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Relationship between Fluidity of Cement Paste with Fluoride Ion and Type of Superplasticizer

Kazuki Matsuzawa^{1*}, Masahiro Miyauchi² and Etsuo Sakai³

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Abstract

Fluoride ions decrease the fluidity of cement paste containing superplasticizer. This paper discusses the fluidity decrease from the influence of fluoride on the solid and liquid phases in cement paste, and investigates the difference between allylether-type and methacrylate-type polycarboxylate-based superplasticizers in cement paste containing fluoride ions. Regarding the solid phase, addition of fluoride ions generates fine particles, resulting in adsorption of superplasticizer on the fine particles. Regarding the liquid phase, addition of fluoride ions decreased Ca^{2+} concentration and increased SO_4^{2-} concentration; i.e., the adsorption hindrance. Allylether-type superplasticizers preferentially adsorb on the fine particles even with the adsorption hindrance; i.e., they are susceptible to the preferential adsorption. Methacrylate-type superplasticizers were less susceptible, but adsorption was hindered by the adsorption hindrance. When water-cement ratio increased, Ca^{2+} concentration increased and SO_4^{2-} was diluted, resulting in weak adsorption hindrance. Because of these concentration changes, methacrylate-type superplasticizers showed the preferential adsorption at high water-cement ratio.

1. Introduction

Cement calcination requires high-temperature ($> 1450^\circ\text{C}$; $> 1720\text{ K}$) for alite ($\text{Ca}_3\text{SiO}_5 = \text{C}_3\text{S}$) generation and consumes a large amount of energy (Stadler *et al.* 2011). Therefore, low-temperature calcination using sulfate and fluoride compounds has been researched as a countermeasure (Blanco-Varela *et al.* 1986; Kolovos *et al.* 2001; Renó *et al.* 2013; Yoshikawa 2011). Sulfate compounds (e.g., CaSO_4) influence the calcination as fluxes, and fluoride compounds (e.g., CaF_2) influence as mineralizers (Johansen and Christensen 1979; Klemm *et al.* 1979). Fluxes affect the liquid phase, resulting in acceleration of the C_3S generation (Maki and Goto 1982). In contrast, mineralizers affect the solid-phase diagram and widen the temperature range where C_3S can exist to lower temperatures (Blanco-Varela *et al.* 1984). It has been revealed that additions of 1 - 2 mass% CaSO_4 and CaF_2 to the raw materials of cement can result in a temperature decrease of at most 220°C (220 K) (Raina and Janakiraman 1998), which corresponds to about 4.5% reduction in energy consumption (Gardeik 1981). However, sulfate ions and fluoride ions can form soluble or highly reactive compounds (e.g.,

K_2SO_4 and $\text{Ca}_{12}\text{Al}_{14}\text{O}_{32}\text{F}_2 = \text{C}_{11}\text{A}_7\cdot\text{CaF}_2$) during the calcination (Jawed and Skalny 1977; Klemm *et al.* 1979), and these ions elute into cement suspension after the calcination. In addition, fluoride ions are also contained in slags because fluoride compounds are used as fluxes in iron manufacture. When slag is contained in concrete, fluoride ions may elute into the concrete (Mizukami *et al.* 2004).

Sulfate ions hinder adsorption of superplasticizers in cement paste, and the fluidity of cement paste decreases because of this adsorption hindrance (Andersen *et al.* 1986; Nakajima and Yamada 2004; Pourchet *et al.* 2012; Yamada *et al.* 2001). Sulfate ions decrease Ca^{2+} concentration in the liquid phase and competitively occupy adsorption sites on cement particles, resulting in reduction of the number of adsorption sites for superplasticizers. This fluidity decrease with sulfate ions has been investigated for many years. However, the fluidity decrease with fluoride ions has not been researched in detail. The authors have reported that fluoride ion addition decreases the fluidity of cement pastes containing polycarboxylate-based superplasticizers and increases the specific surface area of the solid phase in cement paste (Matsuzawa *et al.* 2015a, 2015b, 2017). This increase in the specific surface area is caused by generation of fine particles containing mainly silicon and oxygen. Some reactions between hydrated calcium silicate and added fluoride ions generate the fine particles, and one of the causes of the fluidity decrease is preferential adsorption of the superplasticizer to the fine particles. Such a fluidity decrease by preferential adsorption also has been reported in cement paste containing montmorillonite (Atarashi *et al.* 2015; Lei and Plank 2012; Ng and Plank 2012).

The influence of these ions can be classified into two

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groups; i.e., the changes in the solid and liquid phase conditions. The adsorption hindrance by sulfate ions can be regarded as a change in the liquid phase condition, but sulfate ions also influence the solid phase. Sulfate ions can react with calcium aluminate and generate hydrated products, resulting in generation of new adsorption sites and some adsorption of superplasticizer on the hydrated products. The influence of the hydrated products is less than the adsorption hindrance for small or moderate amounts of sulfate ions (Matsuzawa *et al.* 2015b). On the other hand, the fine particle generation by fluoride ions can be regarded as a change in the solid phase condition. Montmorillonite addition also can be regarded as a change in the solid phase condition. Here, the influence of fluoride ion addition on the liquid phase condition has not been investigated.

In addition, polycarboxylate-based superplasticizers can be classified into many groups, including allylether-type and methacrylate-type superplasticizers. Allylether-type superplasticizers have maleic acid as the functional group for adsorption and methacrylate-type superplasticizers have methacrylic acid with a single carboxyl functional group. The authors consider that different superplasticizers have different adsorption behaviors to the fine particles. The influence of fluoride on the liquid phase is also considered to depend on the type of superplasticizer. Investigation of the difference between allylether-type and methacrylate-type superplasticizers is important to decrease the influence of fluoride ions. In this paper, the authors investigate the influence of fluoride ion addition on the solid and liquid phases in cement paste and compare adsorption of allylether-type and methacrylate-type superplasticizers in cement paste with fluoride ion addition.

