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Controlling of the adsorption and dispersing force of polycarboxylate-type superplasticizer by sulfate ion concentration in aqueous phase

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Abstract

The dispersing force of polycarboxylate-type superplasticizer (PC) with poly(ethyleneoxide) (PEO) graft chain has been known to degrade by the sulfate ion in the aqueous phase of concrete. Alkaline sulfate contents and calcium sulfates in cement, mixing temperature and time elapsed after mixing, and other various material characteristics as well as environmental conditions affect the sulfate ion concentration. Therefore, it is generally very difficult to keep the sulfate ion concentration constant. In this study, the active control of the sulfate ion concentration in aqueous phase by adding soluble salts containing multiple-charged cations, such as $CaCl_2$ and alkaline sulfate, has been attempted. The adsorption of PC is able to be controlled by adding salts such as $CaCl_2$ and Na_2SO_4. The change of the PC adsorption ratio results directly in the variation of the dispersing force of superplasticizer. It is also indicated that ionic strength in the aqueous phase affects the dispersing force of PC. The dispersing force degrades with the increase in ionic strength and sulfate ion concentration.

Keywords: Superplasticizer; Polycarboxylate; Sulfate ion concentration; Multiple-charged cation; Calcium; Adsorption; Dispersing force; Ionic strength

1. Introduction

Polycarboxylate-type superplasticizer (PC) is one of the indispensable materials for high-fluidity and high-strength concrete because of its superior dispersing force for cement, especially at low water/cement ratios, and its retention effects. However, it has been known that the dispersing force of PC for cement and its time variation are significantly affected by even slight differences in concrete components or mixing conditions. Such instability of the dispersing force is explained by the incompatibility between cement and PC [1–3].

Recently, the reasons for the incompatibility have been studied by many researchers in order to control the fluidity of concrete containing PC [1–13]. It has reported that the alkaline sulfate in cement had the most significant effects on the dispersing force of PC in the case of cements having relatively narrow variation of characteristics, such as normal Portland cements specified by JIS R 5210 [14] as well as various cements with wide variations of characteristics [15]. As for the mechanism, it has indicated that the sulfate ion concentration in cement paste affected the adsorption behavior of PC on cement particles [15,16]. The adsorption of PC decreases in the case of high sulfate ion concentration in aqueous phase because the sulfate ion and PC are adsorbed on cement particles competitively [16].

Although every mechanism is not clarified at present, alkaline sulfate contents and calcium sulfates in cement, other concrete components such as aggregates and their mix proportions, mixing temperature, and time elapsed after mixing, and other various material characteristics as well as environmental conditions affect the sulfate ion concentration in the aqueous phase of concrete. It is not easy to keep the sulfate ion concentration constant in order to control the fluidity of concrete. Thus, it is important to establish a technique to control the sulfate ion concentration in the aqueous phase in order to overcome the incompatibility problems.

In this paper, the sulfate ion concentration has successfully been controlled by the addition of multiple-charged cations and alkaline sulfate. The addition of multiple-charged cations causes the formation of insoluble sulfate salts and removes sulfate ions from the aqueous phase,

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Table 1
Cement character (mass%)

	ig.loss (550°C)	ig.loss (950°C)	insoluble	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	f.CaO
NPC	0.5	2.0	0.2	20.9	4.5	2.9	64.9	1.2	2.0	0.31	0.47	0.6

whereas the addition of alkaline sulfate increases the sulfate ion concentration. The relationship between the sulfate ion concentration and the dispersing force of PC has also been investigated by evaluating the PC adsorption behavior and the stearic size of PC in solution.

2. Experiments

2.1. Materials

The cement used was commercially available normal Portland cement (NPC) in Japan. The cement characters are shown in Table 1. The PC used was the commercial one whose main component was co-polymer of methacrylate containing poly(ethyleneoxide) (PEO) graft chain. Inorganic salts used were reagent-grade NaCl, Na_2SO_4, $CaCl_2$, $MgCl_2$, $SrCl_2$, $BaCl_2$, $CuCl_2$, $FeCl_3$, $AlCl_3$, and $Ca(NO_3)_2$.

2.2. Evaluation

The dispersing force of PC was evaluated by the fluidity of cement paste. The cement paste was mixed at a water/cement ratio (w/c) of 0.35 with the PC dosage of 0.15 mass% (as solid component, added in mixing water) against the mass of cement and w/c of 0.30 with the PC dosage of 0.20 mass%. A Hobart mixer was used for 1 min at low speed and 3 min at high speed. The premix refers to the addition of inorganic salts to the mixing water. The delayed addition means adding inorganic salts after mixing for 1 min at low speed. The flow of cement paste was measured in accordance with the JASS 15 M 103-3.5. The flow pipe used was 50 mm in diameter and 51 mm in height. Flow (F) was measured by averaging the two crossing diameters of the spread. As an index of fluidity, relative flow area ratio (Γ) was calculated by the Eq. (1).

