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# Working Mechanism of Superplasticizer in Cement Paste with Fluoride Ion

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*Scientific paper*

# Working Mechanism of Superplasticizer in Cement Paste with Fluoride Ion

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## Abstract

Low-temperature calcination for cement manufacturing by the addition of fluoride compounds has been researched by many investigators. Although it is possible that fluoride ions elute to the suspension after calcination, there are very few studies about the influence of fluoride ion on the fluidity of cement paste with superplasticizer. This paper describes the influence of fluoride ions on the adsorption mechanism of polycarboxylate based superplasticizer in cement paste. When the amount of KF was increased, the viscosity of the cement paste with superplasticizer and the amount of adsorbed superplasticizer increased. The fluidity with the polycarboxylate based superplasticizer containing more functional groups was more susceptive to KF addition and the amount of adsorbed superplasticizer was larger for the polycarboxylate based superplasticizer containing more functional groups. The specific surface area increased with KF addition. In the case of no KF addition, the hydration of alite was retarded by the addition of polycarboxylate based superplasticizer. In contrast, in the case of KF addition, the hydration of alite was not retarded by the addition of superplasticizer. It is supposed that some types of fine particles were generated by KF addition and the fine particles deprived the cement particles of superplasticizer.

## 1. Introduction

High fluidity concrete is necessary to save labor and reduce the time spent in the construction of concrete. In addition, reduction of the water ratio is required to increase the strength and the durability of the concrete, but sufficient fluidity is required for construction. To keep the fluidity and the durability, polycarboxylate based superplasticizers are used as the air-entraining and high range water-reducing admixture. Polycarboxylate based superplasticizers are comb-type polymers that adsorb to the surface of cement particles by their carboxyl functional groups. Polycarboxylate based superplasticizer stabilizes the dispersion of particles by the steric hindrance effect of the graft chains, and this type of superplasticizer can produce high fluidity with less dosage than other types of superplasticizer. In addition, the molecular structure of polycarboxylate based superplasticizers can be easily modified by changing the monomers.

High temperature condition (>1450°C: >1720 K) is necessary for alite generation in cement manufacturing, and a large amount of energy is consumed in this calcination process. The amount of energy for the calcination is equal to 80% of all energy consumed in cement manufacturing. Furthermore, high temperature calcination results in deterioration of the furnace and NOx emission. Because of these problems, decrease of the calcination temperature and reduction of energy consumption by the addition of sulfate and fluoride compounds have been investigated (Yoshikawa 2011). Compounds that can decrease the calcination temperature are separated into two groups based on the mechanism of the temperature decrease. Fluxes enable decrease of the calcination temperature by affecting the liquid phase diagram, amount of liquid, viscosity of the liquid, and surface energy. Sulfate compounds are potential fluxes. On the other hand, mineralizers enable decrease of the calcination temperature by affecting the solid phase diagram. Mineralizers widen the temperature range in which alite can exist to include lower temperatures. Fluorides are potential mineralizers. There have been many studies of the use of fluxes and mineralizers. For example, Raina and Janakiraman (1998) added $CaSO_4$ and $CaF_2$ to the raw materials of cement, and evaluated the degree of temperature decrease by the amount of free-lime after the calcination. In their research, it has been revealed that fluxes and mineralizers bring about a 220°C temperature decrease at most by the addition of 1–2 mass% $CaSO_4/CaF_2$ to the raw materials. The reduction of the energy consumption ratio in the manufacturing process is about 2.2% for every 100°C temperature decrease (Gardeik 1981). Therefore, the energy reduction ratio is calculated to be about 4.5%

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for the addition of $CaSO_4/CaF_2$ at most. However, when sulfate and fluoride are added to the raw material, it is possible that the sulfate and fluoride ions become soluble by calcination and elute to the suspension.