2. Previous results for allylether-type superplasticizers

Here, the authors discuss the influence of fluoride ion addition on cement paste containing allylether-type superplasticizers using the results of previous studies (Matsuzawa *et al.* 2015a, 2015b, 2017). The results in this section are used in later sections to compare allylether-type and methacrylate-type superplasticizers. **Figure 1** shows the molecular structure of allylether-type superplasticizers (P-34 and P-10). The mean polymerization degrees of graft chains (n) are 34 for P-34 and 10 for P-10. In both P-34 and P-10, the ratio of α -allyl- ω -methoxypolyethylene to maleic acid ($P : Q$) is 1 : 1 and the ratio of styrene (R) is less than 0.015, thus the effect of styrene on the behavior of superplasticizers is negligible. The mean molecular weights (M_w) are 23,100 g/mol for P-34 and 29,100 g/mol for P-10. From a calculation using these molecular weights, the mean number of graft chains ($P = Q$) in one P-34 molecule is 13.8 and that in one P-10 molecule is 47.5. In brief, one P-10 molecule has more functional groups than P-34. In the experiments, ordinary Portland cement (OPC) was used

and the mass ratio of water to OPC (W/C) was 0.32:1. The dosages of P-34 and P-10 were 0.192 mass% of OPC. To add fluoride ions, KF solution was used.

Figure 2 shows the apparent viscosities of cement pastes containing the allylether-type superplasticizers. The method of measurement for the apparent viscosity is explained in Section 3.2. Without addition of KF, the apparent viscosity with P-34 was 569 mPa·s. On the other hand, that with P-10 was 488 mPa·s and it is approximately 0.86 times that with P-34. When KF was added, the apparent viscosities increased in both pastes with P-34 and P-10; i.e., the fluidity decreased. When the dosage of KF was 0.128 mol/kg, the apparent viscosities were 1031 mPa·s for P-34 and 954 mPa·s for P-10. The fluidities increased by approximately 2 times with KF addition.

Figure 3 shows the adsorbed amounts of the al-

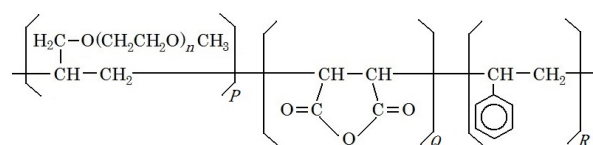


Fig. 1 Molecular structure of allylether-type superplasticizers.

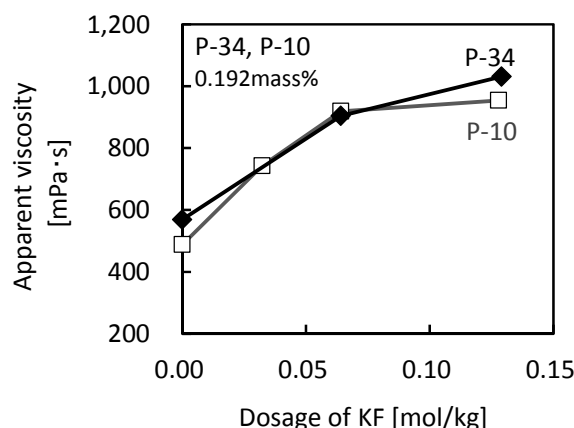


Fig. 2 Influence of KF addition on fluidity of OPC pastes with allylether-type superplasticizers.

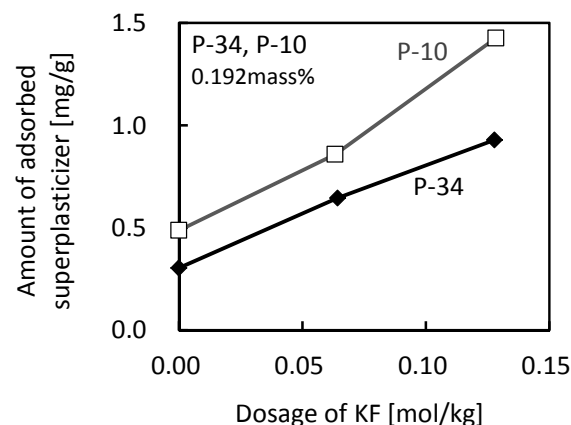


Fig. 3 Influence of KF addition on adsorption of allylether-type superplasticizers in OPC pastes.

Table 1 Composition of OPC. [mass%]

| CaO | SiO ₂ | Al ₂ O ₃ | Fe ₂ O ₃ | SO ₃ | MgO | K ₂ O | Na ₂ O | P ₂ O ₅ | TiO ₂ | MnO |
|-------|------------------|--------------------------------|--------------------------------|-----------------|------|------------------|-------------------|-------------------------------|------------------|------|
| 65.36 | 21.28 | 5.09 | 3.15 | 2.01 | 1.01 | 0.41 | 0.32 | 0.14 | 0.25 | 0.10 |

Table 2 Mineral composition of OPC. [mass%]

| Ca ₃ SiO ₅ | Ca ₂ SiO ₄ | Ca ₃ Al ₂ O ₆ | Ca ₄ Al ₂ Fe ₂ O ₁₀ | CaSO ₄ |
|----------------------------------|----------------------------------|--|---|-------------------|
| 59.8 | 15.9 | 8.2 | 9.6 | 3.4 |

