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Interaction between cement and chemical admixture from the point of cement hydration, absorption behaviour of admixture, and paste rheology

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Abstract

Chemical admixtures can improve the properties of concrete. High performance concrete with high strength, superior fluidity, and self-compactibility can be realized mainly because of chemical admixtures. Rheological properties of fresh concrete can be strongly affected by the combination of cement and chemical admixture, method of admixture addition, or the water-cement ratio. Problems in fluidity, such as stiffening and large slump-loss, occasionally happen under a particular combination of cement and admixture. These phenomena are generally called incompatibilities between cement and chemical admixtures. In this study, the interaction between cement and the chemical admixture types lignin sulfonate, naphthalene sulfonate, melamine sulfonate, amino sulfonate, and polycarboxylate, together with the working factors and mechanisms, are discussed from the viewpoint of cement hydration. Although the polycarboxylate type superplasticizer was considered to have better compatibility in combination with different kinds of cement, the authors show that its compatibility is affected by the amount of alkaline sulfates in cement.

Keywords: Interaction; Chemical admixture; Hydration; Adsorption; Rheology

1. Introduction

Recently, chemical admixtures (organic admixtures), including AE agents, superplasticizers, and AE superplasticizers, have been used for a variety of concretes. The role of the admixture in concrete has therefore become increasingly important each year. For instance, the contribution of the development and improvement of organic admixtures to advanced ultra-high-strength concrete is remarkably larger than that of cement; thus, advanced admixtures play a principal part in concrete instead of cement. Because the amounts of admixture used in high-performance concrete have increased, the cost of admixture is sometimes comparable to that of cement. It is often emphasized that the new admixtures play a more important role in concrete than new cement[1].

Admixtures are, however, not almighty. There are important problems, including the production of stiffness in concrete, variation of initial slump, and large slump loss of concrete prepared using some types of cement with a constant weight of the admixture. Likewise, there is a problem with large variations in the flow of concrete prepared from some kinds of admixture with the same cement. Such phenomena as these are said to be interaction problems between cement and admixture.

In this paper, the authors discuss each interaction mechanism causing the abnormal rheological properties by using lignin sulfonic acid-based AE agent, naphthalene sulfonic acid-based superplasticizer, and polycarboxylic acid-based AE superplasticizer.

2. Interteractions between cement and chemical admixture

The rheological properties of concrete vary largely according to the ingredients, preparation conditions, and the surrounding environment of the concrete. One variable that sometimes affects the rheological properties of concrete is an incompatible interaction between the ingredients. In particular, this paper discusses interactions between cement and admixture because the admixture is an important ingredient in preparing concrete, as mentioned above.

The compatibility of an interaction between cement and admixture is judged on whether the expected rheological properties of concrete are obtained by using cement together with the admixture. Fig. 1 shows the flow of cement paste prepared by adding no admixture (W/C ratio: 40%), β-naphthalene sulfonic acid-based admixture (amount of addition = C × 1.1%. W/C = 30%), and polycarboxylic acid-based admixture (amount of addition = C × 0.8%,

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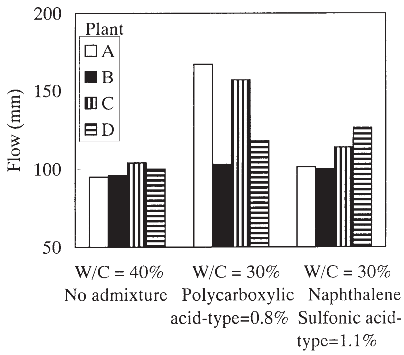

Fig. 1. Fluidity variation in normal Portland cement with different producing plants.

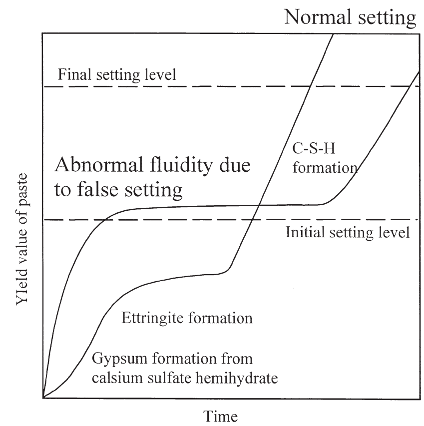

Fig. 3. Normal setting and false setting [4].