$$\Gamma = F^2/50^2 - 1 \tag{1}$$

The solution phase was extracted by centrifugal separation at 13,500 rpm with a rotating radius of 10 cm for 1 min (MC-150, TOMY; Tokyo, Japan) using the same cement paste whose fluidity was evaluated. PC adsorption amount was evaluated by measuring the reduction amount of PC in the aqueous phase before and after mixing. PC concentration in the aqueous phase was measured by a total carbon analyzer (TOC-5000, Shimadzu; Kyoto, Japan). Ion concentrations were measured for ions of sodium, potassium, calcium, sulfate, chloride, and hydroxide. Cations were measured by inductively coupled plasma emission spectrophotometer (SPS4000, Seiko Instruments; Tokyo, Japan). Sulfate and chloride ions were measured by ion chromatograph (ICA-5000, TOA; Tokyo, Japan). The hydroxide ion concentration was measured by titration.

2.3. Steric size of PC

The steric size of PC in the aqueous solution was measured using the laser light-scattering method. The measurement apparatus used was a combined system of size exclusion chromatography (SEC) with two columns of OHpak SB806M (Shodex; Tokyo, Japan), and a multiangle laser light-scattering detector (DAWN-DSP, Wyatt Technology; Santa Barbara, USA). The wavelength of the laser was 633 nm. The detecting limit of molecular size was around 10 nm. This measurement system was controlled, and data were collected and processed by the software attached to the system (ASTRA, Wyatt Technology). The steric size of

Table 2
Chemical structure of synthesized PC

	PEO chain length	Molecular weight (10^4)[a]	Estimated "true" polymer content	COO^-	SO_3^-	PEO chains	Degree of polymerization of the backbone chain
	Mol[b]	Weighted average	Mass%	Groups/average molecule			Groups[c]
SP1	40	9.46	71.6	128	11	41	195
SP2	23	9.75	87.2	234	35	75	353

All values were calculated on the assumption that molecular weights of all polymers took their weight average values.

[a] Molecular weight was measured by a light-scattering method.

[b] Mean number of ethyleneoxide groups.

[c] Mean number of ethylenic monomers/molecule.

PC was calculated using the route of the mean square radius (RMS).

Samples measured were PEO and two kinds of synthesized methacrylic polymer with a graft chain of PEO. The mass average molecular weight of PEO was 120,000. The molecular structure of two graft polymers was evaluated by the method described in Ref. [17], and the result is shown in Table 2. Eluting solutions were 50 and 300 mmol/l of NaCl and 50 and 300 mmol/l of Na_2SO_4.

3. Results and discussions

3.1. Effects of the addition of salts on fluidity change

The adding effects of adding NaCl or Na_2SO_4 on the fluidity of cement paste containing 0.15 mass% of PC at w/c ratio of 0.35 are shown in Figs. 1 and 2. Salts were premixed in mixing water. In Fig. 1, the dosage of salts is indicated by the molar concentrations in the mixing water. The addition of NaCl decreases the fluidity Γ by three per mol/l of NaCl, which corresponds to 2.0 mass% of cement. In the case of Na_2SO_4, although the decreasing effect on the fluidity is saturated over the dosage of 1 mol/l, which corresponds to 5.0 mass% of cement, the decreasing effect for the fluidity Γ is by 15 per mol/l of Na_2SO_4, which is five times larger than the effect of NaCl. The reason for the decrease over 1 mol/l in the saturation of fluidity by the addition of Na_2SO_4 is thought to be due to the saturation of the solubility of Na_2SO_4.

In Fig. 2, the dosage of salts is indicated by the ionic strength in the mixing water. The ionic strength of the solution containing ions is calculated by Eq. (2).

$$I = 1/2\sum(c_i \times z_i^2) \qquad (2)$$

where i is the kind of ion, z_i is the charge number of ion i, and c_i is the molar concentration of ion i. The difference in the fluidity change between the NaCl addition and that of Na_2SO_4 is reduced in this case. Nonetheless, Na_2SO_4 shows a decreasing effect twice as large as NaCl.

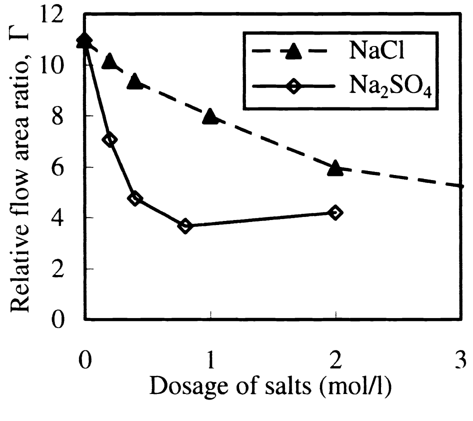

Fig. 1. The effects of salt addition on paste fluidity.