Annotation: These values are calculated by Bogue's equation

lylether-type superplasticizers. The method of measurement for the adsorbed amount is also explained in Section 3.2. Without addition of KF, the adsorbed amounts were 0.30 mg/g for P-34 and 0.49 mg/g for P-10. The adsorbed amount of P-10 was larger than that of P-34, and this corresponds to the result of fluidity measurement. More adsorbed superplasticizer molecules aid in dispersion and result in the higher fluidity. When KF was added, the adsorbed amounts of P-34 and P-10 considerably increased. Independent of the fluoride dosage, the adsorbed amount of P-10 was larger than that of P-34. This should be because one P-10 molecule has more functional groups than P-34. It means the adsorption ability depends on the number of functional groups. Although the adsorbed amount increased with KF addition, the fluidity was decreased (Fig. 2). This means that most of adsorbed superplasticizer molecules do not aid in dispersion of cement particles. When fluoride ions are added to cement paste, fine particles are generated and most of allylether-type superplasticizer molecules adsorb on the particles, resulting in a decrease in the amount of adsorbed superplasticizer on cement particles and a fluidity decrease (Matsuzawa *et al.* 2015a, 2015b, 2017).

3. Experimental investigation

3.1 Materials

Table 1 shows the chemical composition of OPC used in this paper. **Table 2** shows the mineral composition of used OPC calculated using the values in **Table 1** and Bogue's equation. The specific surface area of used OPC was determined to be 0.88 m²/g by the Brunauer-Emmett-Teller (BET) method with N₂ adsorption.

Two methacrylate-type polycarboxylate-based superplasticizers (TI-5 and TI-6: Nippon Shokubai Co., Ltd., Japan) were used. **Figure 4** shows the general molecular structure of methacrylate-type polycarboxylate-based superplasticizers (Plank *et al.* 2015; Sakai *et al.* 2003). In the molecular structure, M represents metal elements

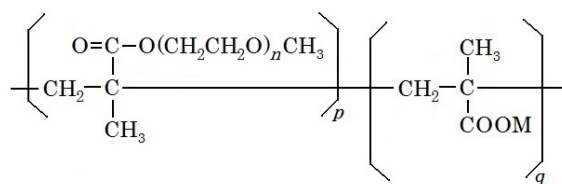


Fig. 4 Molecular structure of methacrylate-type superplasticizers.

(e.g., Na). The actual molecular structures of TI-5 and TI-6 are not exposed but considered to be quite similar to the general molecular structure. Methacrylate-type superplasticizers have poly-ethylene oxide graft chains, similar to allylether-type superplasticizers. However, they have methacrylic acid and differ from allylether-type superplasticizers which usually have maleic acid as functional groups. TI-5 and TI-6 have the same densities of functional groups and the same polymerization degrees of graft chains. On the other hand, the mean molecular weights (M_w) are 10,000 g/mol for TI-5 and 18,900 g/mol for TI-6. This means that one TI-6 molecule has approximately 2 times more functional groups than TI-5. TI-6 can be regarded as the combination of two TI-5 molecules.

The actual amount of fluoride elution from low-calcined cement has not been revealed in detail. However, to clarify the influence of fluoride ions, the authors took account of generation of soluble or highly reactive compounds under the low-temperature calcination and used KF solution for fluoride ion addition into cement paste as the model experiment for fluoride ion elution. KF solution was prepared from KF·2H₂O (98.0%, Sigma-Aldrich) and distilled water. To investigate the influence of potassium, KCl (> 99.5%, Wako Pure Chemical Industries, Ltd.) was used instead of KF·2H₂O in some experiments.

3.2 Methods

To investigate the influence of fluoride ion addition on the liquid phase, W/C was changed from 0.32 to 1.0. Similar to a previous report (Matsuzawa *et al.* 2017), the dosage of superplasticizer was 0.192 mass% of OPC. Based on the mineralizer amount in actual low-temperature calcinations, the dosage of KF was changed from 0 to 0.128 mol/kg (0.744 mass%) of OPC.

A solution with the fixed amounts of superplasticizer and KF was added to OPC, and the paste was mixed by hand with a stainless steel spoon for 5 min at 20°C (293 K). After this 5 min hydration, the OPC paste was mixed with a large amount of acetone to stop hydration. Continuously, the cement-acetone suspension was centrifuged at 8200 m/s² for 10 min, and the solid phase was collected. The collected solid phase was dried under a low pressure (0.01 MPa) for 24 h at 20°C (293 K), and the solid phase was then degassed in N₂ gas flow. The degassing temperature was 40°C (313 K) and the degassing period was in the range of 180 - 300 min to avoid ettringite decomposition (Yamada 2011). Finally, the specific surface area of the degassed solid phase was measured by the BET method with N₂ adsorption using a surface area analyzer (Gemini V2380, Micromeritics, USA).

To measure ion concentrations in the liquid phase of

OPC paste, the mixing time was 5 min at 20°C (293 K), similar to the specific surface area measurements. After the mixing, OPC paste was centrifuged at 8200 m/s² for 10 min, and the liquid phase was extracted. Ion concentrations in the extracted liquid phase were measured using an ion chromatograph (LC-20ADsp prominence, Shimadzu Corporation, Japan) to investigate the influences of fluoride addition and W/C change on the liquid phase. In addition, the amount of adsorbed superplasticizer on the solid phase in the paste was measured by a similar method. The liquid phase was extracted by the centrifugation, and the superplasticizer concentration in the extracted liquid was measured using a total organic carbon analyzer (TOC-L CSH/CSN, Shimadzu Corporation, Japan). Finally, the adsorbed amount was calculated from the difference between superplasticizer concentrations of the added solution and the extracted liquid.

The fluidity of OPC paste was measured using a rotational cylinder viscometer (Haake MARS III Z41-TI, Thermo Fisher Scientific K.K, Japan) at 20°C (293 K). After the 5 min mixing, the fluidity measurement was immediately started and the shear stress was linearly changed from 0 to 200 Pa in 120 s. Similar to a previous report (Matsuzawa *et al.* 2015a), the fluidity of OPC paste was evaluated by the apparent viscosity at a shear stress of 200 Pa. A lower apparent viscosity corresponds to higher fluidity.