Authors have investigated limestone powder ($CaCO_3$) without hydration reactions as a model system, and it was revealed that the fluidity of $CaCO_3$ paste with polycarboxylate based superplasticizer considerably decreased by the addition of sulfate and fluoride ions (Sakai *et al.* 2000). It has been revealed that ions that can form an insoluble salt with the calcium ions, such as sulfate and fluoride ions, decrease calcium ions on the surface of $CaCO_3$ particles. It is thought that polycarboxylate based superplasticizers adsorb to the calcium ions on the surface of particles by their negatively charged functional groups. Therefore, the adsorption of these superplasticizers will be hindered by the decrease of calcium ions on the surface of the $CaCO_3$ particles. This adsorption hindrance effect of inorganic ions decreases the fluidity of the $CaCO_3$ paste with superplasticizers. Although there are many previous studies on $CaCO_3$ paste, the influence of fluoride ions on the fluidity of the cement paste with polycarboxylate based superplasticizer has not been investigated. To perform the low-temperature calcination by mineral salt addition in industry, more effective superplasticizers are desirable and detailed analysis is required about the mechanism of the fluidity change of cement paste by inorganic ions.

In this study, authors discuss the influence of KF addition on the fluidity, amount of adsorbed superplasticizer, specific surface area, and hydration reaction of cement paste with polycarboxylate based superplasticizer. Additionally, authors investigate the mechanism for the fluidity decrease of cement paste with superplasticizer by the fluoride ions addition.

## 2. Experimental investigation

### 2.1 Materials

The polycarboxylate based superplasticizers used in this study (P-10 and P-34) were α-allyl-ω-methoxypolyethylene-maleic anhydrite copolymers with graft chains of polyethylene oxide. **Figure 1** shows the molecular structure of the polycarboxylate based superplasticizers (P-*n*). **Table 1** shows the monomer polymerization ratio of P-*n* ($\alpha$: $\beta$: $\gamma$) and the mean molecular weight of P-*n* measured by gel permeation chromatography analysis. The amount of α-allyl-ω-methoxypolyethylene and maleic acid in both of superplasticizers is 1 to 1. Maleic acid in superplasticizers changes to carboxyl functional groups in cement paste. The ratio of styrene to α-allyl-ω-methoxypolyethylene ($\gamma$) is small and it is considered that styrene doesn't influence on the effect of superplasticizers. The number in the superplasticizers' name indicates the mean polymerization degree ($n$) of the graft chains. P-10 has shorter graft chains and contains more functional groups per unit mass than P-34. The amount of maleic acid contained in P-10 is $994 \times 10^{18}$ per 1 g and the amount in P-34 is $364 \times 10^{18}$ per 1 g. The comb-type polymers may also contain impurities, such as low molecular weight non-grafted polyethylene oxide oligomers. Since these impurities do not act as dispersing agents, their concentration was not included in the total superplasticizer concentration.

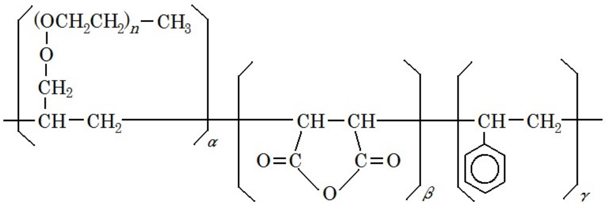

Fig. 1 Molecular structure of P-*n*.

**Table 2** shows the chemical composition ratio of the ordinary Portland cement (OPC) used in this study. **Table 3** shows the mineral composition ratio of OPC calculated by Bogue's equation. For fluoride ions addition, $KF \cdot 2H_2O$ (>95.0%, Wako Pure Chemical Industries, Ltd., Japan) was selected because the influence of potassium on the hydration of cement is small. Moreover, for potassium ions addition, $K_2SO_4$ (>99.0%, Kanto Chemical Co., Inc., Japan) and KCl (>99.5%, Wako Pure Chemical Industries, Ltd., Japan) were used.

