the analysis described in this section focuses on the Γ change of cement paste with a constant PC dosage, as shown in Fig. 7, in order to investigate the mechanism by which fluidity changes with exposure to moist conditions.

b) PC adsorption and fluidity

The change in PC adsorption per mass of the solid phase paste mixed with PC when exposed to moist conditions is shown in Fig. 11. LHC adsorbed more PC than NPC. Adsorption decreased with exposure up to three days and thereafter increased slightly.

The relationship between the amount of PC adsorbed and Γ is shown in Fig. 12. In the case of LHC, there was a positive relationship between them. However, in the case of NPC, the relationship was negative. Thus the behavior differed with the type of cement, and the change in Γ cannot be explained simply in terms of PC adsorption.

c) Effect of surface area of solid phase of paste

The dispersing performance of PC is thought to be more significantly affected by the adsorption per unit surface area of the solid phase ($Ad_{PC/BET}$) than by the actual amount of PC adsorbed. To investigate this, the change in BET specific surface area of the solid phase of paste containing PC (SSA_{PC}) with exposure to moist conditions was examined. The results are shown in Fig. 10(c). When compared with the unexposed cement paste without superplasticizer for each cement type, SSA_{PC} was higher in the case of NPC and was almost the same in the case of LHC. In the NPC case, SSA_{PC} decreased with exposure time, as in the case of NS. In the LHC case, SSA_{PC} reached a maximum value at 1 day and decreased with further exposure to moist conditions.

It is clear that changes in BET specific surface area after exposure to moist conditions varies significantly for different combinations of superplasticizer and cement. Although detailed analysis of the reasons for of such variations is outside the scope of this study, the authors speculate that the addition of a superplasticizer may affect the initial hydration of the cement, and this effect may differ for each type of superplasticizer. Within the time scale of this study, the hydration reactions that need to be considered are the dissolution of calcium sulfate hemihydrate, the deposition of gypsum, the hydration of free lime, the formation of calcium-sulfo-aluminate hydrates such as ettringite by the hydration of C_3A , and similar reactions. In a system without a superplasticizer, it has been reported that the phase composition of hydrates is altered by exposure to moist conditions [20]. Also, Kang *et al.* [21] have demonstrated that PC significantly affects the hydration of C_3A . Changes in initial hydration reactivity and the presence or otherwise of a superplasticizer can both affect the production of initial hydrates, and the effects may be different for NPC and LHC. In this study, the complex changes in the surface area of hydrates resulting from a combination of these two effects were observed. As for the mechanism of this phenomenon, further study will be necessary to elucidate more details.

The relationship between $Ad_{PC/BET}$ and Γ is shown in Fig. 13. The same linear relationship between $Ad_{PC/BET}$ and Γ is seen irrespective of the type of cement and length of exposure to moist conditions. This suggests that the fluidity of a paste is determined by $Ad_{PC/BET}$, which in turn means that the dispersing performance of a superplasticizer is determined by the amount of superplasticizer per surface area of the particles in the dispersing phase, as noted above.

Next, the controlling factor of $Ad_{PC/BET}$ is investigated. Because the PC dosage was constant, SSA_{PC} is examined first. The relationship between SSA_{PC} and $Ad_{PC/BET}$ is shown in Fig. 14. As SSA_{PC} decreased, $Ad_{PC/BET}$ tended to increase with both NPC and LHC. Again, because the PC dosage was constant, the PC adsorbed per unit surface area increased as the surface area of solid phase on which the PC is adsorbed fell.

d) Effect of sulfate ion concentration in aqueous phase

Figure 14 compares $Ad_{PC/BET}$ for NPC and LHC at the same SSA_{PC} . The value of $Ad_{PC/BET}$ for NPC is lower than that for LHC. The mechanism