W/C = 30%) to four types of commercially available, normal Portland cement produced from different plants. The flow values of the four types of cement paste prepared without admixtures are almost the same as each other, while those prepared with admixtures fluctuate widely. The flow values of cement pastes prepared by adding both admixtures to Cement-C are the second highest. The cement paste prepared by adding naphthalene-based admixture to Cement-A shows low fluidity although that prepared using polycarboxylic acid-based admixture shows the highest fluidity. Thus, a phenomenon in which the fluidity of cement paste prepared by adding different admixtures to one type of cement varies according to the type of admixture, while the fluidity of those prepared by adding the same admixture to different cements varies according to the cement, is an example of the interaction problems between cement and the admixture.

The relationship between the amount of the naphthalene sulfonic and polycarboxylic acid-based admixtures added to normal Portland cement and the flow area ratios is shown in Fig. 2 [2]. The flow area ratio is defined as the value obtained by dividing the area difference between the flowing and the original area of cone in 50 mm diameter by the original cone area [3] according to the equation written in Fig. 2. The figure shows that the relationship between the amount of the admixture added and the flow area ratio is linear. The flow area ratio of the cement paste prepared by adding as little as 0.2% of polycarboxylic acid-based admixture is increased enough to improve its fluidity. Meanwhile, the fluidity of cement paste prepared using naphthalene sulfonic acid-based admixture is hardly changed by adding up to 0.8% of the admixture. By adding more than 0.8%, however, the fluidity increases more sharply than that of the cement paste prepared using polycarboxylic acid-based admixture. Finally, both curves meet each other at the addition level of 2% admixture. Thus, the effect of the admixture on the fluidity of cement paste varies according to the type and the amount of the admixture added. Perhaps this is because the fluidization mechanism of cement varies with the kind of admixture. Moreover, the above-mentioned trend sometimes varies with the cement.

Interaction between cement and admixture not only affects the fluidity of cement paste, but also causes a stiffness like pseudo-setting, or remarkable retardation of setting. As mentioned above, there are various causes of abnormal fluidity arising from the interaction problem. Since the organic admixture disperses the cement particles by the surface-activating action between solid and liquid, the amount of the mixing water can be reduced. The admixture is therefore indispensable in preparing concrete, so the interaction problems can be roughly classified in two groups: (1) problems

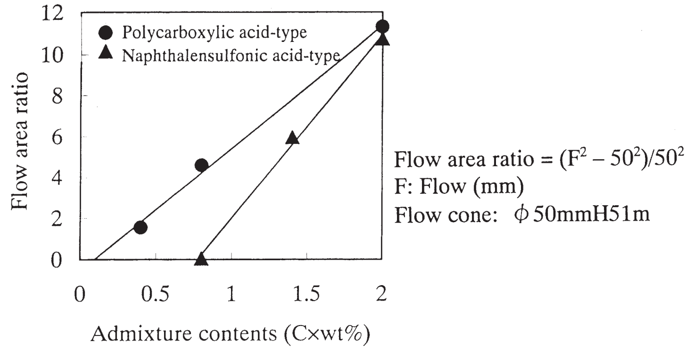

Fig. 2. Fluidity variation with different admixture types [2].

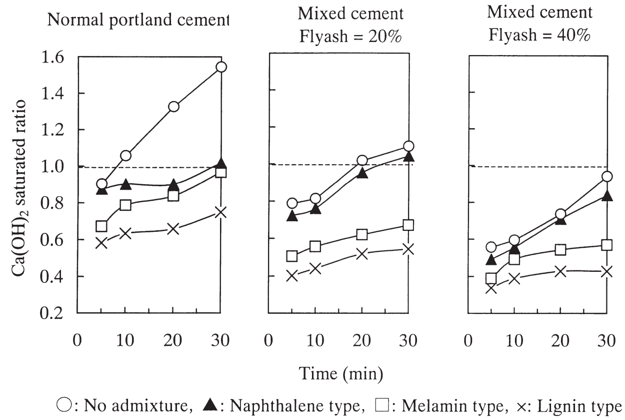

Fig. 4. Time variation of lime-saturation ratio in phase solution [5].

caused by the effect of the admixture's addition on the hydration reaction of cement, and (2) problems caused by the adsorption of the admixture to the cement particles.