### 2.2 Methods

The cement paste for the measurements was made by adding superplasticizer solution and KF solution to OPC. The mass ratio of water to OPC (W/C) was fixed at 0.32. After mixing by hands with a stainless steel spoon in a rubber cup for 5 min, the cement paste was used as the specimen for the experiments. The fluidity of the cement paste was measured by a rotational cylinder viscometer (Haake MARS III Z41-TI, Thermo Fisher Scientific K.K, Japan) at 20°C (293 K). The shear stress was changed from 0.54 Pa to 200 Pa in 120 s and continuously was changed from 200 Pa to 0.54 Pa in 120 s. The fluidity was evaluated by the apparent viscosity at

Table 1 Polymerization ratio and mean molecular weight of P-*n*.

| | $\alpha$ | $\beta$ | $\gamma$ | *Mw* [g/mol] |
|---|---|---|---|---|
| P-10 | 1 | 1.0 | 0.005 | 29100 |
| P-34 | 1 | 1.0 | 0.014 | 23100 |

Table 2 Composition of OPC [mass%].

| CaO | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | MgO | $SO_3$ |
|---|---|---|---|---|---|
| 64.96 | 20.94 | 5.45 | 2.83 | 1.54 | 2.05 |
| $Na_2O$ | $K_2O$ | $TiO_2$ | $P_2O_5$ | MnO | |
| 0.32 | 0.48 | 0.27 | 0.31 | 0.08 | |

Table 3 Mineral composition of OPC [mass%].

| $3CaO \cdot SiO_2$ | $2CaO \cdot SiO_2$ | $3CaO \cdot Al_2O_3$ | $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ |
|---|---|---|---|
| 59 | 16 | 10 | 9 |

Annotation: These values are calculated by Bogue's equation.

the shear stress of 200 Pa and the yield stress of the paste. The yield stress was evaluated by the shear stress in which the shear speed was 1 $s^{-1}$. In the measurement of the amount of superplasticizer adsorbed to the solid, the adsorption time was fixed at 5 min and the temperature was 20°C (293 K). The liquid phase in the paste was separated by centrifuging at 8200 $m/s^2$ for 10 min. After the separation, the unadsorbed superplasticizer concentration was measured using a total organic carbon analyser (TOC-L CSH/CSN, Shimadzu Corporation, Japan). The amount of adsorbed superplasticizer was calculated from the superplasticizer concentration in the initial solution and the liquid phase of the paste. To determine the specific surface area of the solid in the paste, the hydration time was fixed at 5 min and the temperature was 20°C (293 K). The hydration was stopped by acetone, and the solid phase was separated from the liquid by centrifuging at 8200 $m/s^2$ for 10 min. After the separation, the solid phase was dried under low pressure (0.01 MPa) for 24 hours, and the surface area of the solid was measured by the Brunauer–Emmett–Teller (BET) method with $N_2$ adsorption using and a surface area analyser (Gemini V2380, Micromeritics, USA). To determine the hydration reaction of the cement paste, the heat liberation rate of the cement paste was measured using a sandwich-type conduction calorimeter (SCM-12L, Tokyo Riko, Japan). The heat liberation rate was measured from 3 to 90 hours after hydration start at 20°C (293 K).

The range of the amount of KF in the experiments was 0-1.49 mass% of OPC. The amount of fluoride ions contained in 1.49 mass% KF of OPC is equal to the amount of fluoride ions contained in 1 mass% $CaF_2$ of OPC. If the calcination temperature is evaluated in which the free-lime ratio becomes 2 mass% of OPC after calcination, the amount of fluoride ions contained in 1.49 mass% KF of OPC brings a 100°C temperature decrease (Raina and Janakiraman 1998). The concentration of fluoride ions in cement paste from low-temperature calcination is not well-known but authors presume the extreme condition where all fluoride ions elute after the calcination with a 100°C temperature decrease. On the other hand, for the experiments using a fixed amount of $K_2SO_4$, the amount was 2.18 mass% of OPC. The amount of sulfate ions contained in 2.18 mass% $K_2SO_4$ of OPC is equal to the amount of sulfate ions contained in 1 mass% $SO_3$ of OPC. The amount of potassium contained in 2.18 mass% $K_2SO_4$ of OPC is 0.977 mass% of OPC and this amount is almost equal to the amount of potassium in the case where the amount of added KF is 1.49 mass% of OPC (K=1.00 mass% of OPC). Moreover, for the experiments using a fixed amount of KCl, the amount was 1.91 mass% of OPC. At this addition ratio, the amount of potassium is 1.00 mass% of OPC and this amount is equal to the amount of potassium in the case where the amount of added KF is 1.49 mass% of OPC (K=1.00 mass% of OPC).

