Effect of Silicate Ions on the Hydration of $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ with Gypsum

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ABSTRACT

$Na_2Si_2O_5$ added to the solution affects the hydration of $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ with calcium sulfate. The reaction between $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ and $CaSO_4 \cdot 2H_2O$ decrease with increasing amount of $Na_2Si_2O_5$ in solution, owing to low hydraulic reactivity of $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ by the adsorption of silicate ions on the surface of $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ particles. The dissolution rate of $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ particles deceased with the increase of the concentration of silicate ion in solution. When the $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ particles was hydrated in gypsum - $Na_2Si_2O_5$ solution, the hydration was retarded and the rate could not discriminate between formation of ettringite and that of monosulfate, and it stopped in high concentration of silicate ions. However, silicate ion did not any effect on the dissolution rate of gypsum.

Key words : Calcium alumino-ferrite, Hydration reaction, Sodium silicate

1. Introduction

Portland cement consists mainly of alite, belite, aluminate and aluminoferrite.[1] The aluminate and aluminoferrite phases are often referred to as the interstitial phases, and are known to exhibit a broad range of compositions in Portland cement.[2] The aluminoferrite phase also exists as a solid solution, which varies from C_6A_2F to C_6AF_2 in composition. In some cases, the typical composition of the ferrite phase was found to be $Ca_2AlFe_{0.6} Mg_{0.2}Si_{0.15}Ti_{0.05}O_5$ in Portland cement.[3] The content of the ferrite phase in ordinary Portland cement ranges from 5 mass% to 10 mass% with an average of 8 mass%.[4] The ferrite phase is commonly expressed in terms of its ideal composition : $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ (After here, C_4AF). In some cases, the typical composition of the ferrite phase was found to be $Ca_2AlFe_{0.6} Mg_{0.2}Si_{0.15}Ti_{0.05}O_5$ in Portland cement.[3] It has been reported that the hydration products of C_4AF comprise the cubic compound $Ca_3Al_2(OH)_{12}$ called hydrogarnet, which is probably the only stable hydrated calcium aluminate similar to that in the $CaO-Al_2O_3-H_2O$ system above $30°C$.[4,5] It is formed slowly at room temperature by conversion from metastable mono-, di-, and tetracalcium aluminate hydrates, probably by a 'through-solution mechanism' involving the crystallization of $Ca_3Al_2(OH)_{12}$ from solution.[4,5] This transformation process is promoted by increasing temperature or pH. Sersale[6] reported the transformation process of the crystalline habits of calcium aluminum hydroxide under the influence of various factors including temperature, $CaO : Al_2O_3$ ratio in the mother liquid, and pH, etc.

Hydration of $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ in the presence of calcium sulfate result in the initial formation of ettringite. As completely consuming the gypsum, ettringite converts to monosulfate, and unhydrated C_4AF reacts with the liberated calcium sulfate to form additional monosulfate. And also, the hydration to form additional monosulfate probably involves the formation and subsequent conversion of calcium aluminum hydrates. Thereby, the heat evolution curves of these hydrations are divided into two distinct stages of heat evolution[7,8] on the hydration of C_4AF of calcium sulfate. However, the hydration of C_4AF in Portland cement has not yet been clarified. Although C_4AF reacts very rapidly with water, the ferrite phase in Portland cement has low hydraulic reactivity. It is considered that the hydration reaction of C_4AF in Portland cement is affected by other ions, i.e., silicate ions etc. We have focused on silicate ion as the factor having effect on the hydration of C_4AF, because the high concentration of silicate ions from the hydration of calcium silicate compounds is shown during the hydration of Portland cement.

In this research, we discussed the hydration behavior of C_4AF with gypsum in solution with high a concentration of silicate ions.

