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Effects of crystallinity and silica content on the hydration kinetics of $12CaO \cdot 7Al_2O_3$

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Abstract

The effects of $12CaO_7 \cdot Al_2O_3$ crystallinity on the kinetics of hydration reaction were studied by measuring the heat liberated using a conduction calorimeter. The crystallinity of the sample was modified by changing the cooling rate of the sample after synthesis reaction. In addition, the effects of silica addition to $12CaO_7 \cdot Al_2O_3$ glass on kinetics were also investigated. The results indicated that the glass underwent a faster initial kinetic hydration reaction compared with that of crystalline calcium aluminate. The addition of silica, on the other hand, decreased the reaction rates. The results are discussed in terms of the solvation rate of the calcium aluminate phases and the precipitation of the hydrate phases.

Keywords: $12CaO_7 \cdot Al_2O_3$; Hydration reaction kinetics; Cement; Glass

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1. Introduction

Currently, Portland cement is an integral part of many of the buildings and constructions that constitute our daily environment. It is hard to imagine a world without cement, as it is not just the best solution but the only solution in many cases. Cement is, therefore, largely indispensable for sustaining the current development of industrial society.

The setting of Portland cement is a result of the hydration reaction between the cementitious phases and water. The hydration reaction of Portland cement, therefore, is its most important feature since it determines both the mechanical properties and the setting time. There have been many studies on the kinetics of hydration reaction. The hydration rate, in general, is affected by the morphology and size of the particles, the water to cement ratio, the curing temperature and the chemical compositions of the cement. Kondo et al. [1] showed that powders with a narrow particle size distribution increase the hydration rate. They attributed the increase to the enhanced mass transfer rate through the pores of powders with a narrow particle size distribution. Kondo and Daimon [2] studied the effect of curing temperature on the hydration reaction of $3CaO \cdot SiO_2$ during the first stage. The rate of reaction was increased with the increase of the curing temperature, since the reaction is a thermally activated process.

Many studies on the hydration behavior of calcium aluminate phase, C_3A, $C_{12}A_7$, C_4AF, CA, CA_2 etc, have been also conducted. Tsumura and Kawachi [3] reported that the hydration rate of C_3A is accelerated as the water to cement ratio is increased, but that that of C_4AF at the first stage was decreased with the increase of the water to cement ratio. Uchida et al. [4] pointed out in their research that the increase in the molar ratio of CaO/Al_2O_3 caused the amount of heat generated at the first stage of the hydration

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reaction to increase. You et al. [5,6] reported that the hydration rate of C_4AF was affected by the adsorption of silicate ion from the hydration solution, and that the retardation or stopping of the hydration was due to the precipitated layer generated from the adsorption of silicate ion on the surface of the C_4AF. Abdel Razig et al. [7] also reported that glassy $C_{12}A_7$ was less reactive than the crystalline $C_{12}A_7$.

It is believed that the degree of crystallinity and impure contents in the component should change the free energy of the compound, eventually affecting their hydration rate. The present work, therefore, deals with the kinetics of the hydration reaction of $C_{12}A_7$ with different degrees of crystallinity and impurity. Silica was added intentionally to serve as an impurity.

2. Experimental

Reagent-grade $CaCO_3$ and Al_2O_3 (Wako Chemicals Co., Ltd, Japan) were mixed at 12:7 by weight and reacted at elevated temperatures to synthesize $C_{12}A_7$. The degree of crystallinity of the phase was controlled by changing the cooling rate after the synthesis reaction: furnace cooling, air cooling, and quenching into liquid nitrogen. In order to obtain a fully crystalline phase, the mixture was reacted at 1300 °C for 12 h and cooled slowly in a furnace. The sample thus obtained was designated as 'CRYSTAL'. A sample with low-crystallinity was prepared by reacting the mixture at 1600 °C for 1 h, followed by air cooling to ambient temperatures. This was designated as 'MIXTURE'. Glassy $C_{12}A_7$ was prepared by reacting the mixture at 1600 °C for 2 h and quenching into liquid nitrogen. This sample was designated as 'GLASS0'. For the sample preparation, a vertical furnace was used. The reaction mixture was placed in a Pt basket and the sample was dropped into nitrogen liquid for quenching after the synthesis reaction.

To synthesize calcium aluminate glass with a silica impurity, reagent-grade SiO_2 powder was added to the above-mentioned mixture. The amounts of SiO_2 added were 1%, 2%, and 3% mass of the mixture. The samples were designated as 'GLASS1', 'GLASS2', and 'GLASS3', respectively. After grinding the samples, the surface area of the powders was determined using the Blaine air permeability method. Their Blaine fineness was about 1900–2000 cm^2/g. Table 1 summarizes sample designations, chemical compositions, and their thermal histories.