## 3. Results and discussion

### 3.1 Influence of KF addition on fluidity

**Figure 2** shows the relationship between the shear stress and the shear speed of the cement paste with P-10. **Figure 3** shows the relationship between the shear stress and the shear speed of the cement paste with P-34. From the results of the shear stress and the shear speed in **Fig. 2** and **3**, the apparent viscosity and the yield stress were

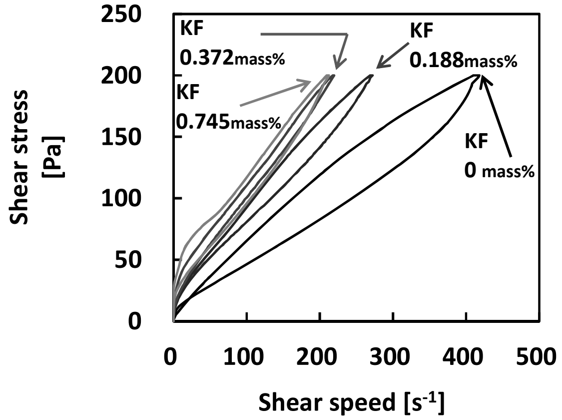

Fig. 2 Relationship between the shear stress and the shear speed of the cement paste with P-10.

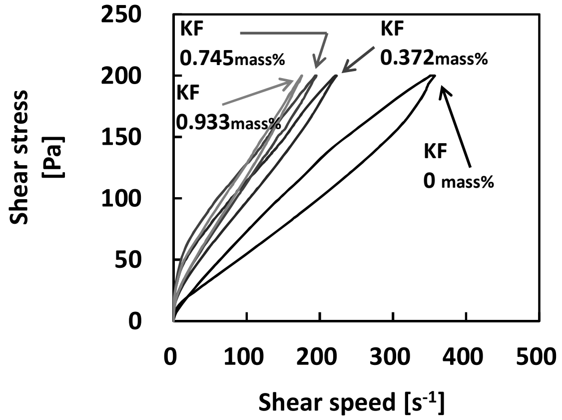

Fig. 3 Relationship between the shear stress and the shear speed of the cement paste with P-34.

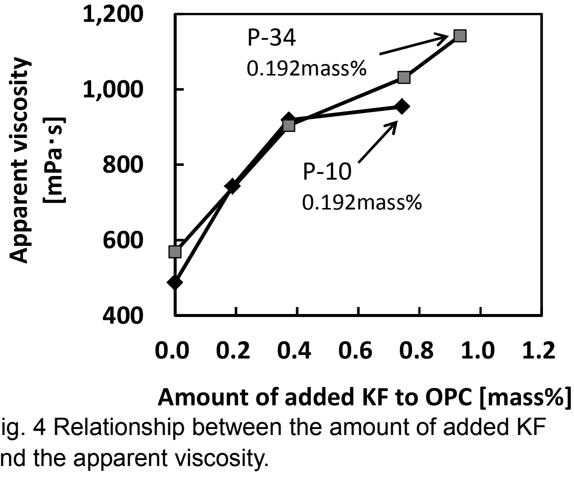

Fig. 4 Relationship between the amount of added KF and the apparent viscosity.

calculated. **Figure 4** shows the relationship between the amount of added KF and the apparent viscosity of the cement paste with polycarboxylate based superplasticizers. **Figure 5** shows the relationship between the amount of added KF and the yield stress of the cement paste with polycarboxylate based superplasticizers. The dosage of P-*n* was fixed at 0.192 mass% of OPC.