3. A case using lignin sulfonic acid-based admixture

Using the lignin sulfonic acid-based AE agent sometimes causes a large slump loss of concrete made with specified fly ash cement. Normal and abnormal setting processes are depicted in Fig. 3 [4]. The setting of cement paste is caused by the combination of the hydration of the interstitial phase, including C_3A and C_4AF, and the hydration of alite. The stiffness corresponds to the accelerated hydration of the interstitial phase, as shown in Fig. 3. The hydration of the interstitial phase occurs mainly in the hour just after mixing with water. This hydration is affected by the concentration of Ca^{2+}, OH^- and SO_4^{2+} in the mixing water. The concentration of those ions depends upon the amounts of alkali sulfate, gypsum, and free lime in the cement just after mixing with water; after that, it depends upon the hydration reaction of alite. The hydration of the interstitial phase is affected in particular by the lime-saturation ratio. Since small crystals of ettringite, which are produced in high ion concentration conditions, cover the unreacted interstitial phase, the hydration reaction rate slows down. On the contrary, in low ion concentration conditions large amounts of ettringite are produced in the shape of large needles. In this case, the hydration of the interstitial phase continues to produce large amounts of ettringite, which causes the stiffness and pseudo-setting [4]. Rapid slump loss of concrete is a problem that begins within one hour after mixing with water and depends upon the hydration reaction during this time interval. Therefore, it is related to the large production of ettringite from the interstitial phase.

The variation over time of the lime-saturation ratio, calculated from the concentration of Ca^{2+} and OH^- in the mixing water, is shown in Fig. 4 [5], in which normal Portland cement, or 20%- or 40%- fly-ash-blended cement are used in combination with lignin sulfonic, melamine sulfonic, or naphthalene sulfonic acid-based admixtures. The variation over time of the lime-saturation ratio in the case using lignin sulfonic acid-based AE agent is smaller than those in the case using either no admixture, or melamine- or naphthalene-based admixtures. This is because lignin sulfonic acid-based admixture takes up Ca^{2+} from the mixing water. And since fly ash fixes Ca^{2+}, the concentration of Ca^{2+} in the concrete containing fly ash and lignin sulfonic acid-based admixture is greatly lowered. Based on these results, the phenomena of slump loss and stiffness are thought to be caused by the production of large amounts of ettringite.

The stiffness produced by the fixation of Ca^{2+} supplied from cement has been mentioned above. However, it is also produced by a lesser supply of Ca^{2+} from cement. Ca^{2+} is supplied mainly by the dissolution of free lime (f-CaO) during the mixing process. It is therefore necessary to retain sufficient free lime (0.5% or greater) in cement to prevent stiffness in concrete prepared using lignin sulfonic acid-based admixture together with fly ash cement.

4. Cases using β-naphthalene sulfonic acid-based admixture

4.1. Large fluctuation in fluidity according to the cement

The fluidity of mortar and concrete prepared by adding a constant amount of the naphthalene sulfonic acid-based admixture fluctuates greatly sometimes, according to the lot, grade, and type of cement. The sulfonic acid-based organic admixtures containing a hydrophilic group, such as the sulfonic group, and a hydrophobic group, such as lignin and naphthalene ring, are adsorbed on cement particles. The admixtures give cement particles a negative potential through the effect of sulfonic group dissociation. The cement particles are thus electrostatically repulsed from each other, fluidizing the paste. Accordingly, the water-reducing effect is observed only when the admixture is adsorbed on the sur-