The hydration reaction of the samples was conducted at 20 °C in a conduction calorimeter (model: TCC-2, Tokyo Piko Co., Ltd., Japan). The weight of the samples was 5 g and the water to cement ratio was 1. The measurement by calorimeter started with internal mixing with water. The rate of heat evolution during the hydration reaction of each sample was measured for up to three days using the calorimeter. The morphology of the hydrated phases formed on the surface of the cement particles was examined using a scanning electron microscopy (SEM, model: S-806c, Hitachi, Japan). In addition, the hydrated products were characterized via X-ray diffraction (XRD) analysis (model: Geiger flex, Rigaku Co., Ltd., Japan).

Table 1
Sample name, chemical composition of reactants, and condition of their thermal treatment

Reactant	CaO/Al_2O_3 mole ratio	SiO_2/mass%	Synthesis
CRYSTAL	12/7	0	1300 °C for 12 h: annealed
MIXTURE	12/7	0	1600 °C for 2 h: cooled slowly
GLASS0	12/7	0	1600 °C for 2 h: quenched
GLASS1	12/7	1	1600 °C for 2 h: quenched
GLASS2	12/7	2	1600 °C for 2 h: quenched
GLASS3	12/7	3	1600 °C for 2 h: quenched

3. Results and discussion

The XRD patterns of the synthesized samples are shown in Figs. 1 and 2. As noted in Fig. 1, a highly crystalline phase was detected with the CRYSTAL sample. With the

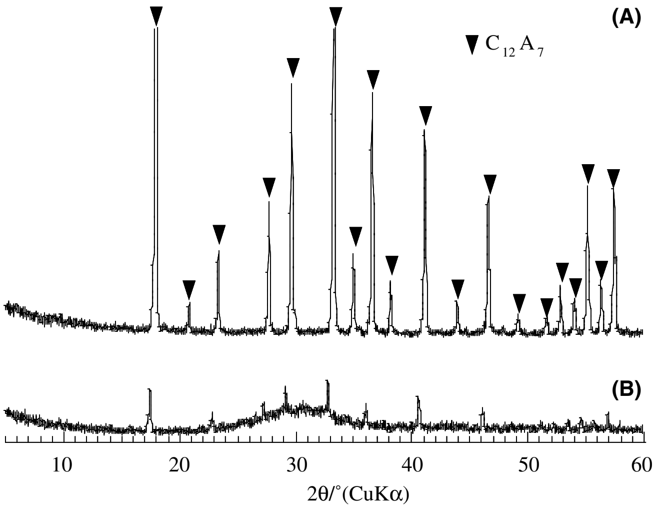

Fig. 1. X-ray diffraction patterns of (A) CRYSTAL and (B) MIXTURE.

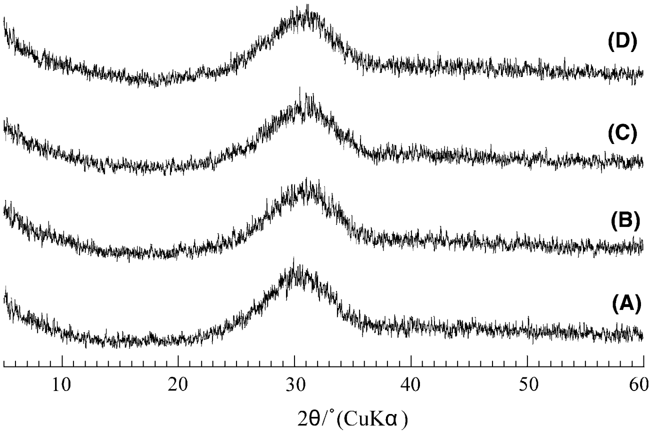

Fig. 2. X-ray diffraction patterns of (A) GLASS0; (B) GLASS1; (C) GLASS2; and (D) GLASS3.

sample designated as the MIXTURE, on the other hand, peaks from the crystalline phase were low in intensity and were mixed with a broad peak from a glass phase. This observation suggests that the sample consisted of crystalline and the glass phase mixture. With the samples quenched into liquid nitrogen, only the broad peaks from the glass were detected, irrespective of the silica content in the sample (as shown in Fig. 2).

The peak shift of the glassy phase with the change in silica content was analyzed in more detail. As the silicate content increased from 0% to 3% mass, the peak diffraction angle increased almost linearly from 30.2 to 31.4; the peak shift of the glassy phase with the change in silica content was analyzed by checking the mid point (2θ per degree) of the full-width half-maximum of the XRD peak. The mid points (2θ per degree) measured are summarized in Table 2. In other words, the average lattice constant decreased with the increase in silica content. The shift of the diffraction angle, therefore, is believed to have arisen as a result of the substitution of aluminum atoms by smaller diameter silicon atoms added to the glass.