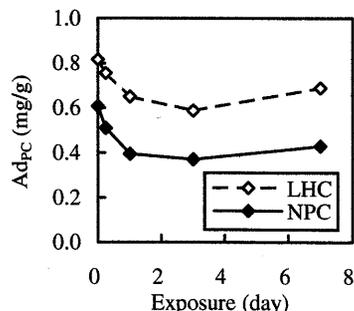


Fig. 11 Effect of exposure on adsorption of PC

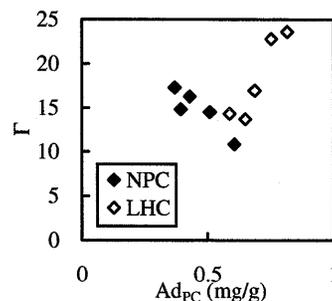


Fig. 12 Relationship between PC adsorption and fluidity

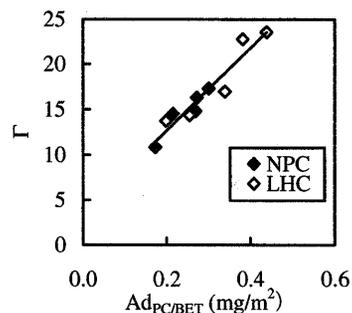


Fig. 13 $Ad_{PC/BET}$ and fluidity

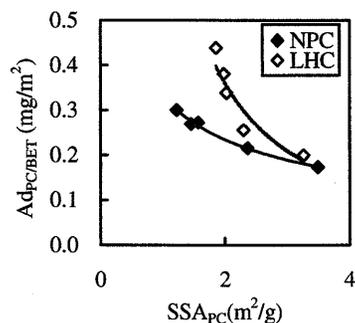


Fig. 14 BET S.S.A. of the solid phase of paste with PC and PC adsorption per BET S.S.A.

behind this phenomenon is examined in terms of adsorption equilibrium.

The PC is thought to be in adsorption equilibrium at the surface of the cement hydrates in competition with sulfate ions. This implies that the adsorption state is affected by sulfate ion concentration. To check this, the sulfate ion concentration was measured, and the results are shown in Fig. 15. The aqueous phase of a cement paste is saturated state with lime and gypsum, and the sulfate ion concentration is strongly affected by the alkaline content, as determined by the content of alkaline sulfates in the cement. Because the alkaline sulfate content of LHC is lower than that of NPC, as shown in Table 1, the sulfate ion concentration is lower in the case of LHC than in the case of NPC. As for the effect of exposure to moist conditions, sulfate ion concentration increased for first 0.25 days of exposure in the case of both cements. With lengthier exposure, the change in sulfate ion concentration was limited. The initial difference in sulfate ion concentrations of LHC and NPC is three times greater than the change seen as a result of exposure to moist conditions.

Based on these results, the reason for $Ad_{PC/BET}$ being smaller in the case of NPC than in the case of LHC can be discussed. As mentioned above, the PC dosage was constant, so $Ad_{PC/BET}$ increased when the surface area was small. The size of this increase depends on the sulfate ion concentration, because PC competes with sulfate ions for adsorption. In the case of a higher sulfate ion concentration, the amount of PC adsorbed on the solid surface is less, even where the PC dosage is constant. As a consequence of this mechanism, the $Ad_{PC/BET}$ value of NPC, which has a higher sulfate ion concentration, is less than that of LHC, which has a lower sulfate ion concentration.

The effect of sulfate ion concentration in the aqueous phase of the paste is shown in Fig. 16. This figure, based on published data [23], shows the change in PC adsorption in a PC-dosed NPC paste (PC dosage = 0.8 mass%; water-cement ratio = 0.30) when the sulfate ion concentration is altered by the addition of soluble calcium salt to the mixed cement paste. By adding calcium salt in this manner, it can be assumed that the surface area of the solid phase of the paste remains constant, so the data for PC adsorption in reference [23] were converted to $Ad_{PC/BET}$ by dividing by the SSA_{PC} values of unexposed NPC paste.

Based on this data, the $Ad_{PC/BET}$ values in Fig. 14 were normalized to a constant sulfate ion of 100 mmol/l. That is the ratio of $Ad_{PC/BET}$ at two different sulfate ion concentrations was used for the normalization; for example, $Ad_{PC/BET}$ was 0.31 mg/m^2 when the sulfate ion concentration was 50 mmol/l and 0.25 mg/m^2 when the sulfate ion concentration was 100 mmol/l, so the ratio is 1.25. All data in Fig. 14 were normalized to the case of 100 mmol/l of sulfate ion concentration. The results are shown in Fig. 17.