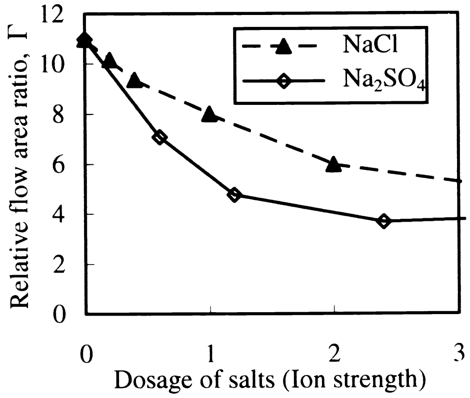

Fig. 2. The effects of ion strength on paste fluidity.

3.2. Decreasing mechanism of the dispersing force of PC by salts

3.2.1. PC adsorption

In order to investigate the mechanism of the above difference, the PC adsorption ratio was evaluated. The results are shown in Fig. 3. In the case of the Na_2SO_4 addition, the PC adsorption ratio decreases with the increase in ionic strength. In the case of NaCl addition, the PC adsorption ratio is almost independent of the ionic strength. The relationship between the PC adsorption ratio and Γ is shown in Fig. 4. There is a linear relationship between the PC adsorption ratio and Γ in the case of Na_2SO_4, suggesting that the mechanism of the Γ decrease by Na_2SO_4 addition is caused by the decrease in PC adsorption. In the case of NaCl, it is necessary to consider some other mechanisms since the PC adsorption ratio is almost independent of the addition of NaCl.

The dispersing force of PC is caused by adsorption layers on particles. The adsorption layer of PEO gives particles repulsive force by its hindrance effect. The hindrance effect is related to the steric thickness of the adsorption layer [18]. Therefore, it is necessary for PC to be adsorbed on cement particles and to expand the structure in aqueous phase in order to exhibit the dispersing force. In the case of NaCl addition, the decrease of Γ may be caused by the shrinking in the steric size of PC because the adsorption ratio is the same regardless of the amount of NaCl added. In the case of Na_2SO_4, the larger decrease of Γ is thought to be caused by the decrease of the PC adsorption ratio as well as the shrinking effect.

Uchikawa et al. [19] suggested that the adsorption portion of PC on cement particles was the carboxylic group. The adsorption of PC on cement particles by the carboxylic group may be prevented by the competitive adsorption between the sulfate ion and dissociated carboxylic group on cement particles. The effects of salt addition on the sulfate ion

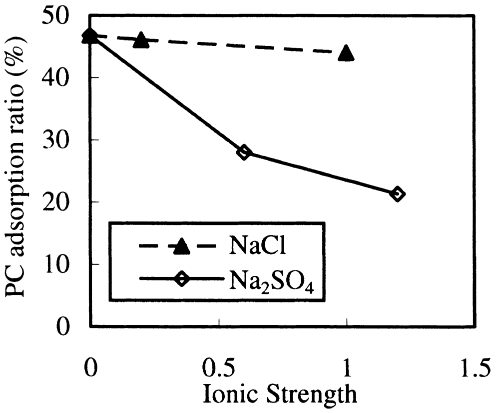

Fig. 3. Effects of ionic strength on PC adsorption.

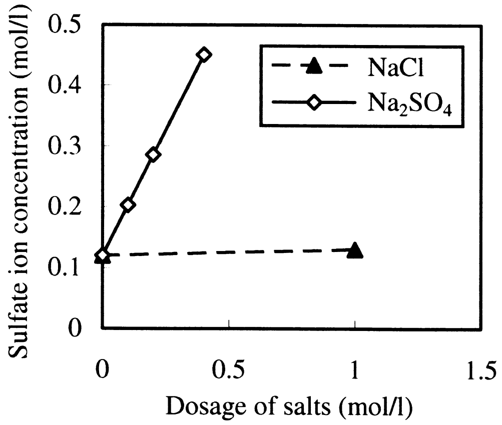

Fig. 5. Effects of salt addition on the sulfate ion concentration.

concentration are shown in Fig. 5. The addition of Na_2SO_4 increases the sulfate ion concentration linearly. The effect of NaCl addition on the sulfate ion concentration is limited. The relationship between the sulfate ion concentration and the PC adsorption is shown in Fig. 6. In the case of Na_2SO_4, PC adsorption is significantly affected by the sulfate ion concentration, suggesting that competitive adsorption with the sulfate ion is occurring.

3.2.2. Steric size of PC

Another factor affecting the dispersing force of PC is the steric size in aqueous solution. Ohta and Uomoto [20] showed that the steric structure of PC shrunk in highly saline solutions. In this paper, steric sizes of PEO and PC in aqueous solution of various ionic strengths were evaluated by the light-scattering method. Ionic strength was adjusted by adding NaCl and Na_2SO_4.