4. Results and discussion

4.1 Influence of fluoride ion addition on specific surface area of solid phase

First, this section discusses the influence of fluoride ions on the solid phase in OPC paste. **Figure 5** shows the change of the specific surface area with KF addition. TI-5 was used in this experiment as a representative superplasticizer, and the dosage of TI-5 was 0.192 mass% of OPC.

Without addition of KF, the specific surface area was approximately 1.35 m²/g independent of W/C. The spe-

cific surface area of unhydrated OPC was 0.88 m²/g, thus it increased by 1.5 times with 5 min hydration. This increase in the specific surface area should originate from the early hydrated products. On the other hand, the specific surface area with 0.128 mol/kg KF was 1.91 m²/g at W/C of 0.32, and it decreased with increasing W/C. When W/C > 0.50, the specific surface area was approximately 1.75 m²/g, and there was no change in the specific surface area with increasing W/C. Although 0.128 mol/kg KF is equal to 0.744 mass% only, the increase in the specific surface area with KF addition was larger than 0.40 m²/g and this corresponds to 45% of the initial specific surface area. Such a large increase in the specific surface area indicates generation of finer particles than cement particles (Matsuzawa *et al.* 2017), and this is the influence of fluoride ion addition on the solid phase. In addition, this experiment shows that the liquid phase condition is not dominant for the fine particle generation with fluoride addition. For example, when W/C = 0.32, it is considered that the increase in the specific surface area of 0.40 (1.75 - 1.35) m²/g is not related to the liquid phase and 0.16 (1.91 - 1.75) m²/g is related to the liquid phase.

4.2 Influence of fluoride ion addition on ion concentrations of liquid phase

Next, the influence of fluoride ions on the liquid phase in OPC paste is discussed. Similar to the measurements for the specific surface area, TI-5 was used as a representative superplasticizer and the dosage was 0.192 mass%. In this section, the paste with KCl was also investigated for comparison. Three cations (K⁺, Na⁺, and Ca²⁺) and two anions (SO₄²⁻ and Cl⁻) were detected in OPC paste by ion chromatography. K⁺ and Na⁺ naturally exist in OPC as the sulfate or the soluted elements in calcium silicates (Jawed and Skalny 1977; Yamaguchi and Takagi 1969), therefore they can be detected even in the paste without KF or KCl. There is no difference in Na⁺ concentrations for pastes with/without KF, thus the result is not discussed. Ca²⁺ elutes from cement particles owing to hydration of cement or dissolution of calcium sulfates. SO₄²⁻ also elutes from cement particles owing to dissolution of sulfates. Incidentally, F⁻ concentration was also measured, but it was below the measurement limit even in the paste with KF. Therefore, the figure for fluoride ion concentration is omitted. It is supposed that all of the added fluoride ions became solid matter in the 5 min mixing.

Figure 6 shows the relationship between K⁺ concentration and W/C. **Figure 7** shows the total amount of K⁺ in the liquid phase, which corresponds to the product of concentration and water amount. At a certain W/C, K⁺ concentration was higher in the paste with KF or KCl than without them; i.e., K⁺ concentration increased with the potassium salt addition. Both KF and KCl increased K⁺ concentration, and the concentrations were almost equal in both pastes with KF and KCl. Therefore, the increase in K⁺ concentration should be caused by the

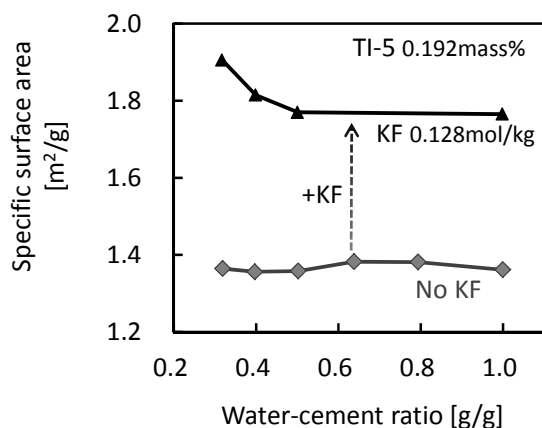


Fig. 5 Influence of KF addition on specific surface area of solid phase in OPC paste.

potassium addition, and the influence of anions (F^- and Cl^-) is considered to be negligible. Although K^+ concentration decreased with increasing W/C, the total amount of K^+ was almost constant independent of W/C. The total amounts were approximately 30 mmol/kg of OPC in the pastes without the potassium salts and approximately 94 mmol/kg in the pastes with the salts. Therefore, it is supposed that the decrease in K^+ concentration with increasing W/C is just caused by dilution.

Figure 8 shows the relationship between Cl^- concentration and W/C. **Figure 9** shows the total amount of Cl^- in the liquid phase. Cements naturally contain a small amount of Cl^- , but Cl^- concentration in the paste without KCl was below the measurement limit. On the other hand, Cl^- could be detected in the paste with KCl. This result is different from that for F^- ; i.e., F^- was not detected even in the paste with KF. Although Cl^- concentration decreased with increasing W/C, the total amount of Cl^- was almost constant independent of W/C. Therefore, it can be said that the decrease in Cl^- concentration with increasing W/C is just caused by dilution, similar to K^+ concentration.