In this figure, the difference between NPC and LHC is less than in Fig. 14. This means that the reason for the lower $Ad_{PC/BET}$ value of NPC compared with LHC at the same SSA_{PC} can be attributed to the difference in sulfate ion concentration. However, the behavior of NPC and LHC does not coincide exactly even in Fig. 17.

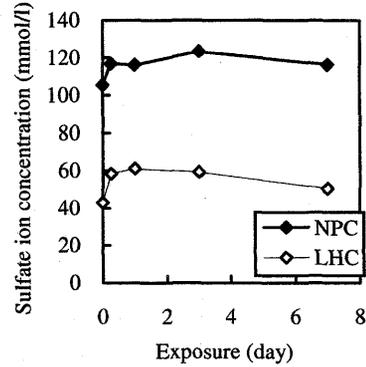


Fig. 15 Change in sulfate ion concentration in aqueous phase of paste with NPC with exposure

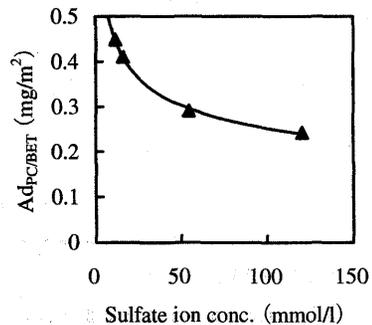


Fig. 16 Effect of sulfate ion concentration on PC adsorption per BET S.S.A.

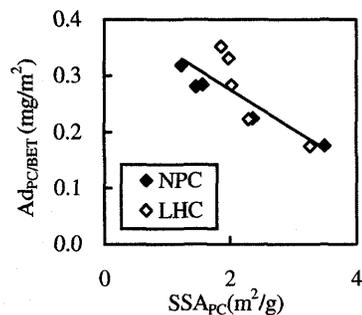


Fig. 17 Relationship between SSA_{PC} and $Ad_{PC/BET}$ with consideration of difference in sulfate ion concentration

This may be explained by ambiguity in the effect of sulfate ions on PC adsorption behavior when the surface area and the phase composition of the hydrates are modified with exposure to moist conditions. In other words, it can be expected that the hydrate composition would change through exposure of the cement to moist conditions, and the effect of sulfate ions on PC adsorption onto each different hydrate may be different.

e) Mechanism by which initial hydration reactivity affects dispersing performance of PC

Based on the discussion above, the mechanism by which the initial hydration reactivity of the cement affects PC performance is summarized. The fluidity of paste dosed with PC is determined by $Ad_{PC/BET}$ regardless of the cement type and initial hydration reactivity. Since PC acts as a dispersant immediately upon adsorption onto the solid phase, SSA_{PC} plays an important role. Changes in the initial hydration reactivity cause variations in SSA_{PC} , and these in turn cause a change in $Ad_{PC/BET}$ under conditions of constant PC dosage. On the other hand, PC adsorption on the solid phase is in a state of equilibrium determined by the balance of PC and sulfate ion concentrations in the aqueous phase. Consequently, differences in the relationships between SSA_{PC} and $Ad_{PC/BET}$ in the cases of NPC and LHC are thought to derive from difference in sulfate ion concentration. In short, in order to discuss the mechanism by which initial hydration reactivity affects the performance of PC, it is important to consider changes in the specific surface area of the solid phase of the cement paste and in the concentration of sulfate ions in the aqueous phase of the paste, and these changes result from variations in the initial hydration reactivity of the cement.

4. Conclusion

Initial hydration reactivity affects the dispersing performance of PC. The mechanism of this behavior was investigated from the viewpoint of PC adsorption behavior. The cements used in the investigation were NPC and LHC, and initial hydration reactivity was controlled with exposure of the cement to moist conditions. NS was also examined by referring to the literature.