The relationship between the elution time and the RMS and that between the elution time and the intensity of the differential refractive index (RI intensity) for PC2 with the eluting solution of 50 mmol/l Na_2SO_4 is shown in Fig. 7. The steric size of PC was evaluated by the RMS at the peak top of RI intensity. RI intensity represents the amount of PC corresponding to the size when separated by SEC. Based on the principle of SEC, shorter elution time corresponds to larger molecular size in the eluting solution. Because the measurement limit of this apparatus for RMS is around 10 nm, RMS signals under 10 nm are scattered as shown in Fig. 7. The RMS at the peak top of RI intensity was decided by extrapolating the relationship between the elution time and the RMS in the range of relatively shorter elution time from 14.5 to 16.5 min. In the case of Fig. 7, the steric size of PC2 in the solution of 50 mmol/l Na_2SO_4 is estimated as 5.2 nm.

The relationships between the ionic strength of the eluting solution and steric size of the polymers are shown in Fig. 8. The steric size of PEO is almost constant, irrespective of ionic strength. Although the sizes of PC in 300 mmol/l Na_2SO_4 solution cannot be decided because they are too small to measure by this method, the steric sizes of PC1 and PC2 decrease with the increase in ionic strength. Although the molecular weights of both PCs are almost the same, the steric size of PC2 is larger than that of PC1. The shrinking amount of PC2 is larger than that of PC1 with the same change in ionic strength. These differences are thought to correlate to their chemical

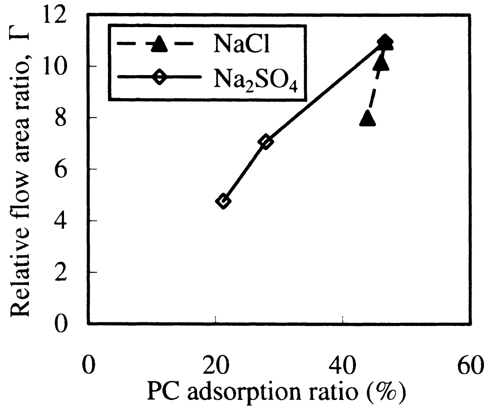

Fig. 4. Relationship between PC adsorption and paste fluidity.

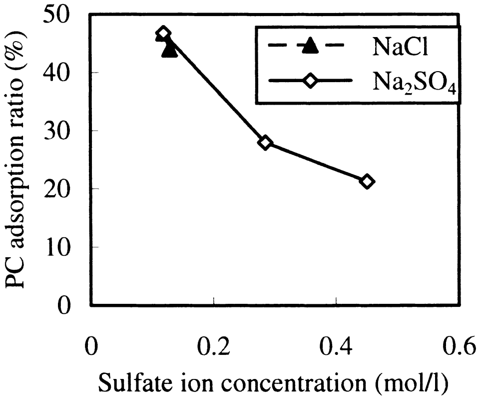

Fig. 6. Relationship between sulfate ion concentration and PC adsorption.

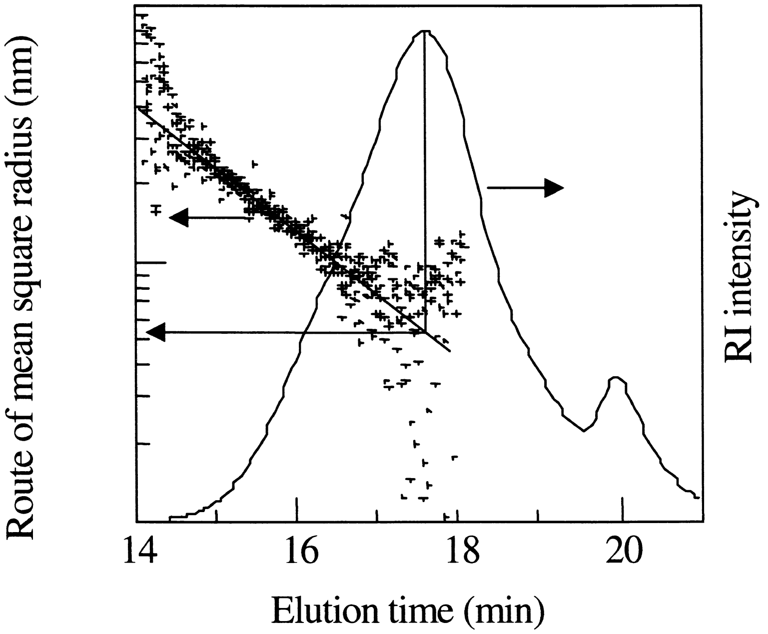

Fig. 7. Steric size of PC2 in the aqueous solution containing 50 mmol/l of Na_2SO_4 by light scattering.

structures. PC2 has a longer trunk chain and shorter graft chains compared to PC1.