As previously reported (Matsuzawa *et al.* 2013, 2014), when the amount of added KF was increased, the apparent viscosity of the cement paste with P-*n* increased. Moreover, the yield stress of the cement paste with superplasticizer is increased by KF addition. Comparing P-10 with P-34, the increase in the degree of yield stress with P-10 by KF addition was larger than with P-34. Moreover, in the case of 0.93 mass% KF addition to P-10/OPC, the yield stress of cement paste was greater than 200 Pa. In contrast, in the case of 0.93 mass% KF addition to P-34/OPC, the yield stress of cement paste was 20 Pa. Therefore, the fluidity of cement paste with the polycarboxylate based superplasticizer with more functional groups (P-10) was more susceptive to KF addition. This result is different from the result of $CaCO_3$, where it has been reported that the fluidity of $CaCO_3$ paste containing the polycarboxylate based superplasticizer with more functional groups is less susceptive to inorganic ion addition (Atarashi *et al.* 2004; Sakai *et al.* 2003).

### 3.2 Influence of KF addition on the amount of adsorbed superplasticizer

**Figure 6** shows the relationship between the amount of added KF and the amount of P-*n* adsorbed per unit mass solid. **Figure 7** shows the relationship between the amount of added KF and the amount of P-10 adsorbed per unit area. The dosage of P-*n* was fixed at 0.192 mass% of OPC.

When the amount of added KF was increased, the amount of adsorbed P-*n* increased. In particular, when the amount of added KF was 1.49 mass% of OPC, the amount of adsorbed P-10 was 92% of the dosage of P-10. Although the amount of adsorbed P-*n* increased with KF addition, the fluidity of the paste with P-*n* decreased with KF addition, as shown in **Figs. 4** and **5**. This result is also different from the result of $CaCO_3$, where the amount of adsorbed superplasticizer was decreased by the adsorption hindrance of inorganic ion addition (Sakai *et al.* 2001). The adsorption hindrance mechanism cannot explain the decrease in fluidity with KF addition to cement paste with P-10. The results of the fluidity and the amount of adsorbed superplasticizer suggest other mechanisms influence the fluidity. Comparing P-10 with P-34, the amount of adsorbed P-10 was larger than the amount of adsorbed P-34. Authors suggest that the difference of adsorbed amount relates to the number of functional groups in the superplasticizer. It is supposed that P-10 has stronger adsorption ability than P-34 because P-10 has more functional groups than P-34.

### 3.3 Influence of KF addition on the BET specific surface area

**Figure 8** shows the relationship between the amount of added KF and the BET specific surface area of the solid in the paste with superplasticizers. The dosage of P-10 was fixed at 0.192 mass% of OPC.

When the amount of added KF was increased, the specific surface area increased. Authors suggest that the

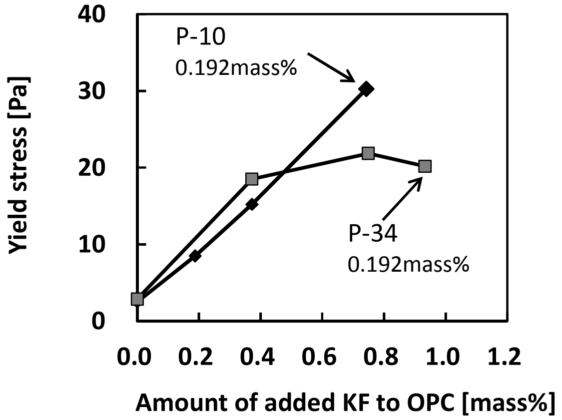

Fig. 5 Relationship between the amount of added KF and the yield stress.

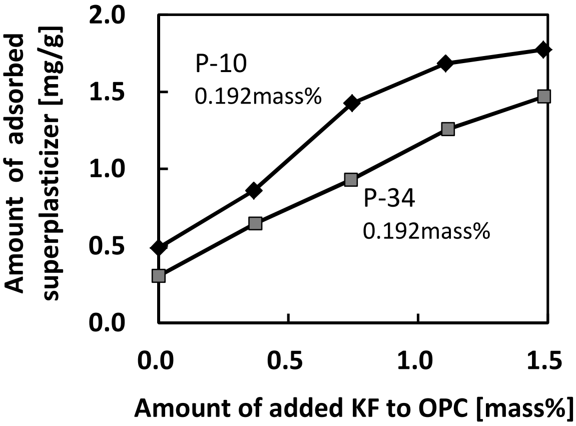

Fig. 6 Relationship between the amount of added KF and the amount of adsorbed P-*n* per unit mass solid.