Table 1
Admixture adsorption amount on cement constituting phases (mg/g) {6}

	Admixture adsorption amount		Mineral phase				
Admixture type	%	mg/g	C_3S	C_2S	C_3A	C_4AF	CaO
Naphthalene sulfonic acid	2.0	20	5.9	11.1	19.6	19.6	19.2
	20	200			190	186	134
Lignin sulfonic acid	0.5	5	2.5	2.6	4.7	4.5	4.2
	5	50			47.6	11.7	28.0

face of cement particles. A cement particle may contain cement minerals including alite (C_3S) and belite (C_2S), as well as aluminate phase (C_3A), ferrite phase (C_4AF), alkali sulfate, f-CaO and gypsum in interstitial phase. Table 1 reveals that the admixture is not evenly adsorbed on cement particles but rather is adsorbed according to the kind of cement mineral. It is adsorbed less on alite and belite, while adsorbed much more on C_3A, C_4AF, and f-CaO [6]. In particular, the naphthalene sulfonic acid-based admixture shows much more uneven adsorption on the clinker minerals than the lignin sulfonic acid-based admixture.

To keep the fluidity high using a constant amount of the admixture, it is desirable that the admixture is evenly distributed and adsorbed on the surfaces of cement particles. In paste prepared using a constant amount of admixture, the relationship between the amount of admixture adsorbed on cement and the paste flow is shown in Fig. 5 [6]. The smaller the adsorption of naphthalene sulfonic acid-based admixture on cement, the larger the flow value of cement paste is. The admixture is so unevenly adsorbed on cement containing much C_3A and f-CaO that the amount of the admixture adsorbed on alite and belite is relatively decreased, thereby lowering the fluidity of the paste. The more even the adsorption of admixture on cement is, the lower the total amount of the admixture adsorbed on the cement is, and the higher the fluidity of the paste is. Thus, the amount of the admixture adsorbed on cement sometimes fluctuates greatly according to the mineral composition of clinker, the type of gypsum, and the contents of the other ingredients in cement. The amount of naphthalene sulfonic acid-based admixture adsorbed on cement has a larger range in the adsorptivities of the admixture to the cement minerals, and the fluidity of paste prepared by adding a constant amount of this admixture fluctuates more than with the other admixtures. The fluidity of paste prepared from cement with an extremely low content of free lime together with the naphthalene sulfonic acid-based admixture is often high just after adding the mixing water. The fluidity of paste prepared using moderate-heat Portland cement together with an admixture is higher than paste made with normal Portland cement in the same manner. The same phenomenon also is observed in the fluidity of paste prepared using the amino sulfonic acid-based admixture because this admixture is relatively unevenly adsorbed on the cement minerals.

4.2. Higher fluidity of paste prepared from cement stored for a longer time

The fluidity of paste prepared using "stale" cement stored for a long time is sometimes high, even with the addition of a small amount of the naphthalene sulfonic acid-based admixture. The flow of cement paste using cement weathered forcibly by exposure to an environment of 20°C and RH80%, and prepared using a constant amount of the naphthalene sulfonic and polycarboxylic acid-based admixtures is shown in Fig. 6 [7]. The fluidity of the cement paste prepared using the polycarboxylic acid-based admixture is somewhat lowered by using weathered cement, whereas the flow of the paste prepared using the naphthalene sulfonic acid-based admixture is improved with the increase in weathering time. The BET specific surface area of cement increases—although the amount of the naphthalene sulfonic acid-based admixture adsorbed decreases—with the increase in weathering. The specific surface area is increased because the cement particles are covered with hydrates newly produced by hydration reaction. Since the activity of the interstitial phase is lowered and the free lime is converted to calcium hydroxide through the weathering, the amount of the admixture adsorbed on those compounds is reduced. Since the amount of the naphthalene sulfonic acid-based admixture adsorbed on the interstitial phase is remarkably reduced by weathering as mentioned above, the admixture is effectively adsorbed on the main ingredients such as alite and belite, hence the fluidity of cement is extremely improved [7]. Surface-modified cement treated with the forced weathering for high-strength concrete is being developed based on the experimental results mentioned above [8].