Because the size of PEO is independent of the ionic strength, the shrink of PC is thought to be caused by the trunk structure. The ratios of carboxylic groups in the trunk chains are 0.655 and 0.662 for PC1 and PC2, respectively. The degrees of trunk polymerization are 195 and 353 for PC1 and PC2, respectively. The ratios of carboxylic groups of two PCs are similar, whereas the trunk chain of PC2 is longer than that of PC1. The trunk chain expands in aqueous solutions by the dissociation of the carboxylic group because the dissociation generates the electrostatic repulsive force between carboxylic groups. The dissociated state is expected to change depending on the ionic strength. In higher ionic solutions, since the dissociation is less, the repulsive force between carboxylic groups is weaker. Based on this consideration, the size of PC2 with longer trunk chains decreases more by the change in ionic strength than that of PC1 with the shorter trunk chain. The decrease in the steric size of PC is thought to result in the decrease in the dispersing force of PC.

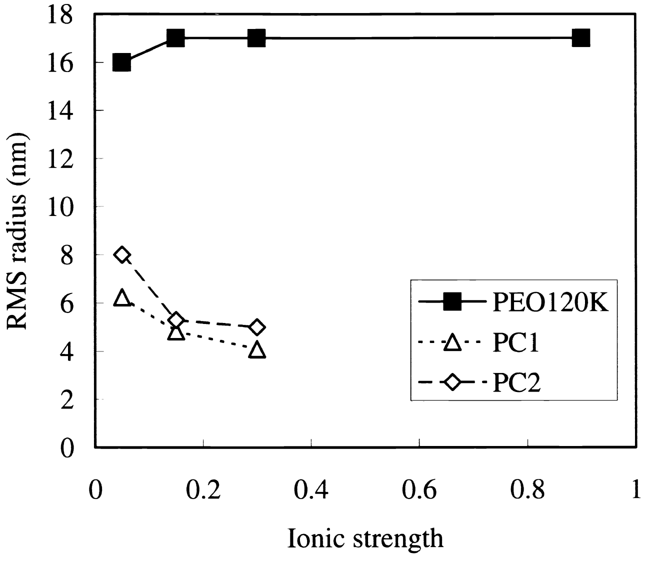

Fig. 8. Effects of ionic strength on the steric size of PEO and PC in aqueous solution.

It is very important to point out that the effect of salt addition on the steric size of PC depends on the ionic strength regardless of the kind of salt, NaCl or Na_2SO_4. When the ionic strength of added salts are equal, the decreasing effect of Γ by Na_2SO_4 is twice larger than that by NaCl, as shown in Fig. 2. Therefore, in the case of Na_2SO_4 addition, it is necessary to take into account other mechanisms, such as competitive adsorption between PC and sulfate ion.

3.2.3. Contributing ratios of competitive adsorption and ionic strength

Both ionic strength and competitive adsorption with the sulfate ion seems to affect the dispersing force of PC. Comparing the contribution ratios of both effects on the decrease of Γ, Na_2SO_4 and NaCl decrease Γ by six and three per ionic strength, respectively. Assuming the decrease of Γ by NaCl results from the ionic strength alone and the decrease of Γ by Na_2SO_4 is caused by both ionic strength and competitive adsorption with the sulfate ion, the effect of the decrease of Γ by ionic strength is equivalent to that by competitive adsorption with sulfate

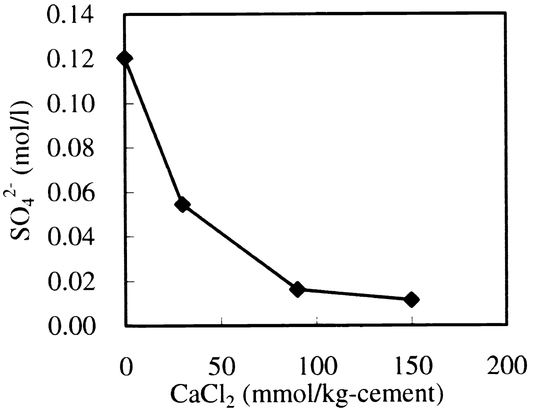

Fig. 9. Effects of $CaCl_2$ addition on sulfate ion concentration.

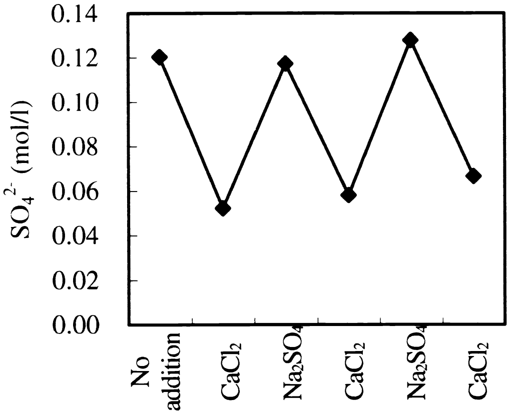

Fig. 11. Salt-adding effect on sulfate ion concentration.

ion in this experimental condition. In the cases of different types and dosages of PC, the contributing ratio of both effects may be different because the adsorption equilibrium state between PC and the sulfate ions depends on the adsorption force and the concentration of PC.