Figure 10 shows the relationship between Ca^{2+} concentration and W/C. **Figure 11** shows the total amount of Ca^{2+} in the liquid phase. At a certain W/C, Ca^{2+} con-

centration with KF addition was lower than that without potassium salts. In contrast, Ca^{2+} concentration with KCl addition was higher than that without potassium salts. When Ca^{2+} concentration without the salts is normalized to 100%, Ca^{2+} concentration with KF is approximately 70% and that with KCl is approximately 130%. KF and KCl are potassium salts, but there is a large difference in Ca^{2+} concentrations with KF and KCl. Therefore, the decrease in Ca^{2+} concentration with KF addition must originate from fluoride ions. In addition, independent of potassium salt addition, Ca^{2+} concentration increased with increasing W/C from 0.32 to 0.80 and slightly decreased with increasing W/C from 0.80 to 1.0. In particular, the total amount of Ca^{2+} increased monotonically with increasing W/C. This result is different from that for K^+ . Independent of the potassium salt addition, the total amount of Ca^{2+} increased by approximately 4 times with increasing W/C from 0.32 to 1.0.

Figure 12 shows the relationship between SO_4^{2-} concentration and W/C. **Figure 13** shows the total amount of SO_4^{2-} in the liquid phase. At a certain W/C, SO_4^{2-} concentration with KF addition was higher than that without potassium salts; i.e., SO_4^{2-} concentration increased with KF addition. In contrast, SO_4^{2-} concentra-

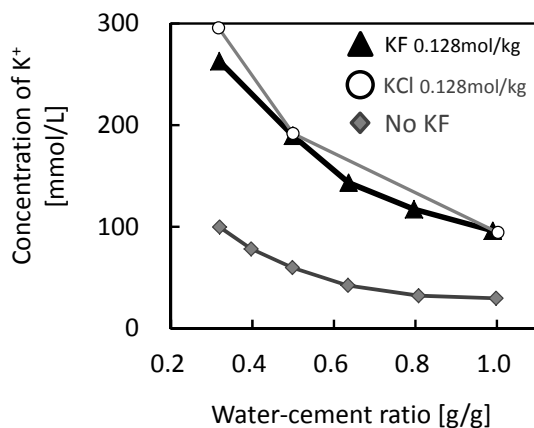


Fig. 6 Influence of potassium salt addition on potassium ion concentration.

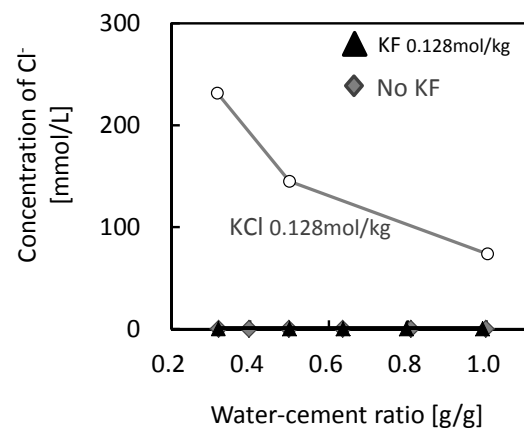


Fig. 8 Influence of potassium salt addition on chloride ion concentration.

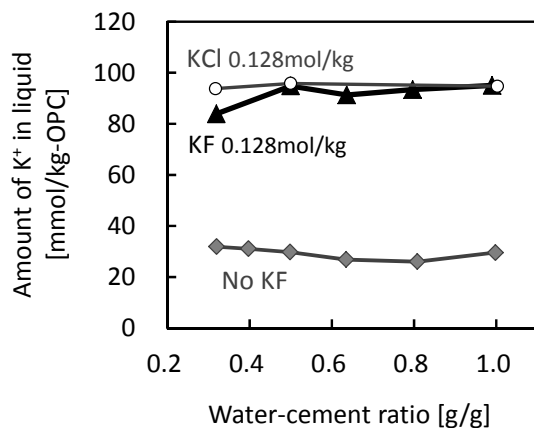


Fig. 7 Influence of potassium salt addition on amount of potassium ion.

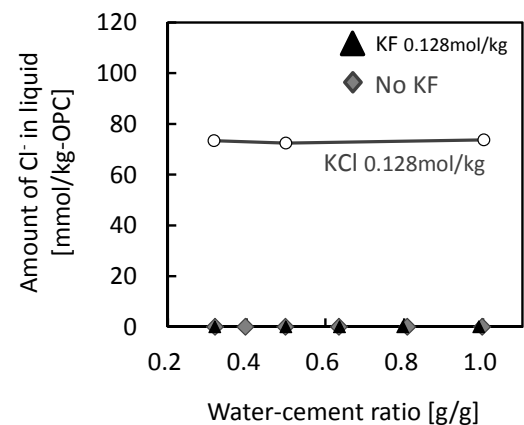
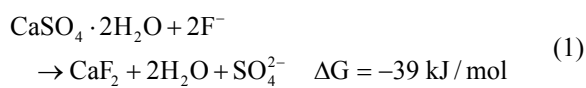


Fig. 9 Influence of potassium salt addition on amount of chloride ion.

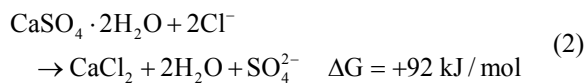
Table 3 Gibbs free energies of substances in Eqs. 1 and 2. [kJ/mol]

| $F^-_{(aq)}$ | $Cl^-_{(aq)}$ | $SO_4^{2-}_{(aq)}$ | CaF_2 | $CaCl_2$ | $CaSO_4 \cdot 2H_2O$ | $H_2O_{(l)}$ |
|--------------|---------------|--------------------|---------|----------|----------------------|--------------|
| -278.8 | -131.3 | -744.5 | -1175.6 | -748.8 | -1797.5 | -237.2 |

tion with KCl addition was the same as that without potassium salts; i.e., SO_4^{2-} concentration was not changed by KCl addition. From these results, fluoride ions must be the cause of SO_4^{2-} concentration increase with KF addition. It is supposed that there are some reactions between the sulfates in OPC and the added fluoride ions. Here, the authors consider $CaSO_4 \cdot 2H_2O$ as a representative sulfate in OPC paste, and a reaction between fluoride ions and $CaSO_4 \cdot 2H_2O$ is discussed. It is Eq. 1 and spontaneous.



