Effects of Chemical Admixtures on the Silicate Structure of Hydrated Portland Cement

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1. Introduction

Much has been studied on the effects of chemical admixture for concrete upon hydration reactions. The mechanisms are often described in terms of fluidity, adsorption characteristics and interactions between chemical admixtures, calcium ion and hydration products such as aluminates [1-2].

The authors have reported a study of changes in silicate structure of hydraulic binders, such as ordinary portland cement (OPC) and pulverized blast furnace slag, during hydration and carbonation using trimethylsilylation technique[3-4].

In this study, high-range water reducing agent of polycarboxylic acid type (PC) and β-naphthalenesulfonic acid type (NS) are studied in terms of mechanisms of their influences on silicate structure of hydrated cement.

2. Experiments

2.1 Materials used

The OPC used in this experiment was a commercial product. Type of the chemical admixture used, polycarboxylic acid type (PC) and β-naphthalenesulfonic acid type (NS), were also commercially available products.

2.2 Test methods

(1) Hydration of OPC with chemical admixture

Aqueous solution of the chemical admixtures was prepared at three levels of concentrations: 5.00 grams per liter, 2.50 gram per liter and 1.25 gram per liter for each type of the admixture. A 5.00 grams of OPC was introduced to each 100 ml solution and then stirred to proceed a powder phase hydration. After the hydration for a specified time, the hydrated specimens were subjected to a suction filtration, and the separated solid component was dehydrated and dried with methanol and acetone.

(2) Determination of silicate structure with TMS method

The hydrated OPC specimen was subjected to TMS-derivatization developed by Suginohara [5-6]. The treated specimens were introduced to a gas chromatography of Shimazu GC-14B and fractions of the type of silicate anion, from monomer to hexamer, were obtained. Peak areas of the gas chromatogram were used to determine each mass.

(3) Determination of total organic carbon (TOC) content in aqueous solution

Liquid phases separated in the process (1) were used to determine total

organic carbon content in the liquid phase using Shimazu TOC-V

(4) Determination of calcium ion concentration in aqueous solution

Effects of chemical admixture on the calcium ion in the liquid phase were examined. The liquid phase separated in the process (1), or calcium hydroxide saturated solution instead, was subjected to a determination of calcium ion concentration using ion chromatography Shimazu LC-10A.

3. Result and discussion

3.1 Influences of chemical admixture on hydration heat liberation rate of OPC

With an increase in concentration of PC type chemical admixture, a slight secondary exothermal peak was observed during the measurement of hydration heat liberation rate with the conduction calorimeter as shown in Fig.1. However for NS type chemical admixture, a delay in the secondary exothermal peak was observed at high concentration of 5.00 grams per liter while there was almost no difference in heat liberation profile with that of single OPC at low concentrations as shown in Fig. 2.

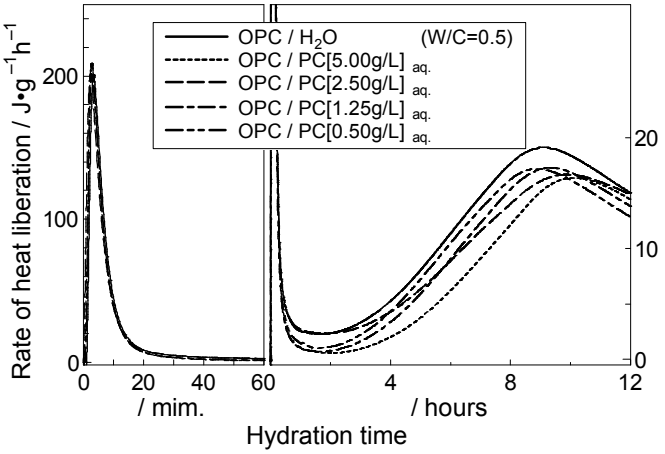

Figure 1. Rate of heat liberation of OPC added PC solutions.