Considering actual concrete, the possible contributions are compared as follows. Chlorine content in cement is restricted to lower than 0.1 mass% by EN 197–1:2000, European standard for common cement. Therefore, the maximum ionic strength due to alkaline chloride in cement paste at w/c ratio of 0.20 is calculated as only 0.14. The effect of alkaline chloride is negligible, judging from Fig. 2. Alkaline oxide content in cement is restricted to lower than 0.75 mass% by JIS R 5201, Japanese standard for Portland cement. Assuming the entire amount of alkaline exists as alkaline sulfate, the sulfate ion molar concentration and ionic strength in cement paste at w/c ratio of 0.20 is calculated as 0.60 and 1.81 mol/l, respectively. Judging from Fig. 2, the dispersing force of PC can be changed three times depending on the amount of alkaline sulfate in cement.

3.3. Controlling of sulfate ion concentration and PC adsorption by Ca salts

It has become clear that ionic strength and the sulfate ion concentration affects the dispersing force of PC. Although it seems to be difficult to decrease the soluble alkaline concentration, the sulfate ion concentration may be decreased by using the solubility equilibrium of gypsum as shown in Eq. (3).

$$[Ca^{2+}][SO_4^{2-}] = 2.4 \times 10^{-5} \tag{3}$$

The increase in the calcium ion concentration is expected to reduce the sulfate ion concentration.

The sulfate ion concentration change in cement paste containing 0.20 mass% PC at w/c of 0.30 by the addition of $CaCl_2$ is shown in Fig. 9. By the addition of $CaCl_2$, the sulfate ion concentration in the paste decreases. The relationship between the sulfate ion concentration and PC adsorption ratio is shown in Fig. 10. The PC adsorption ratio increases with the decrease in the sulfate ion concentration.

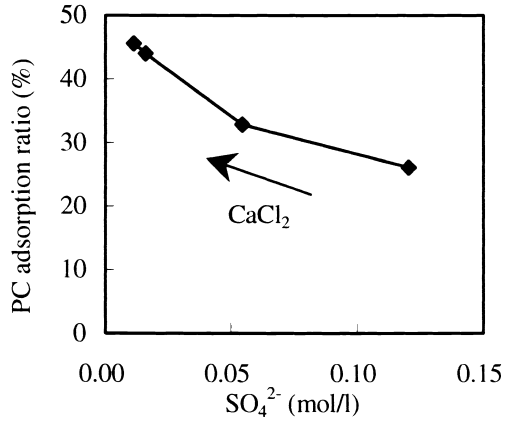

Fig. 10. Sulfate ion concentration and PC adsorption.

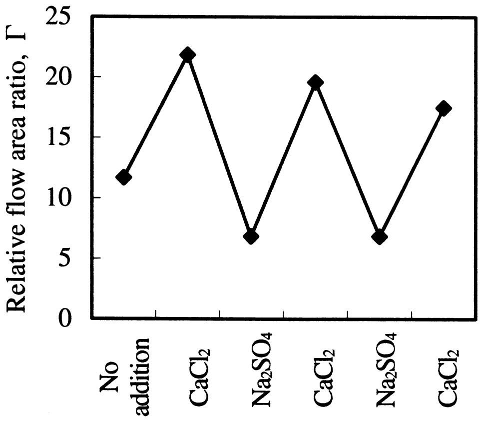

Fig. 12. Salt-adding effect on paste fluidity.

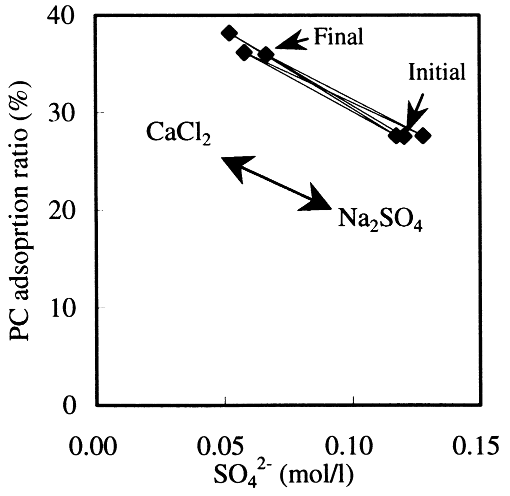

Fig. 13. Sulfate ion concentration and PC adsorption.

From the above results, it is possible to control the sulfate ion concentration in cement paste and the PC adsorption ratio by adding $CaCl_2$ and Na_2SO_4.