In contrast, a reaction between chloride ions and $CaSO_4 \cdot 2H_2O$ is Eq. 2, and it is nonspontaneous.



The standard formation Gibbs energies of the substances in Eqs. 1 and 2 are shown in **Table 3** (Dean

1998). Incidentally, a similar result is obtained from the reactions of $CaSO_4 \cdot 0.5H_2O$. From these calculations, it is supposed that the increase in SO_4^{2-} concentration with KF addition is caused by reactions between fluoride ions and calcium sulfates in OPC. SO_4^{2-} concentration did not increase with KCl addition, because chloride ions cannot react with calcium sulfates.

Although SO_4^{2-} concentration decreased with increasing W/C, the total amount of SO_4^{2-} was almost constant independent of W/C. The total amounts were approximately 20 mmol/kg of OPC in the paste without KF and approximately 50 mmol/kg with KF. Therefore, it is supposed that the decrease in SO_4^{2-} concentration with increasing W/C is just caused by dilution. In addition, 0.128 mol/kg KF addition resulted in 18 - 31 mmol/kg SO_4^{2-} elution. From Eq. 1, 2 mol fluoride ions result in 1 mol sulfate ions elution. Therefore, the amount of fluoride ions that reacted with sulfates should be 36 - 62 mmol/kg; i.e., 28-48% of added fluoride ions. The authors did not detect CaF_2 particle generation in the previous report (Matsuzawa *et al.* 2017), but Eq. 1 indicates CaF_2 generation from this amount of fluoride ions.

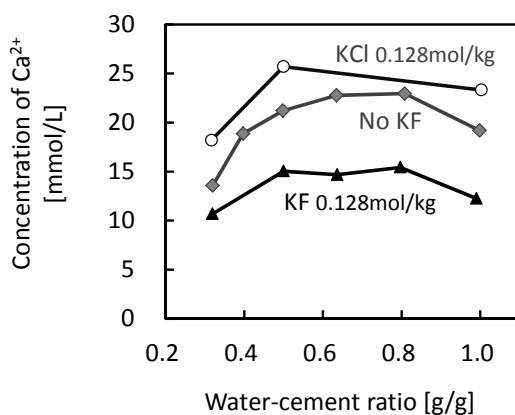


Fig. 10 Influence of potassium salt addition on calcium ion concentration.

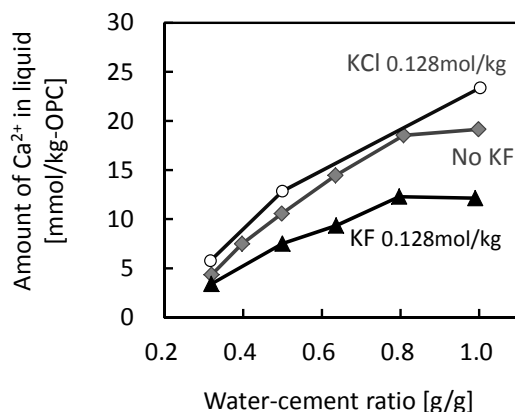


Fig. 11 Influence of potassium salt addition on amount of calcium ion.

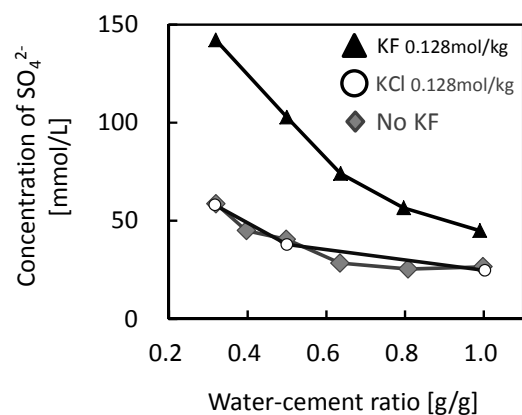


Fig. 12 Influence of potassium salt addition on sulfate ion concentration.

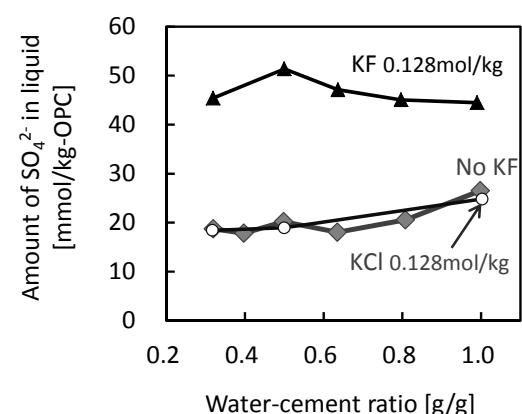


Fig. 13 Influence of potassium salt addition on amount of sulfate ion.

The fine particles containing silicon and oxygen should be generated by the remaining fluoride ions (52 - 72% of the dosage).

From these results, it is revealed that the influence of fluoride ion addition on the liquid phase is a decrease in Ca^{2+} concentration and an increase in SO_4^{2-} concentration. Ca^{2+} relates to the number of adsorption sites for polycarboxylate-based superplasticizers. On the other hand, SO_4^{2-} competitively occupies the adsorption sites and reduces the number of adsorption sites. These changes in the concentrations are considered to cause the adsorption hindrance of superplasticizer. However, adsorption of allylether-type superplasticizers is not susceptible to this adsorption hindrance (Section 2). In addition, it is also revealed that the influence of increasing W/C is an increase in Ca^{2+} amount and SO_4^{2-} dilution.