2. Experimental Procedure

The synthesized C_4AF, ground to powder form with specific surface area of 0.1 and 0.3 $m^2 \cdot g^{-1}$ was blended with calcium sulfate hydrate; $CaSO_4 \cdot 2H_2O$. The blended ratio

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of C$_4$AF/gypsum was 9/1 for mass%. The solution with silicate ions was prepared by using reagent-grade Na$_2$Si$_2$O$_5$, supplied by Wako Chemicals Co., Ltd. The addition amount of Na$_2$Si$_2$O$_5$ was expressed as mass% of the solution. The mixture of which C$_4$AF with 0.1 m^2 · g^{-1} was mixed with gypsum (hereafter we call them merely mixture), was hydrated in distilled water and in pre-dissolved Na$_2$Si$_2$O$_5$ solution. The hydration rates of mixtures as a function of time were measured by using conduction calorimeter. The ratio of W/C (water/Mixture) in the experiment of conduction calorimeter was 1. After the measurement of heat evolution, the hydration of pastes was stopped with acetone, and then, the hydrates formed during the measurement of conduction calorimeter were identified by X-ray diffractometry with graphite-monochromatic Cu Kα radiation.

We ran three series experiments of liquid phase analyses. The first experiment was that concentration of ions was measured in various liquid of slurries (W/C = 10) of which mixture was hydrated in distilled water and in Na$_2$Si$_2$O$_5$ solutions various concentrations. In this analysis, the concentrations of Ca and Al ions were analyzed by using atomic absorption analyzer (AAS). And XRD analysis of the solid phase filtered from slurries was carried out to identify the hydrates at certain hydration time.

In the second series, the solubility of CaSO$_4$ · 2H$_2$O was independently investigated in various Na$_2$Si$_2$O$_5$ solutions. The concentration of sulfate ions was determined by weighing the BaSO$_4$ precipitated, when BaCl$_2$ was added to liquid phase of hydration.

In the third series, when the C$_4$AF having 3000 cm^2 · g^{-1} of surface area was hydrated in the CaSO$_4$-Na$_2$Si$_2$O$_5$ saturated solution, the behaviors of ion concentrations were observed. From this research, the hydration behavior of C$_4$AF in Portland cement will be discussed. CaSO$_4$-Na$_2$Si$_2$O$_5$ saturated solution was prepared by adding calcium sulfate hydrate and sodium silicate to freshly distilled water, stirring for 24 h in a sealed poly-ethylene bottle, and filtering through a 0.2 μm filter to remove solid. The initial ions concentrations of CaSO$_4$-Na$_2$Si$_2$O$_5$ saturated solution are shown in Table 1. This experiment was carried out with stirring at 25 ± 1°C using a solution-to-cement weight ration of 20. C$_4$AF was the only solid initially present. Hydrates formed during C$_4$AF hydration for 24 h in this solution were observed by using X-ray diffractometry and SEM.

3. Results and Discussion
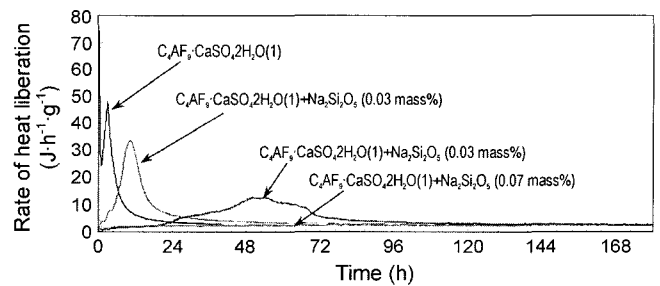
Fig. 1 shows the heat evolution rates of mixtures of C$_4$AF

Table 1. Initial Solution Compositions of Solution

	CaSO$_4$-Na$_2$Si$_2$O$_5$ solution (mmol · dm^{-3})
[Ca^{2+}]	7.5
[SO$_4$$^{2-}$]	15.5
[Si^{4+}]	4.2

Fig. 1. The rates of heat evolution when C$_4$AF is hydrated with calcium sulfate in distilled water or in various Na$_2$Si$_2$O$_5$ solution.

and calcium sulfate hydrated in distilled water and in Na$_2$Si$_2$O$_5$ solution of various concentrations. When mixture was hydrated in distilled water, the rate curves showed the presence of first peak and second peak within 12 h of hydration, while when mixture was hydrated in Na$_2$Si$_2$O$_5$ solution, only one peak was presented. From these results, the formation of ettringite and conversion from ettringite to monosulfate could be deduced when mixture hydrated in distilled water, because two distinct peaks were shown in the paste.