3.4. Relationship between PC adsorption and fluidity

The method of controlling the sulfate ion concentration mentioned above is based on the solubility equilibrium of gypsum. This method is thought to be reversible. Considering that the PC adsorption on cement particles is competitive adsorption with the sulfate ion, the increase and decrease in the sulfate ion concentration results in the decrease and increase in PC adsorption, respectively. Then, the sulfate ion concentration and the fluidity of paste were examined by the repetitious addition of $CaCl_2$ and Na_2SO_4 to the mixed cement paste. Salts were added to the same cement paste in sequence after the first contact between cement and water at about 10-min intervals. After the addition of salts, the paste was remixed using a Hobart mix at high speed for 1 min. The last batch of tests was measured about 1 h after the first contact with water.

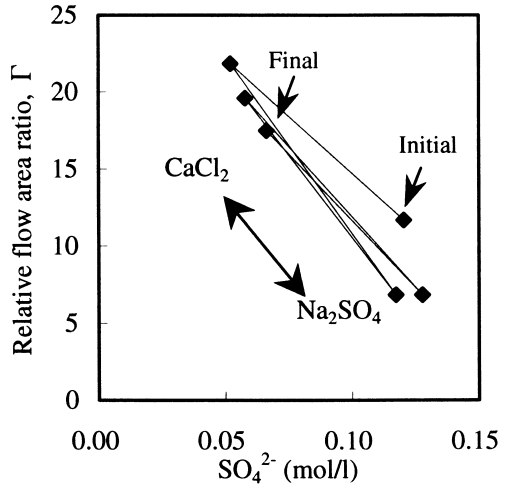

Fig. 14. Sulfate ion concentration and paste fluidity.

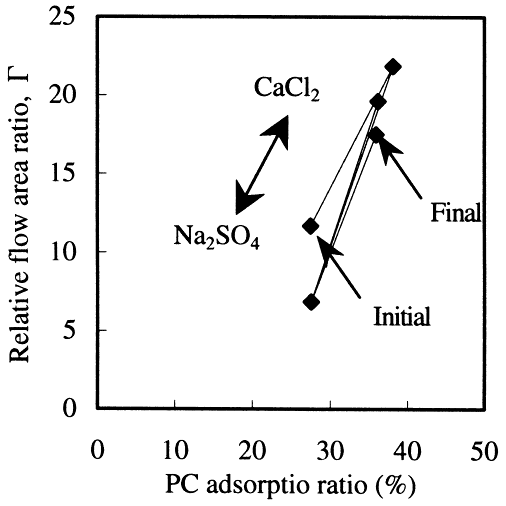

Fig. 15. PC adsorption and paste fluidity.

The sulfate ion concentration changes by salt addition are shown in Fig. 11. The addition of $CaCl_2$ decreases the sulfate ion concentration and the addition of Na_2SO_4 increases the sulfate ion concentration. The sulfated ion concentration reversibly decreases and increases by the repetitious addition of the two salts. The average level of sulfate ion concentration slightly increases by the repetitious addition.

The relationship between the addition of the salts and Γ is shown in Fig. 12. Contrary to the case of the sulfate ion concentration as shown in Fig. 11, Γ decreases with the increase in the sulfate ion concentration and Γ increases with the decrease in the sulfate ion concentration. Although the average level of Γ decreases by the repetitious addition of salts, the decrease of Γ by each addition of Na_2SO_4 is three to four times larger than the average decrease.

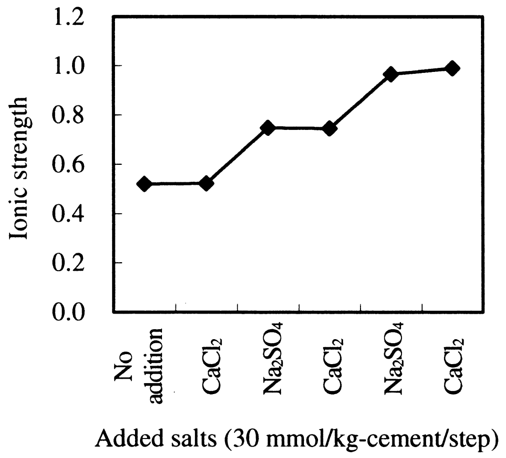

Fig. 16. Salt-adding effect on ionic strength in solution phase in paste.

The effect of the addition of $CaCl_2$ and Na_2SO_4 is expressed by the relationship with the sulfate ion concentration, as shown in Fig. 13. The effect of the addition of $CaCl_2$ and Na_2SO_4 on the PC adsorption ratio functions reversibly. The relationship between the sulfate ion concentration and Γ is shown in Fig. 14. The effects of adding the sulfate ion on Γ are reversible as a whole. When investigated in more detail, Γ level slightly decreases by the repetitious addition of salts, especially by the addition of Na_2SO_4.