- 1) In the case of paste containing NS, fluidity increased with exposure to moist conditions irrespective of the type of cement. This occurs because the critical dosage falls and the dispersing ability rises. In the case of PC, although the fluidity of NPC paste increased slightly after exposure to moist conditions, the fluidity of LHC decreased significantly. This decrease in the LHC case derives from a fall in dispersing ability and the fact that the critical dosage remains constant even when the initial hydration reactivity falls.
- 2) The increased fluidity of paste posed with NS after exposure to moist conditions is thought to be caused by the higher $Ad_{PC/BET}$, which in turn results from reduced absorption into initial hydrates and the lower SSA_{NS} caused by lower initial hydration reactivity.
- 3) The fluidity of paste dosed with PC exhibits a single positive correlation with $Ad_{PC/BET}$ irrespective of cement type and initial hydration reactivity. This result demonstrates that the effect of initial hydration reactivity on $Ad_{PC/BET}$ is important in analyzing the influence of initial hydration reactivity on PC dispersing performance.
- 4) Although $Ad_{PC/BET}$ was affected by changes in SSA_{PC} caused by changes in the initial hydration reactivity of cement, NPC showed lower $Ad_{PC/BET}$ than LHC for the same SSA_{PC} . This difference can be explained to some degree by considering differences in sulfate ion concentration. Because sulfate ions and PC compete for adsorption onto the surface of the initial hydrates, and because of the higher sulfate ion concentration in the aqueous phase of the NPC paste than in LHC-paste, $Ad_{PC/BET}$ of NPC is lower than that of LHC.

References

- [1] Hanehara, S. and Yamada, K., "Interaction between cement and chemical admixture from the point of cement hydration, admixture adsorption and paste rheology", *Cement and Concrete Research*, Vol. 29, No. 8, pp. 1159-1165, 1999
- [2] Hattori, K., Okada, E. and Mizumuna, T., "Characteristics of normal Portland cement and its dispersion by superplasticizer", *JCA Proceedings of Cement & Concrete*, No. 38, pp. 122-125, 1984 (in Japanese)
- [3] Aictin, P. C., Jolicoeur, C. and MacGregor, J. G., "Superplasticizers: How they work and why they occasionally don't", *Concrete International*, Vol. 5, pp. 45-52, 1994
- [4] Yamaguchi, O., Nakajima, Y., Sugaya, H. and Takahashi, M., "The fluidity of pastes and mortars containing various types of water-reducing agent", *JCA proceedings of Cement & Concrete*, No. 49, pp. 216-221, 1995 (in Japanese)
- [5] Nawa, T., Eguchi, H. and Hukaya, Y., "Effect of alkali sulfate on the rheological behavior of cement paste