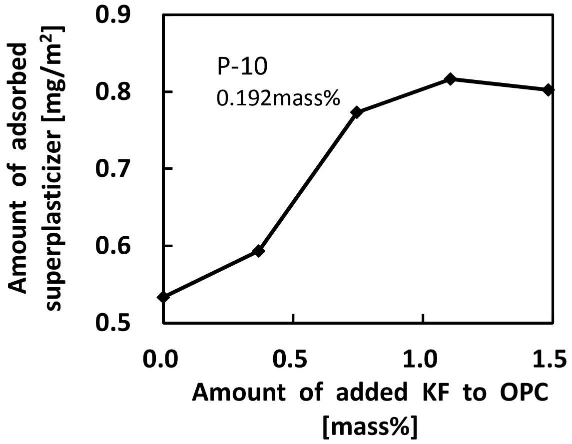

Fig. 7 Relationship between the amount of added KF and the amount of adsorbed P-10 per unit area.

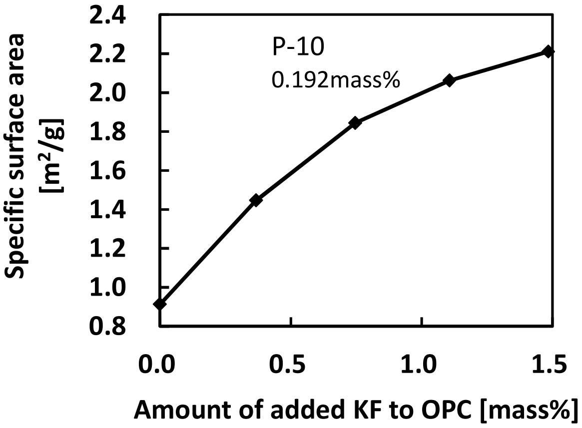

Fig. 8 Relationship between the amount of added KF and the specific surface area of the solid in the paste.

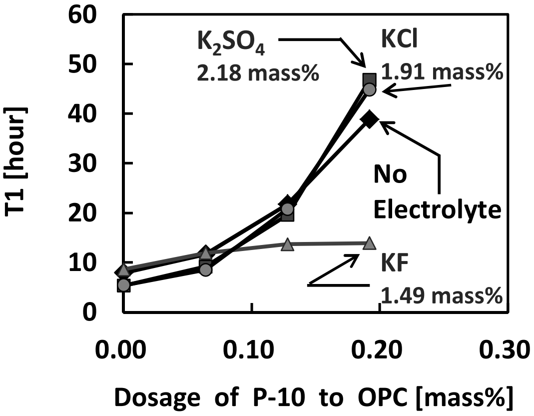

Fig. 9 Relation between the dosage of P-10 and T1.

cause of the increase of specific surface area is some types of fine particles generation by the reaction regarding the added fluoride ions. It is supposed that the increase in the amount of adsorbed superplasticizers is related to the cause of the increase of specific surface area. The decrease in fluidity and the increase in the amount of adsorbed superplasticizers on the solid with KF addition suggest that superplasticizers preferentially adsorbed to the fine particles generated by KF addition, resulting in the decrease of the amount of adsorbed superplasticizers on the cement particles and the fluidity decrease of cement paste.

This preferential adsorption mechanism can explain the difference in the decrease of fluidity with KF addition. It is suggested that P-10 more preferentially adsorbed to the fine particles than P-34 because P-10 has more functional groups than P-34. Authors can consider that the stronger adsorption ability of P-10 than P-34 resulted in the stronger susceptibility of P-10 to KF addition.

### 3.4 Influence of P-10 addition on the hydration of cement paste

**Figure 9** shows the relationship between the dosage of P-10 and the time in which the heat liberation rate of cement paste was largest (T1).