4.3. Large fluctuation of fluidity according to the addition time

It is known that the rheological properties of concrete are improved by delaying the addition of an organic admixture

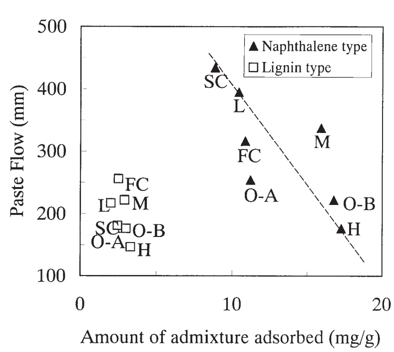

Fig. 5. The relationship between the admixture adsorption on cement and the paste flow [6].

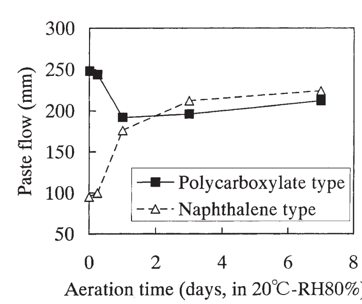

Fig. 6. Fluidity change of high-belite cement paste with admixture by surface aeration [6].

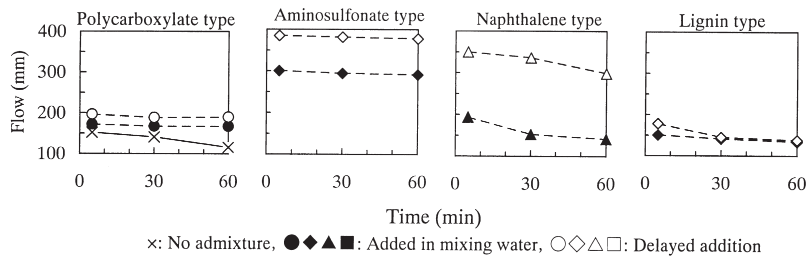

Fig. 7. The effect of admixture type and the admixture addition time on the paste flow of normal Portland cement (20°C,W/C = 0.27) [9].

until after mixing with water, rather than adding both simultaneously. [9]. It is therefore believed that the delayed addition of the admixture, including the two-stage mixing, is an effective method for decreasing the W/C ratio of concrete and increasing its strength [10]. For normal Portland cement paste prepared by either simultaneous or delayed addition, the variation of the flow value over time and the setting times are shown in Fig. 7 [9] and Fig. 8 [9], respectively. The flow value of the cement paste prepared by delayed addition is larger than that of the cement paste prepared by simultaneous addition. The effect of the addition method depends, however, upon the type of the admixture: the effect of delayed addition of the naphthalene sulfonic and amino sulfonic acid-based admixtures is larger, while that of the lignin sulfonic and polycarboxylic acid-based admixtures is smaller. Although the setting of cement paste is slowed by the addition of the admixture, the delayed addition of it retards the setting of cement paste more than simultaneous addition. In the same way as in the flow, the delayed addition of the naphthalene sulfonic and amino sulfonic acid-based admixtures retards the setting of cement paste greatly, while that of the lignin sulfonic and polycarboxylic acid-based admixtures retards the setting less [9].

As mentioned above, the admixture is more easily adsorbed on the interstitial phases than on alite or belite. Since the delayed addition of the admixture reduces the uneven adsorption, more organic admixture is adsorbed on alite. It is believed that clinker produced from normal Portland cement contains 50% or more alite by weight as well as by specific surface area. The dispersion effect of cement particles is increased by the effective adsorption of the admixture to alite, accounting for a large content in clinker. The amounts of the admixture adsorbed on cement by simultaneous addition and delayed addition are listed in Table 2 [9]. Any type of admixture is adsorbed less by delayed addition than by simultaneous addition. The polycarboxylic and lignin sulfonic acid-based admixtures have lower reduction rates than the naphthalene sulfonic and amino sulfonic acid-based admixtures.