However, when mixture was hydrated in Na$_2$Si$_2$O$_5$ solution, the rate could not discriminate between formation of ettringite and that of monosulfate. It was shown that the rate of hydration was delayed by the increasing amount of Na$_2$Si$_2$O$_5$ in solution. Particularly, the hydration of mixture did not occur in 0.07 mass% Na$_2$Si$_2$O$_5$ solution.

Fig. 2 shows X-ray diffraction of hydrates after the measurement by calorimeter; 7 d of hydration. When mixture was hydrated in distilled water and in 0.03 and 0.05 mass% Na$_2$Si$_2$O$_5$ solution, the formed amount of hydrates differed from each other, that is, monosulfate (Ca$_4$Al$_2$(OH)$_{12}$ · (SO)$_4$ ·
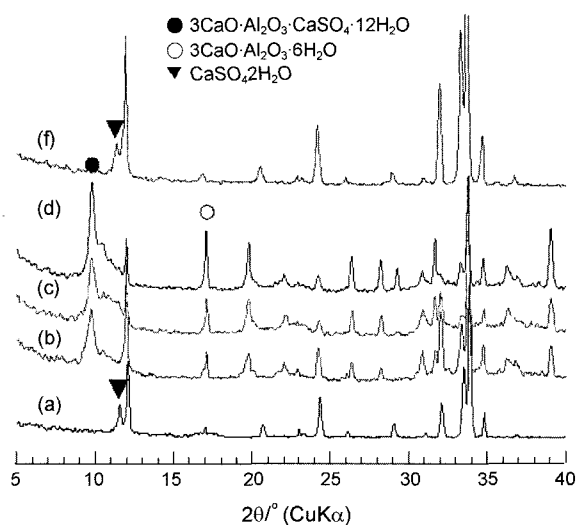
Fig. 2. XRD patterns of mixture hydrated mixture : (a) in 0.07 mass% Na$_2$Si$_2$O$_5$ solution, (b) in 0.05 mass% Na$_2$Si$_2$O$_5$ solution, (c) in 0.03 mass% Na$_2$Si$_2$O$_5$ solution, (d) in H$_2$O after 7 d, and (f) unhydrated mixture.
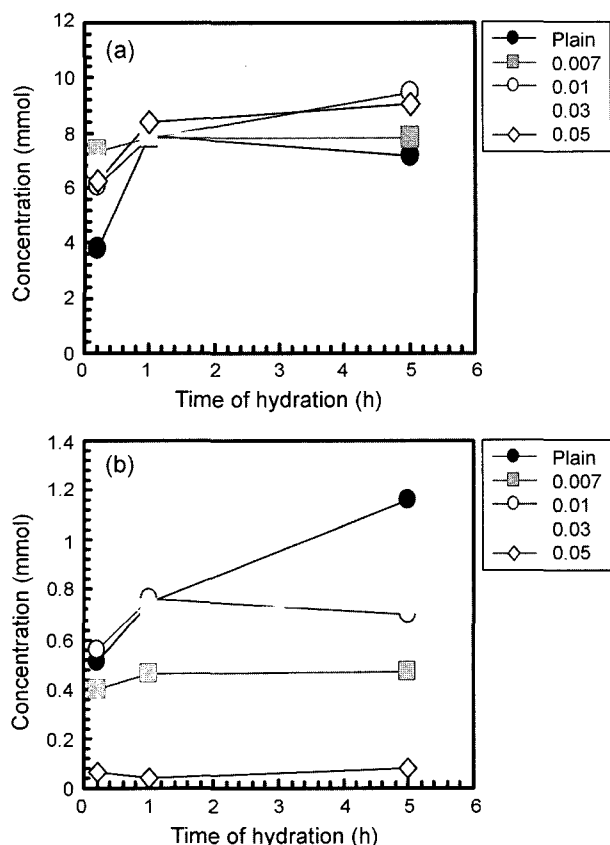
Fig. 3. Change in concentration of (a) Ca ions and (b) Al ions during C_4AF hydration with gypsum in various solution.