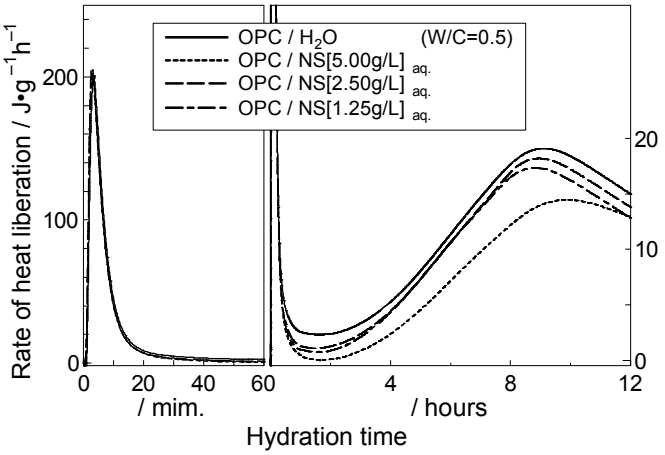

Figure 2. Rate of heat liberation of OPC added NS solutions.

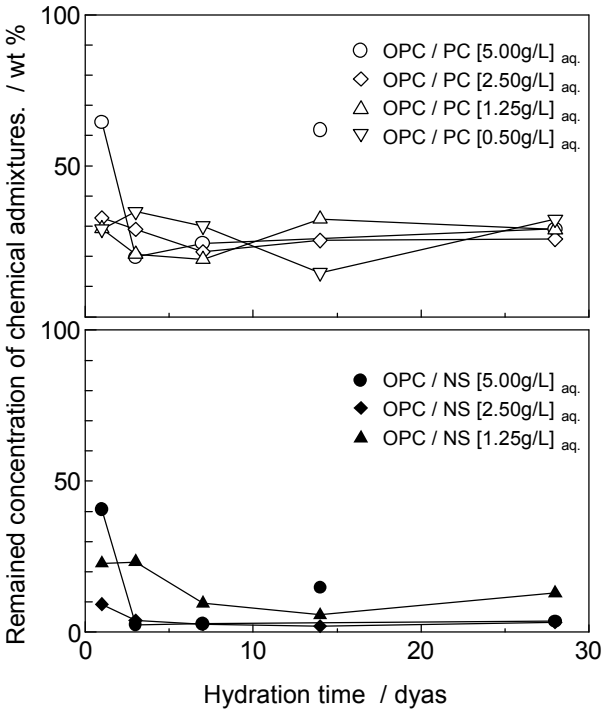

Figure 3. Remained concentration of chemical admixtures in liquid phases.

3.2 Adsorption capability of chemical admixture assessed by residual TOC

TOC was determined for samples of liquid phase separated after hydration. As shown in Fig. 3, a major part of the both organic admixtures was adsorbed on the solid phase, i.e. cement particles, except for a case of the highest dosage (5.00 grams per liter) at an age of 1-day. Particularly in NS type, TOC was completely absent in the liquid phase while approximately 20 percent of PC type was remained. Because the TOC concentration in the liquid phase showed almost no change after a period immediately after mixing, 1-day for major cases and at most 3-day for the highest dosage, it results that adsorption of the chemical admixture on OPC surfaces is completed in a short period after mixing and concentration of the chemical admixture shows almost no change subsequently. The dispersion mechanism of NS type chemical admixture is attributed to electrostatic repulsion forces between electric double layers originated from the adsorption of the admixture molecules while that of PC type admixture is attributed to steric effects over the long distance from the cement particle surfaces thanks to the graft chains of admixture molecules.

Difference in the residual TOC concentration in the liquid phase may suggest that PC type chemical admixture remains both in solid and liquid phase and the latter may contribute to a further dispersion of cement particles by its steric effect. The residual PC type chemical admixture may also contribute to fluidity of the liquid phase resulting in higher fluidity of PC type solution than that of NS type.