The fluidity-improving effect of delayed addition of the amino sulfonic and naphthalene sulfonic acid-based admixtures is larger than that of the lignin sulfonic and polycarboxylic acid-based admixtures. This is because the adsorption of the admixture on the surface of interstitial phase is mitigated by the instantaneous eluviation of Ca from the interstitial phase brought into contact with the mixing water, and the deposition of ettringite by the reaction of the interstitial phase with sulfate ions on its surface. The uneven adsorption of the admixture is, therefore, reduced: it is evenly adsorbed on all the cement particles, whereupon the cement particles are repelled by each other and the fluidity is improved.

It is indicated that the setting time correlates with the concentration of Ca^{2+} in the liquid phase. It is believed that the setting of cement paste begins at the time when the concentration of Ca^{2+} reaches a constant value [4]. The delay of the setting of cement paste is attributed to the substantial decrease in the concentration of Ca^{2+} in the liquid phase by a chelate produced through the reaction of Ca^{2+} with the unadsorbed admixture remaining in the liquid phase. A large delay in the setting of cement paste after the delayed addition of the admixture is attributed to the substantial decrease of the concentration of Ca^{2+}, instead of an increase in the concentration of admixture in the liquid phase.

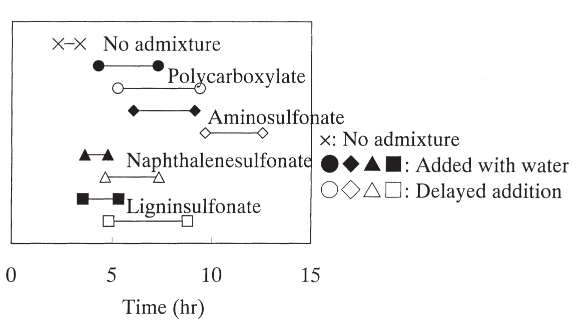

Fig. 8. The effect of admixture type and the admixture addition time on the setting of normal Portland cement (20°C,W/C = 0.27) [9].

Table 2
Admixture adsorption amount on normal Portland cement [9]

Admixture type	Amount added	Adsorption amount: Simultaneous addition	Adsorption amount: Delayed addition
Polycarboxylate	10.0	6.6	6.1
Amino sulfonate	20.0	12.0	7.7
Naphthalene sulfonate	10.0	7.0	5.5
Lignin sulfonate	2.5	1.0	0.9

Table 3
The effect of Na_2SO_4 on paste viscosity with polycarboxylate type admixture [14]

Type of cement	Na_2SO_4 (R_2O%)	Viscosity (10^{-3}Pa·s)		
		5 min	30 min	60 min
High-belite content	0	238	284	286
	0.2	364	464	494
	0.4	616	>800	>800
Normal Portland	0	334	383	395
	0.2	>800	>800	>800
	0.4	>800	>800	>800
High/early strength	0	550	574	648
	0.2	>800	>800	>800
	0.4	>800	>800	>800

5. The case using polycarboxylic acid-based admixture

The newly developed polycarboxylic acid-based admixture provides concrete with high fluidity even in small quantities of admixture, and with low viscosity and high slump retention even at low W/C ratios [11, 12]. The use of the admixture is, therefore, rapidly spreading. It is indispensable—especially for high-fluidity concrete prepared at low W/C ratios. Since the naphthalene sulfonic acid-based admixture contains formalin, it is anticipated that its use will be prohibited in Europe. Under this circumstance, the polycarboxylic acid-based admixture will be the principal admixture used in the 21st century.

The difference in dispersion mechanisms between the sulfonic acid-based admixture and the polycarboxylic acid-based admixture will be mentioned later. The sulfonic acid-based admixture including β-naphthalene sulfonic acid-formalin condensate is an anionic surface active agent. Accordingly, it is adsorbed on cement particles, which are provided with negative potential because the sulfonic group in the molecular structure has negative potential in water. Cement paste prepared from the cement particles with negative potential is fluidized because the cement particles with negative potential are electrostatically repelled by each other. Polycarboxylic acid-based admixture is a nonionic surface active agent with zero potential. The side chains of polyethylene oxide (EO) extending on the surface of cement particles in the form of the brush of a comb migrate in water and the cement particles are dispersed by the steric hindrance of the side chains.