4.3 Influence of fluoride ion addition on fluidity and adsorption in cement paste with methacrylate-type superplasticizers

Figure 14 shows the apparent viscosities of cement pastes containing methacrylate-type superplasticizers (TI-5 and TI-6). Without addition of KF, the apparent viscosity with TI-5 was 304 mPa·s. On the other hand, that with TI-6 was 229 mPa·s; i.e., approximately 0.75 times that with TI-5. Similar to the allylether-type superplasticizers, a superplasticizer having more functional groups (TI-6) showed a higher fluidity. When KF was added, the apparent viscosities of the pastes with TI-5 and TI-6 increased, similar to the allylether-type superplasticizers. When the dosage of KF was 0.128 mol/kg, the apparent viscosities were 889 mPa·s for TI-5 and 734 mPa·s for TI-6. The fluidities increased by approximately 3 times with KF addition. Although this degree of fluidity increase is larger than that of P-34 and P-10 (approximately 2 times), TI-5 and TI-6 showed still higher fluidity than P-34 and P-10 (1031 and 954 mPa·s).

Figure 15 shows the adsorbed amounts of methacrylate-type superplasticizers. Since the hydration time was 5 min only, the authors presumed that the mass of the

solid phase did not change with the hydration. Therefore, the amount of adsorbed superplasticizer per unit mass of the solid corresponds to the total amount of adsorbed superplasticizer in the paste. If all of the superplasticizer molecules adsorb on the solid phase, the adsorbed amount would be 1.92 mg/g. Without addition of KF, the adsorbed amounts were 1.07 mg/g for TI-5 and 1.37 mg/g for TI-6. The adsorbed amount of TI-6 was larger than TI-5, and this corresponds to the difference in the apparent viscosities. When KF was added, the adsorbed amounts of TI-5 and TI-6 decreased; i.e., the preferential adsorption was not shown. This result is different from that for the allylether-type superplasticizers (P-34 and P-10), and it is similar to the adsorption hindrance caused by sulfate ion addition (Andersen *et al.* 1986; Nakajima and Yamada 2004; Pourchet *et al.* 2012; Yamada *et al.* 2001). The authors consider that this adsorption hindrance with fluoride ion addition is caused by the changes in ion concentrations. The decrease in Ca^{2+} concentration and the increase in SO_4^{2-} concentration with fluoride addition are considered to cause strong adsorption hindrance for methacrylate-type superplasticizers. Independent of the fluoride dosage, the amount of adsorbed TI-6 was larger than that of TI-5. This is also because TI-6 has more functional groups than TI-5.

The adsorbed amounts of both methacrylate-type superplasticizers (TI-5 and TI-6) were quite larger than those of allylether-type superplasticizers (P-34 and P-10). Adsorbed amounts without KF were 1.07 mg/g for TI-5 and 1.33 mg/g for TI-6 (Fig. 15). In contrast, adsorbed amounts are only 0.30 mg/g for P-34 and 0.49 mg/g for P-10 (Fig. 3). Therefore, the adsorption abilities of TI-5 and TI-6 should not be weaker than P-34 and P-10. However, TI-5 and TI-6 did not show the preferential adsorption even P-34 and P-10 show it. From these results, the authors consider that the adsorption behaviors of allylether-type and methacrylate-type superplasticizers are related to the type of functional groups rather than the number of functional groups (adsorption ability). It is supposed that maleic acid easily adsorbs to the fine particles generated with fluoride but methacrylic acid does not. Thus, the allylether-type su-

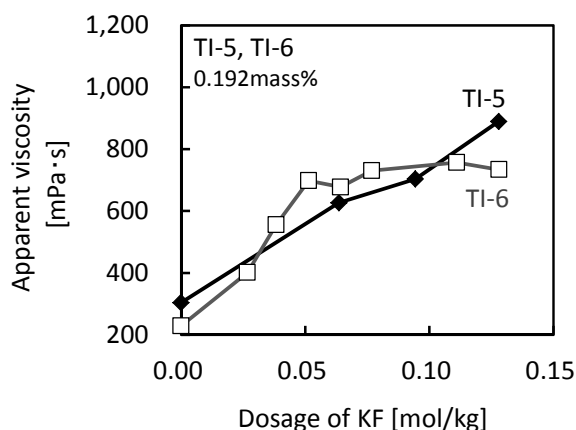


Fig. 14 Influence of KF addition on fluidity of OPC pastes with methacrylate-type superplasticizers.

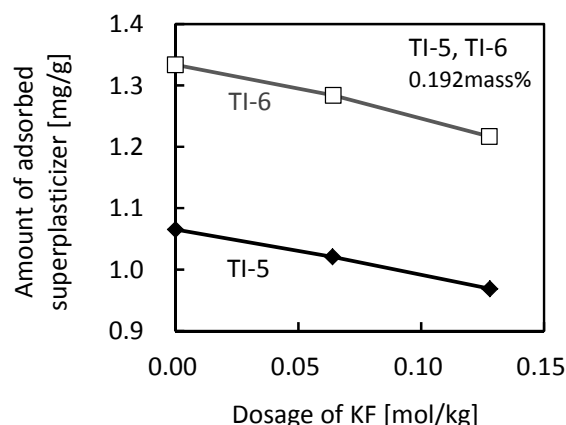


Fig. 15 Influence of KF addition on adsorption of methacrylate-type superplasticizers in OPC pastes.

perplasticizers show the preferential adsorption even though the changes in ion concentrations with fluoride addition hinder adsorption, but the adsorption of methacrylate-type was just hindered. This difference in the adsorption behaviors of superplasticizers is similar to that reported for cement paste containing silica fume. Allylether-type superplasticizers preferentially adsorb on silica fume rather than cement particles but methacrylate-type superplasticizers do not show the preferential adsorption (Schröfl *et al.* 2012). The fine particles generated with fluoride ion addition contain mainly silicon and oxygen, similar to silica fume (Matsuzawa *et al.* 2017). Therefore, it is reasonable that the adsorption behaviors in cement paste with fluoride ion addition and cement paste with silica fume are the same.