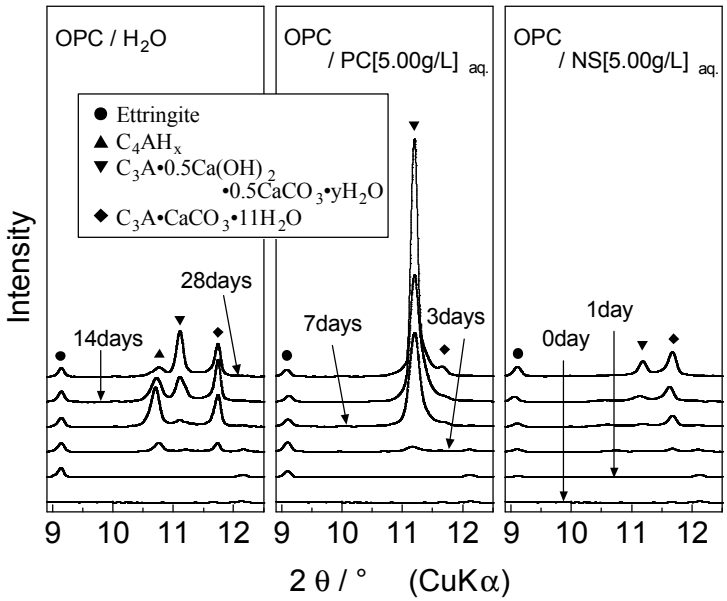

Figure 4. XRD patterns of OPC added PC or NS solutions.

3.3 Changes in mineral phase by chemical admixture

An X-ray diffraction corresponding to the (001) plane of $Ca(OH)_2$ was observed in solutions of single OPC and both types of chemical admixture with the development of hydration. However in the latter case, hydration seemed to be retarded by the chemical admixtures because no distinct diffraction peak of $Ca(OH)_2$ was detected at the age of 1-day, except for a solution with PC type of 0.50 grams per liter, in contrast to single OPC solution that exhibited the diffraction peak at the age of 1-day. In the later ages, the diffraction intensity differs greatly according to the type of chemical admixture. NS type showed lower intensity than OPC while that of PC type, particularly at high dosage, was higher than that of OPC. XRD patterns of ettringite and other hydrates by solution with a concentration of 5.00 grams per liter are shown in Fig. 4

3.4 Influences of chemical admixture on silicate structure

Chain length distribution of silicate anions of OPC hydrated in an aqueous solution of PC type chemical admixture was determined with TMS method and is shown in Figs.5-7. At early stage of hydration up to 7-day, monomers decreased and dimmer increased among silicate anions but significant influence of the type of chemical admixture was confirmed as shown in Figs. 5. In PC type solutions with higher dosages of 5.00 and 2.50 grams per liter, changes in silicate anion polymerization was largely inhibited at the age of 1-day, while in those with lower dosages of 1.25 and 0.50 grams per liter, no such influence was observed. Also in NS type solutions, nearly the same tendency was observed but the polymerization of silicate anion was more or less inhibited over the entire range of dosage when compared with the control solution.

Changes in chain length distribution of silicate anions at later stages are shown in Fig. 6. At the age of 28-day, polymerization of silicate anions in NS type solutions generally developed more significantly than

that of single OPC and than that with lower dosages.