Fig. 4. The solubility of $CaSO_4 \cdot 2H_2O$ in $Na_2Si_2O_5$ solution.
—●— $CaSO_4 \cdot 2H_2O$ in water
--○-- $CaSO_4 \cdot 2H_2O$ in 0.05 mass% $Na_2Si_2O_5$

$6H_2O$), hydrogarnet ($4CaO \cdot Al_2O_3 \cdot 6H_2O$) and calcium aluminum hydrates ($4CaO \cdot Al_2O_3 \cdot nH_2O$, 10.5~11.5θ/°), etc. But no hydration products appeared in the paste of mixture hydrated in 0.07 mass% $Na_2Si_2O_5$ solution. From above results, it was found that $Na_2Si_2O_5$ added had large effect on the hydration of C_4AF with gypsum.

Fig. 3(a) and (b) show the solubility of mixture in various solutions. The concentrations of Ca ions did not change with added $Na_2Si_2O_5$ (Fig. 3(a)), whereas the Al ion concentration falls significantly with increasing amount of added $Na_2Si_2O_5$ in solution (Fig. 3(b)). In the solution containing 0.05 mass% $Na_2Si_2O_5$, the concentration of Al ions becomes markedly low; under 0.1 mmol $\cdot$ dm^{-3}. From above results, the high concentration of Ca ions appeared in solution with high $Na_2Si_2O_5$ concentration as shown in Fig. 3(a). This contradicts that when C_4AF was independently hydrated in solution with high $Na_2Si_2O_5$ concentration, the concentration of Ca ions decrease, and approximately zero in 0.05 mass% $Na_2Si_2O_5$ solution as shown in Fig. 3(a).[9]

Fig. 4 shows the solubility of $CaSO_4 \cdot 2H_2O$ in $Na_2Si_2O_5$ solution. The solubility of $CaSO_4 \cdot 2H_2O$ was not almost affected by $Na_2Si_2O_5$ addition. Therefore, the high concentration of Ca ions in the slurry mixture hydrated in $Na_2Si_2O_5$ solution is due to the dissolution of $CaSO_4 \cdot 2H_2O$. Also, the reaction between C_4AF and $CaSO_4 \cdot 2H_2O$ is diffi-

cult to occur in $Na_2Si_2O_5$ solution owing to non-reactivity of C_4AF.

Fig. 5 shows the change in intensities of X-ray diffraction for unhydrated C_4AF, gypsum and monosulfate during mixture hydration in various solutions. As the consumption of unhydrated C_4AF and gypsum, the formation of monosulfate significantly increases in distilled water. However, the consumed amount of unhydrated C_4AF and gypsum in solution decreases, and the formation of monosulfate also decreases with $Na_2Si_2O_5$ in solution. When 0.05 mass% $Na_2Si_2O_5$ was added to hydration solution, the consumption of C_4AF and gypsum, and the formation of monosulfate did not occur in solution.