4.4 Relationship between water-cement ratio and adsorption hindrance for methacrylate-type superplasticizers

In Section 4.3, it is revealed that methacrylate-type superplasticizers are less susceptible to the preferential adsorption but more susceptible to the adsorption hindrance with fluoride ion addition. Here, it is expected that the adsorption behavior of methacrylate-type superplasticizers changes at high W/C, because the adsorp-

tion hindrance should be weak.

Figures 16 and 17 show the relationship between W/C and the adsorbed amounts of methacrylate-type superplasticizers. Similar to Section 4.1 and 4.2, the dosage of KF was 0.128 mol/kg. First, when W/C was low (W/C = 0.32), the amount of adsorbed TI-5 in OPC paste without KF was 1.07 mg/g, and that with 0.128 mol/kg KF was 0.97 mg/g; i.e., the adsorbed amount decreased with fluoride addition. Adsorbed TI-6 also decreased from 1.33 to 1.22 mg/g with KF addition. These results are also noted in Section 4.3. In contrast, when W/C was high (W/C = 1.0), adsorbed TI-5 increased from 0.92 to 1.24 mg/g with KF addition. The adsorbed amount of TI-6 at W/C=1.0 also increased from 1.17 to 1.51 mg/g with KF addition. These results show that the adsorption behavior of methacrylate-type superplasticizers considerably changes with W/C. The authors consider that the increase in Ca^{2+} concentration and the SO_4^{2-} dilution with increasing W/C canceled out the adsorption hindrance with fluoride addition and permitted the preferential adsorption of methacrylate-type superplasticizers.

5. Summary and conclusion

- (1) Fluoride ion addition increased the specific surface area of the solid phase in OPC paste, as reported in previous reports. This indicates generation of fine particles, and it is the influence of fluoride ions on the solid phase. On the other hand, fluoride ion addition decreased Ca^{2+} concentration and increased SO_4^{2-} concentration in the liquid phase of OPC paste. These changes in the ion concentrations may be caused by reactions between calcium sulfates in OPC and added fluoride ions, and it is the influence of fluoride ions on the liquid phase.
- (2) The fluidity of cement pastes with methacrylate-type superplasticizers was decreased by the fluoride ion addition, similar to the pastes with allylether-type superplasticizers. However, although the adsorbed amounts of allylether-type superplasticizers are increased by fluoride addition, those of methacrylate-type superplasticizers were decreased. The adsorption behavior of allylether-type superplasticizers is related to the preferential adsorption to the fine particles, resulting in the fluidity decrease. In contrast, it is supposed that the adsorption behavior of methacrylate-type superplasticizers is related to the adsorption hindrance caused by the changes in the ion concentrations. The authors consider that the difference between allylether-type and methacrylate-type originates from the type of functional groups.
- (3) With the increase in water-cement ratio, Ca^{2+} concentration increased but SO_4^{2-} was diluted, resulting in weakening of the adsorption hindrance. Because of these changes in the ion concentrations, the adsorbed amounts of methacrylate-type superplasticizers considerably changed with water-cement ratio.

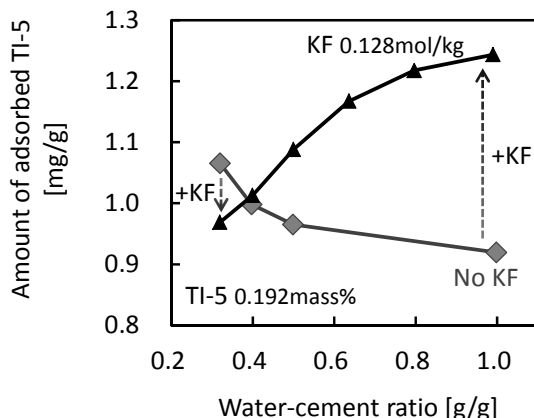


Fig. 16 Influences of KF addition and water-cement ratio on adsorption of TI-5.

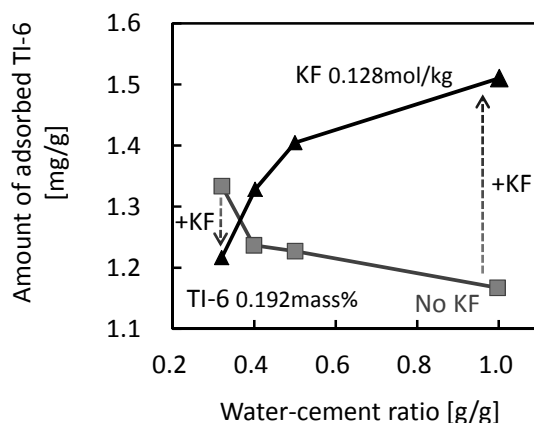


Fig. 17 Influences of KF addition and water-cement ratio on adsorption of TI-6.

When water-cement ratio was low, the adsorbed amount was decreased by fluoride ion addition because of the adsorption hindrance. In contrast, when water-cement ratio was high, the adsorption hindrance was canceled out and the adsorbed amount was considerably increased by fluoride.

- (4) Allylether-type superplasticizers are susceptible to the preferential adsorption even with the influence of the adsorption hindrance at low water-cement ratio. In contrast, methacrylate-type superplasticizers are susceptible to the liquid phase condition. To discuss the adsorption behavior of methacrylate-type superplasticizers in cement paste with fluoride ions, both fine particle generation and ion concentrations must be taken into account.

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