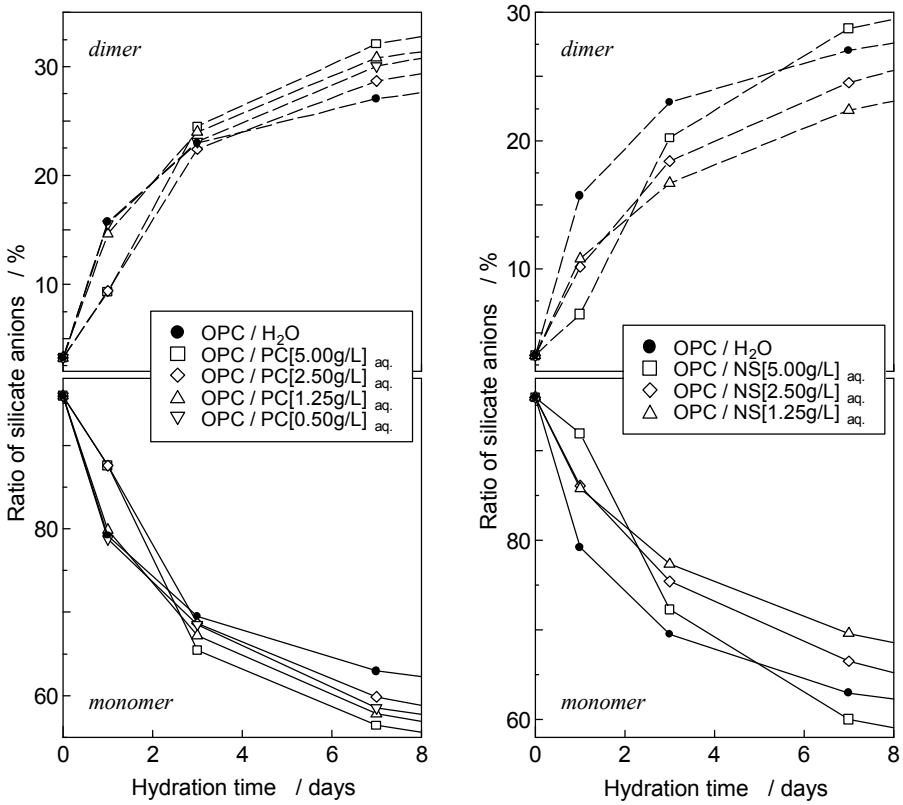

Figure 5. Chain length distribution of *monomer* and *dimer* on hydration of OPC with PC or NS solutions. [early stage (1-7days)]

The polymerization developed at higher dosages of both NS and PC solutions. However, it is at the highest dosage of 5.00 grams per liter that the polymerization developed more than that of single OPC, and in other dosages, the development was equal or less compared to that in single OPC solution. Overall effects of chemical admixture on the polymerization of silicate anion were retardative particularly from monomer to dimmer at early stage of hydration. This has been attributed to, as reported in the previous studies, the adsorption of chemical admixture on the OPC surfaces. However, the retardation effect at early stage of hydration does not work out at later stages where polymerization developed more significantly in solutions of high dosage than in single OPC solution. This could lead to another mechanism other than that of adsorption-retardation.

3.5 Influences of chemical admixture on Ca^{2+} ion concentration in aqueous solution

A possible mechanism other than adsorption-retardation is the formation of a metastable chelate between molecules of the chemical admixture and a metal ion eluted form the OPC surfaces. Supposing that a cation in the aqueous solution, particularly Ca^{2+}, can form a complex with molecules of the chemical admixture and affect the hydration of OPC, the aqueous solution separated from the solid phase as described in 2.2 (1) was subjected to ion chromatography (IC) to determine Ca^{2+}

concentrations. However in the OPC-based solutions, Ca^{2+} ions eluted in the solution may be consumed during the formation of calcium hydroxide, ettringite, CSH gels and other hydrates resulting in a variation of concentration.

Thus an imitated suspension consisting of $Ca(OH)_2$ and the chemical admixtures was prepared and the Ca^{2+} concentrations was determined as shown in Figs. 7. It was confirmed that the Ca^{2+} ion concentration varied, though slightly, with the dosage of the chemical admixture. The Ca^{2+} ion concentration increased with an increase in concentration of the chemical admixture particularly in a solution with high dosage.

Taking above findings into account, effects of chemical admixture, particularly at high dosage, on the hydra- tion reactions of OPC can be discussed: the chemical admixture may promote the polymerization of silicate anion by influencing the Ca^{2+} ion elution at later stage of hydration, while it inhibits hydration by adsorption on the OPC surfaces at early stage. The molecules of the chemical admixture may probably form a metastable complex with Ca^{2+} ion resulting in a decrease of Ca^{2+} ion in the solid phase. When only silicate phases are considered, this may lead to formation of a CSH gel with low CaO/SiO_2 ratio and hence the silicate chain length distribution shows a shift to the longer side.