Fig. 6 indicates the change of concentrations of calcium ions and sulfate ions and amount of adsorption of silicate ions during C_4AF hydration in the $CaSO_4$-$Na_2Si_2O_5$ saturated solution. The concentration of Ca ions slightly decreased from 7.5 to 6 mmol $\cdot$ dm^{-3} within 3 – 4 h. After 5 h of hydration, the consumption of Ca ions reduced. The con-
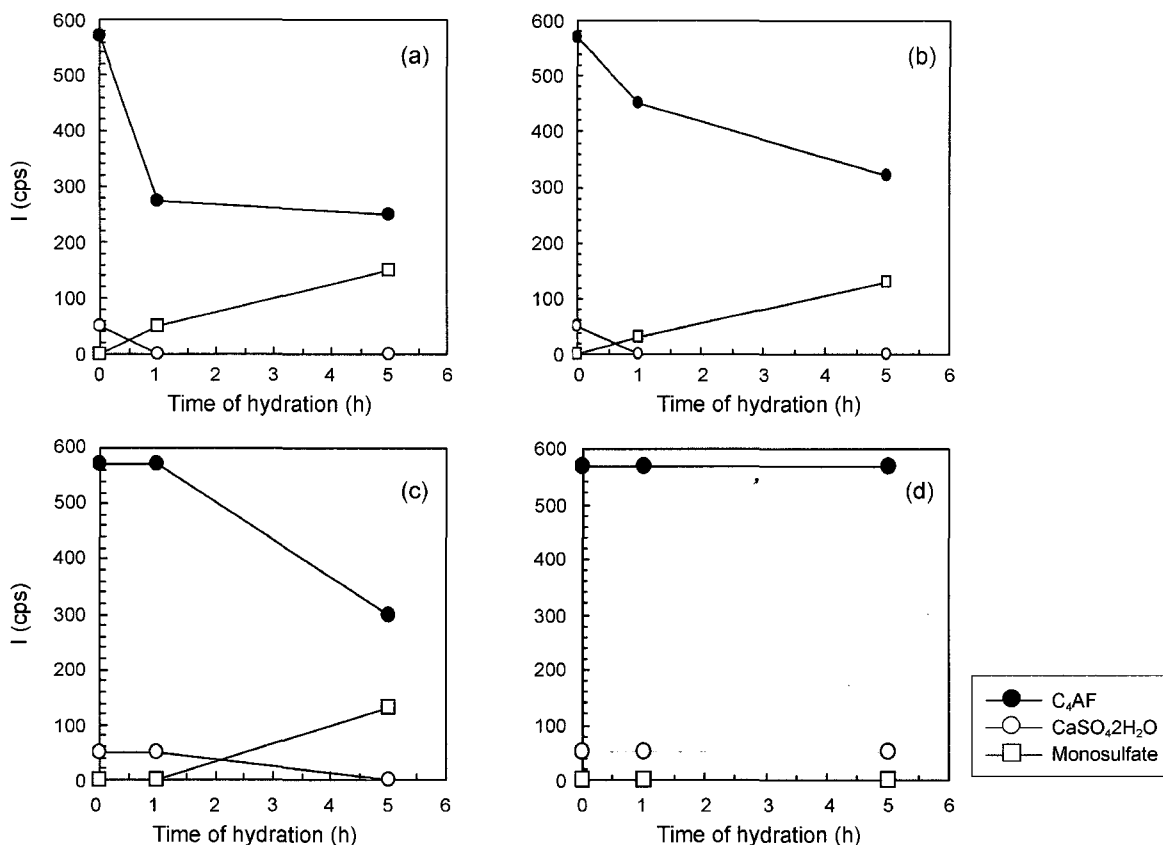
Fig. 5. X-ray diffraction intensity of solids felted from various slurries containing $Na_2Si_2O_5$ at prescribed time :
(a) in distilled water, (b) in 0.007 Na_2Si_2O solution, (c) in 0.01 Na_2Si_2O solution, and (d) in 0.05 Na_2Si_2O solution.

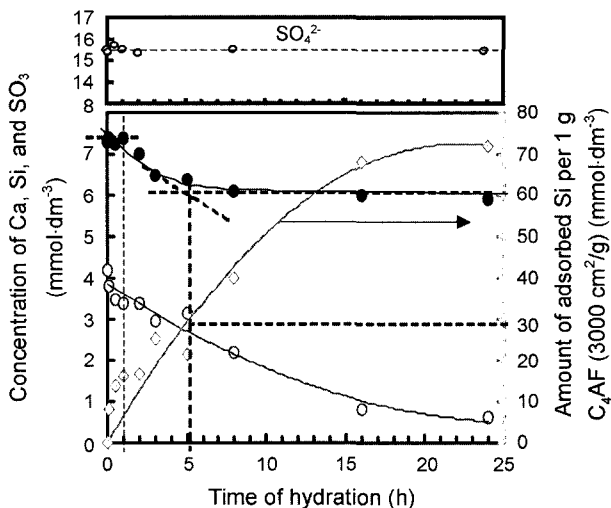**Fig. 6.** Change in the ionic concentrations of calcium, aluminum and silicate in solution when C_4AF was hydrated in $CaSO_4 · 2H_2O - Na_2Si_2O_5$ saturated solution.