The relationship between the PC adsorption ratio and Γ is shown in Fig. 15. Γ changes in proportion to the PC adsorption ratio as a whole. When investigated in more detail, Γ level slightly decreases by the repetitious addition of salts, especially by Na_2SO_4, which is similar to the relationship between Γ and the sulfate ion concentration, as shown in Fig. 14. The change in ionic strength by the addition of salts is shown in Fig. 16. The ionic strength is calculated from the data of ion concentration measurements for ions, such as sodium, potassium, calcium, sulfate, chloride, and hydroxide. The ionic strength is almost independent of the addition of $CaCl_2$ and it increases by the addition of Na_2SO_4. The increase of ionic strength by Na_2SO_4 corresponds to the slight decreases in Γ observed in Figs. 14 and 15. The nonlinear behavior of Γ may be affected by the ionic strength.

3.5. *Effects of various multiple-charged cations*

The above discussion is based on the sulfate ion controlled by $CaCl_2$. Other multiple-charged cations are expected to exhibit the same effects as calcium. Then, the effects of adding other salts of multiple-charged cations were examined. Salts were added in the mixed paste at w/c of 0.3 and PC dosage of 0.20 mass%. The results are shown in Fig. 17.

By the addition of salts, the fluidity increases up to a constant dosage depending on the charge number. The fluidity decreased with over dosage. As an example, the mechanism of fluidity change by $CaCl_2$ is discussed. Although the sulfate ion concentration decreases by the addition of $CaCl_2$, the effect is saturated around 100 mmol/kg cement of $CaCl_2$, as shown in Fig. 9. Further addition of $CaCl_2$ increases only the ionic strength, which might lower the fluidity.

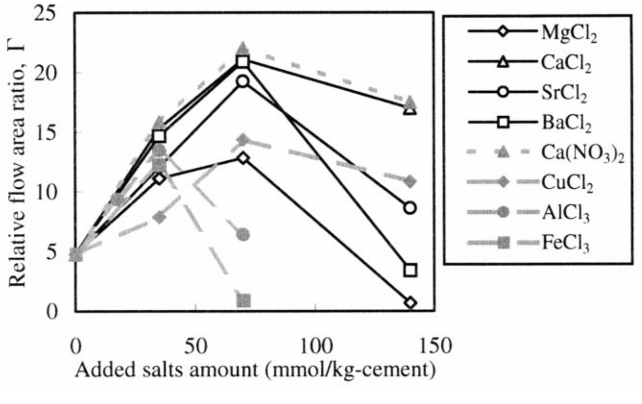

Fig. 17. Adding effects of various salts on paste fluidity.

Regardless of the kind of ions, the optimum dosages of salts that show the highest fluidity are the same as long as the charge numbers are the same. However, each maximum value of Γ is varied depending on the kind of salts. Comparing the same alkaline earth elements, Γ is higher in the order of Ca salts = $BaCl_2 > SrCl_2 >> MgCl_2$. In the case of $CuCl_2$, the behavior around the optimum value is different from alkaline earth elements although the optimum dosage is same.

The effect of the type of anion is examined by changing the pair anion of Ca. The effect of calcium nitrate is similar to that of chloride. The effect of the kind of anions seems to be insignificant. As for the application to concrete, nitrite salt that has a rust preventive effect may be preferable because the nitrate may cause corrosion of steel reinforcements.

The addition of soluble cations whose charge number is three also increases the fluidity. However, the optimum dosage of the triple-charged cation is less than that of double-charged cations, and the maximum value of Γ of triple-charged cation is lower than that of double-charged cations.

4. Conclusions

Controlling the sulfate ion concentration in aqueous phase, which has been known to affect the dispersing force of PCs, was attempted. By controlling the sulfate ion concentration, the relationship between the PC adsorption behavior on cement particles and the paste fluidity was investigated.

1. The fluidity of cement paste containing PC decreases by the addition of NaCl and Na_2SO_4. Comparing the dosages by the same ionic strength, the decreasing effect of Na_2SO_4 is twice as large as that of NaCl.
2. It is possible to control the sulfate ion concentration in the aqueous phase of cement paste by adding soluble multiple-charged cations, such as CaC_{l2}, and soluble sulfate, such as Na_2SO_4.
3. The increase in sulfate ion concentration decreases both the PC adsorption ratio and the fluidity of cement paste and vice versa.
4. Based on the measurement results of the steric size of polymers by the light scattering, although the steric size of PEO in aqueous solution is constant and independent of the ionic strength, that of PC decreases with the increase of ionic strength.
5. The decrease in the dispersing force of PC by the addition of salts is considered to result from the shrinking in the steric size of PC by the increase of ionic strength and the competitive adsorption between the carboxylic group of the PC and sulfate ion.

6. The amounts of multiple-charged cations added to the mixed cement paste have an optimum value to show the high fluidity depending on the charge number.

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