- containing a superplasticizer”, in: Malhotra, V. M. (ed.), “Proceedings of the 3rd CANMET/ACI International Conference on Superplasticizers and Other Chemical Admixtures in Concrete”, ACI, SP-119, pp. 405-424, 1989
- [6] Yamada, K., Hanehara, S. and Matsuhisa, M., “Two working parameters representing the dispersing mechanism of a superplasticizer –Critical dosage and dispersing ability–”, *Concrete Research and Technology*, Vol. 10, No. 3, pp. 61-68, 1999 (in Japanese)
- [7] Yamada, K., Ogawa, S. and Hanehara, S., “Working mechanism of poly-beta-naphthalene sulfonate and polycarboxylate superplasticizer types from the point of cement paste characteristics”, V. M. Malhotra (ed.), 6th CANMET/ACI International Conference on Superplasticizers and Other Chemical Admixtures in Concrete, SP195, ACI, pp.367-382, 2000
- [8] Kato, H. and Yoshioka, K., “Effect of sulfate ions on the adsorption behavior and dispersing performance of superplasticizers”, *JCA Proceedings of Cement & Concrete*, No. 53, pp. 115-117, 1999 (in Japanese)
- [9] Coppola, L., Troli, R., Zaffaroni, P. and Collepardi, M., “Influence of the sulfate level in the clinker phase on the performance of superplasticized concretes”, in: Malhotra, V. M. (ed.), “4th CANMET/ACI/JI Inter. Symp. on Advances in Concrete Technology” (ACI, SP-179), pp. 271-281, 1998
- [10] Negishi, K., Nakajima, Y., Sugaya, H. and Goto, T., “Effects of polymorphism of calcium sulfate and soluble alkalis on the fluidity of cement paste containing polycarboxylic acid superplasticizer”, *Cement Science and Concrete Technology*, No. 52, pp. 152 – 175, 1998 (in Japanese)
- [11] Yamada, K., Hanehara, S. and Matsuhisa, M., “Fluidizing mechanism of cement paste including polycarboxylate-type superplasticizer analyzed from the view point of adsorption behavior of superplasticizer, *Proceedings of JCI*, Vol. 20, No. 2, pp. 73-78, 1998 (in Japanese)
- [12] Satoh, H., Kitagawa, K and Yamato, F., “The chemical structure and performances of a new type of high range AE water-reducing agent”, *JCA Proceedings of Cement & Concrete*, No. 49, pp. 222-227, 1995 (in Japanese)
- [13] Nawa, T., “Effects of cement characteristics on the fluidity of mortar containing a dispersant”, Doctorate Thesis, Tokyo Institute of Technology, 1992 (in Japanese)
- [14] Yamada, K., “Study on working mechanism of polyether-type cement dispersant based on early cement hydration and composition variation of solution phase”, Doctorate Thesis, Tokyo Institute of Technology, 2000 (in Japanese)
- [15] Yamada, K., Hanehara, S. and Honma, K., “The effects of naphthalene sulfonate type and polycarboxylate type superplasticizers on the fluidity of belite-rich cement concrete”, K. Ozawa and M. Ouchi (ed.), *Proceedings of the International Workshop on Self-Compacting Concrete*, Concrete Engineering Series, JSCE, Vol. 30, pp. 201-210, 1988.
- [16] Massazza, F. and Costa, U., “Effect of superplasticizer on C₃A hydration”, *Proceedings of 7th International Congress on the Chemistry of Cement*, Paris, IV, pp. 529 – 534, 1980
- [17] Bonen, D. and Sarkar, S. L., “The superplasticizer adsorption capacity of cement pastes, pore solution composition, and parameters affecting flow loss”, *Cement and Concrete Research*, Vol. 25, No. 7, pp. 1423-1434, 1995
- [18] Uchikawa, H., Sawaki, D. and Hanehara, S. “Influence of kind and added timing of organic admixture on the composition, structure and property of fresh cement paste”, *Cement and Concrete Research*, Vol. 25, No. 2, pp. 353-364, 1995
- [19] Nakajima, Y., Negishi, K. and Goto, T., “Influence of calcium sulfate on early hydration of cement paste containing superplasticizer”, *Cement Science and Concrete Technology*, No. 51, pp. 288-293, 1997 (in Japanese)
- [20] Yamada, K., Hanehara, S. and Honma, K., “Change in hydraulic reactivity of cement by aeration and false setting”, *Concrete Research and Technology*, Vol. 9, No. 2, pp. 91-99, 1998 (in Japanese)
- [21] Yamada, K., Ozu, H. and Yano, M., “Adsorption behavior of polycarboxylate-type superplasticizer on cement hydrates and the effect of sulfate ions”, *Cement Science and Concrete Technology*, No. 54, pp.79-86, 2000 (in Japanese)
- [22] Kang, J., Ohba, Y., Sakai, E. and Daimon, M., “Influence of superplasticizers on hydration in the Ca₃Al₂O₆ – CaSO₄·2H₂O – CaO system”, *Cement Science and Concrete Technology*, No. 54, pp.22-27, 2000 (in Japanese)
- [23] Yamada, K., Ogawa, S. and Hanehara, S., “Controlling the adsorption and dispersing force of polycarboxylate-type superplasticizer by sulfate ion concentration in aqueous phase”, *Cement and Concrete Research*, Vol. 31, No. 3, pp. 375-384, 2001