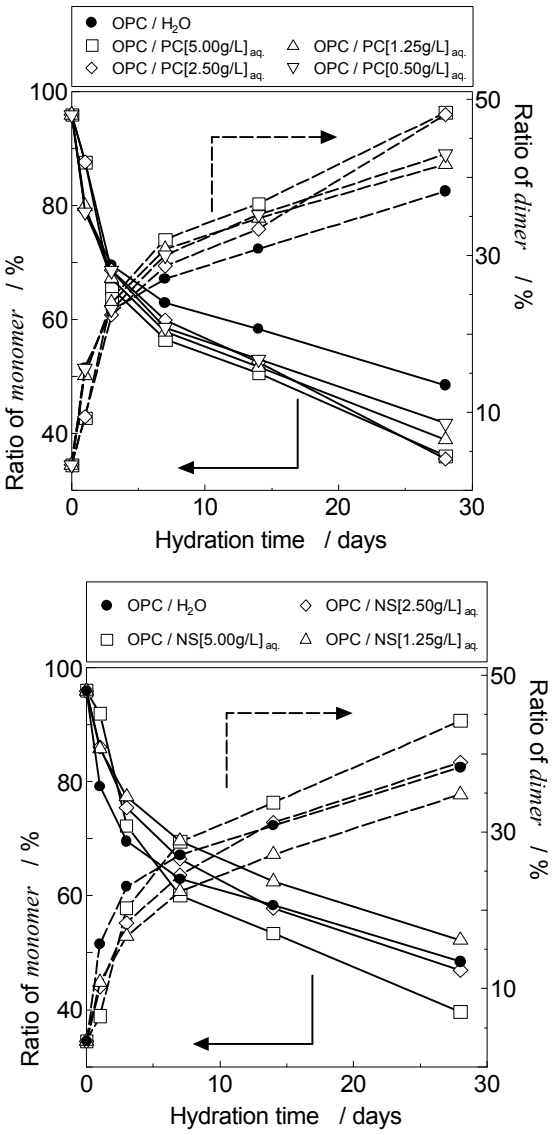

Figure 6. Chain length distribution of *monomer* and *dimer* on hydration of OPC with PC or NS solutions. [later stage (--28days)]

The polymerization of silicate chains may influence the development of strength of mortar and concrete. The influence of chemical admixture on strength has been attributed to a water-reducing effect of the admixture but the results in this study may imply that the chemical admixture could also contribute to the strength development in terms of silicate anion polymerization.

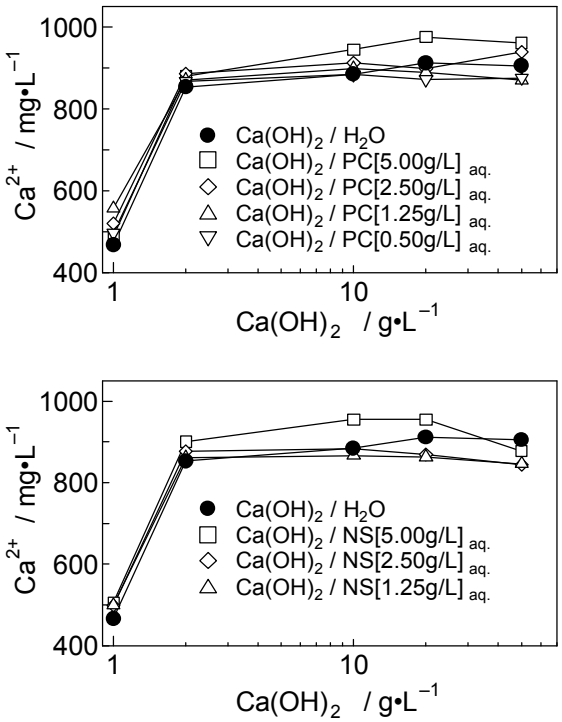

Figure 7. Ca^{2+} concentration in PC or NS solutions dispersed $Ca(OH)_2$.

4. Conclusions

Influences of two types of chemical admixture, NS and PC type, on the hydration of OPC were studied and the following conclusions are derived.

(1) Adsorption behavior of chemical admixtures on the OPC surfaces differed from the type: NS type was entirely consumed by adsorption on the OPC while PC type remained in the liquid phase contributing to a high fluidity of mixes with PC type.

(2) Addition of chemical admixtures greatly influenced on the hydration of OPC at early ages: it showed a tendency of inhibiting the hydration as the dosage increased. Polymerization of silicate anions was retarded except for a case of low dosage of PC type.

(3) The chemical admixture may promote the polymerization of silicate anion by influencing the Ca^{2+} ion elution at later stage of hydration, while it inhibits hydration by adsorption on the OPC surfaces at early stage. The molecules of the chemical admixture may probably form a metastable complex with Ca^{2+} ion resulting in a decrease of Ca^{2+} ion in the solid phase. When only silicate phases are considered, this may lead to formation of a CSH gel with low CaO/SiO_2.

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