In the case of no electrolytes addition, when the dosage of P-10 was increased, T1 increased and the hydration reaction was retarded. Additionally, in the case of 2.18 mass% $K_2SO_4$ addition to OPC (=0.977 mass% potassium addition to OPC), T1 increased by P-10 addition. Moreover, in the case of 1.91 mass% KCl addition to OPC (=1.00 mass% potassium addition to OPC), T1 increased by P-10 addition.

In contrast, in the case of 1.49 mass% KF addition to OPC (=1.00 mass% potassium addition to OPC), when the dosage of P-10 was increased, the hydration reaction was not retarded.

The influence of P-10 addition on T1 in the case with $K_2SO_4$ and KCl addition was different from the case with KF addition. This suggests that the cause of the hydration reaction not being retarded by P-10 addition was not potassium ions addition but fluoride ions addition in the case of KF addition. These results also suggest that P-10 preferentially adsorbed to the fine particles generated by fluoride ions addition and the amount of P-10 adsorbed to cement particles decreased with fluoride ions addition.

## 4. Summary and conclusion

(1) When KF was added to the cement paste with polycarboxylate based superplasticizers, the apparent viscosity of the cement paste and the amount of adsorbed superplasticizer to the solid in the paste increased. This suggests that the adsorption hindrance mechanism by ions does not explain the viscosity increase with KF addition to cement paste.

(2) The fluidity of the cement paste with the polycarboxylate based superplasticizer with more functional groups was more susceptive to KF addition than the polycarboxylate based superplasticizer with less functional groups.

(3) In contrast to $CaCO_3$ paste in which the fluidity decrease can be explained by the adsorption hindrance mechanism by inorganic ions, it is suggested that the cause of the fluidity decrease in cement paste with KF addition was the preferential adsorption of superplasticizer to some types of fine particles generated by fluoride ion addition.

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### References

Atarashi, D., Sakai, E., Honda, S., Itoh, A. and Daimon, M., (2004). "Adsorption and dispersion mechanisms of comb-type superplasticizer containing grafted polyethylene oxide chains." *Journal of the Ceramic Society of Japan*, Supplement 112-1, PacRim5 Special Issue, 112(5), 1304-1307.

Gardeik, H. O., (1981). "Effect of the clinkering temperature on the specific energy consumption in cement clinker burning." *Zement Kalk Gips*, 34, 169-174.

Matsuzawa, K., Atarashi, D., Miyauchi, M. and Sakai, E., (2013). "*The 8th International Symposium on Cement & Concrete Proceedings* [CD-ROM]." Nanjing/China.

Matsuzawa, K., Atarashi, D., Miyauchi, M. and Sakai, E., (2014). "Influence of sulfate ion and fluoride ion on the fluidity of cement paste with polycarboxylate based superplasticizer having different molecular structures." *Cement Science and Concrete Technology*, Japan Cement Association, 67, 59-64. (in Japanease)

Raina, K. and Janakiraman, L. K., (1998). "Use of mineralizer in black meal process for improved clinkerization and conservation of energy." *Cement and Concrete Research*, 28, 1093-1099.

Sakai, E., Atarashi, D., Kawakami, A. and Daimon, M., (2003). "Influence of molecular structure of comb-type superplasticizers and Inorganic Electrolytes on the Dispersion Mechanisms of Limestone poder." *ACI SP-217*, 381-392.

Sakai, E., Kawakami, A. and Daimon, M., (2001). "Dispersion mechanisms of comb-type superplasticizers containing grafted poly(ethylene oxide) chains." *Polymerization Processes and Polymer Materials* II, WILEY-VCH, Macromol. Symp., 175, 367-376.

Sakai, E., Kawakami, A., Hamamoto, H., Honda, S., Itoh, A. and Daimon, M., (2000). "Influence of various types of inorganic salts on dispersion mechanisms of comb-type polymer containing graft polyethylene oxides chains." *Journal of the Cement Society of Japan,* 108(10), 904-908. (in Japanese)

Yoshikawa, T., (2011). "Low-temperature sintering technology for cement clinker using mineralizers and fluxes." *Journal of Research of the Tiheiyo Cement Corporation*, 161, 66-73. (in Japanese)