The interaction problem of the polycarboxylic acid-based admixture is a phenomenon in that the amount of the admixture added to cement varies largely according to the kind of cement. Since this type of admixture is used for concrete prepared at low W/C ratios, a small difference in the dispersibility of the admixture changes the fluidity remarkably. Yamaguchi et al. [13] analyzed the relationship between the character of cement and its rheological properties in combinations of the polycarboxylic acid-based admixture with 18 types of cement, and found that soluble alkali in cement correlates highly to the fluidity of cement. Matsuhisa and Yamada et al. [2] elucidated a detailed analysis of variance in which 80% of the variation of fluidity of cement paste prepared using the polycarboxylic acid–based admixture depends upon the content of alkali sulfate, one of the soluble alkali in cement. Yamamoto et al. evaluated the viscosities of cement pastes prepared by adding alkali sulfate and confirmed that the fluidity is lowered by increasing the amount of alkali sulfate, as shown in Table 3 [14]. It is inferred from this that the fluidity of mortar and concrete prepared from cement with high content of alkali sulfate will be extremely low, even when polycarboxylic acid-based admixture is used. This phenomenon is explainable by the indication [15] that the EO chains, contained in the admixture as an ingredient with the dispersion action, are shrunk by using mixing water containing a lot of sulfate ions, thereby decreasing the steric repulsion. The authors examined the effect of the addition of various types of inorganic salts on the fluidity of cement paste prepared using the polycarboxylic acid-based admixture, as shown in Fig. 9. It became clear that the adsorptivity of the admixture on cement is remarkably reduced by adding the sulfate ion, although chlorides did not change the adsorptivity of the admixture [16]. The relationship of the amount of the polycarboxylic acid-based admixture adsorbed on cement to the fluidity was examined. Fig. 10 reveals that the amount of the admixture adsorbed on cement is 47%, and the flow of the cement paste is as high as 173 mm, when the addition of ion to the mixing water is

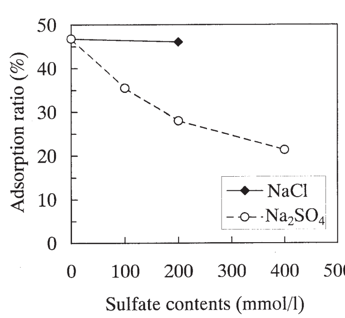

Fig. 9. The effect of salts on the adsorption ratio of polycarboxylic acid type admixture [16].

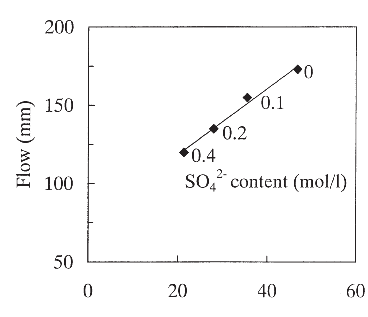

Fig. 10. The effect of alkali sulfate on the relationship between the admixture adsorption ratio and the fluidity of normal Portland cement [16].

zero. Adjusting the concentration of sodium sulfate in the mixing water to 0.1, 0.2 and 0.4 mol/l, the amount of the admixture adsorbed is reduced and the fluidity is also reduced, corresponding to the order of concentration of sodium sulfate described above. It is inferred from this that the lowering of the fluidity of cement paste by adding alkali sulfate is attributed to the reduction of the amount of the admixture adsorbed on cement caused by adding the sulfate ions.

6. Summary

The rheological properties and the strength of concrete are essential properties required for concrete. Cement and admixtures are able to cause sharp variations in fluidity and produce stiffness, depending upon the combination of cement and admixture. This paper describes the mechanism of the interaction problem between commercially available types of cement and admixtures. Higher properties are required for concrete, and applications of lower W/C ratio are being collected. Researchers are, therefore, always attempting to develop new admixtures. When new admixtures are developed, an interaction problem must be anticipated. Researchers in the fields of cement, admixture, and concrete are approaching the time when they will have to collaborate with each other to demonstrate the maximum properties of cement and admixture, disregarding industrial borders, to develop efficient concrete technologies.

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