Fig. 7. X-ray diffraction of C_4AF hydrated in $CaSO_4 · 2H_2O$ - $Na_2Si_2O_5$ saturated solution for 24 h.

centration of silicate ions also decreased in hydration time, due to the adsorption of silicate ions on the surface of C_4AF particles. The amount of silicate ions adsorbed on the surface of C_4AF particles with 3000 cm² · g⁻¹ reached approximately 30 mmol · dm⁻³ within 5 h. This amount presents
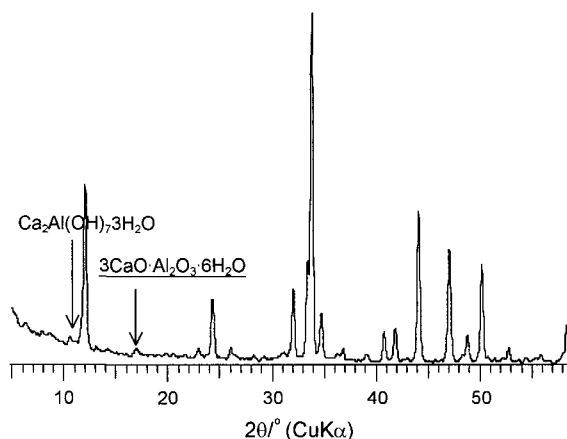
that of silicate ions adsorbed on the surface of C_4AF with 3000 cm² · g⁻¹ in the previous study.[9] The consumption rate of Ca ions in $CaSO_4$-$Na_2Si_2O_5$ saturated solution reduced from this time. After this time, the consumption of Ca ions is expected to occur by complexation with silicate ions in solution. The consumption of SO_4^{2-} ion did not almost appear in the solution.

Fig. 7 shows the X-ray diffraction of C_4AF hydrated in

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Fig. 8. SEM pictures of C_4AF hydrated in $CaSO_4 \cdot 2H_2O$ - $Na_2Si_2O_5$ saturated solution for 24 h : (a) surface where no hydrates formed, and (b) and (c) surface where hydrates formed.

$CaSO_4$-$Na_2Si_2O_5$ saturated solution for 24 h. There are not large differences from that of unhydrated C_4AF. However, although very small amount, calcium aluminate hydrates ($4CaO \cdot Al_2O_3 \cdot 6H_2O$, $17.2\theta f$ and $4CaO \cdot Al_2O_3 \cdot nH_2O$, 10.5 – $11.5\theta f$) were formed.

Fig. 8 presents the SEM picture of C_4AF particles hydrated in $CaSO_4$-$Na_2Si_2O_5$ saturated solution for 24 h. Hydrates were not shown in a large portion of C_4AF surface (Fig. 8(a)), but partially, the gel hydrates and card house were produced, but that amount was very little.

It is believed from above research that when sufficient silicate ions are adsorbed on the unhydrated C_4AF particles, the hydraulic reactivity of C_4AF particle with gypsum decreased remarkably. Therefore we believe that the low hydraulic reactivity of C_4AF in Portland cement is due to the adsorption of silicate ion, existing in hydration solution, on its surface.

4. Conclusions

The hydration of tetracalcium aluminoferrite was retarded by silicate ions in solution, and it stopped in high concentration of silicate ions, which can be explained the hydration of C_4AF in Portland cement that has low hydraulic reactivity by the high concentration of silicate ions. Silicate ion added in the solution affects the hydration of C_4AF with calcium sulfate, which is suppressed the reaction between C_4AF and $CaSO_4 \cdot 2H_2O$ due to the adsorption of silicate ions on the surface of C_4AF particles. From above discussion, it is concluded that the low hydraulic reactivity of C_4AF in Portland cement is due to the adsorption of silicate ion on its surface.

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