Table 2
The peak diffraction angle of the XRD by checking the mid point (2θ per degree) of full-width half-maximum with the change in silica contents

Content of SiO_2	0	1	2	3
Mid point (2θ per degree) of FWHM	30.2	30.8	31.2	31.4

FWHM: full-width half-maximum.

The rates of heat liberation that were measured during the hydration reaction are shown in Fig. 3. With all the samples, two exothermic peaks were observed with an intermediate dormant period, as shown in Fig. 3(A). The rate of heat generation at the first peak was much larger than that at the second peak. The first peaks were observed within 30 min of making contact with the water for the hydration reaction and are shown in Fig. 3(B) in greater detail. The maximum heat liberation rate, $R_{\max}$, depended on the degree of crystallinity and the silica content of the sample. The $C_{12}A_7$ glass, in general, showed higher hydration rates when compared with those of the crystalline $C_{12}A_7$. Furthermore, the addition of silica to the $C_{12}A_7$ glass decreased the rate. Table 3 summarizes the effect of the silica content on the $R_{\max}$ of the glasses. The $R_{\max}$ of the glasses decreases with an increase in the amount of silica added. The result indicates that the addition of silica appeared to inhibit the hydration of glass at the first stage.

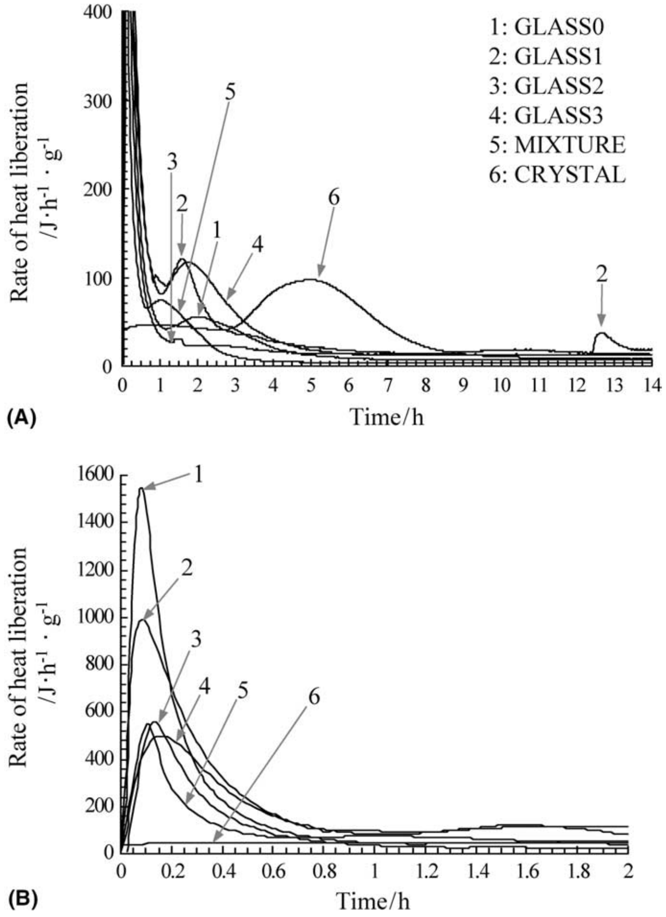

Fig. 3. The rate curves of heat liberation recorded by conduction calorimeter, (A) within 14 h and (B) within 2 h.

Table 3
Effect of silicate ion on the $R_{\max}$ of glasses within 30 min of hydration

Content of SiO_2	0	1	2	3
$R_{\max}$ ($J\ h^{-1}\ g^{-1}$)	1550	1000	570	560

Fig. 4(A) and (B) show the total heat liberated (THL) during the hydration reaction. Fig. 4(A) is a time-integration of the curves in Fig. 3(A). The $C_{12}A_7$ glass without the addition of silica, GLASS0, appeared to have the largest THL at the first stage of the hydration reaction. The order of THL was the same as that for: $R_{\max}$: GLASS0 > GLASS1 > GLASS2 and 3 > MIXTURE > CRYSTAL. When the curves were integrated over three days, the order of THL was radically changed: GLASS1 > GLASS2 and 3 > CRYSTAL > GLASS0 > MIXTURE. These changes are explained by the observation of the fracture surface of the samples that were hydrated for 30 min. Fig. 5 shows the morphologies of the hydrated layer on the surface of each sample after 30 min of hydration reaction. With the GLASS0 sample, two characteristic hydrated layers were noted (Fig. 5(A)). The first layer (inner layer) appeared gelatinous and was approximately 50–100 μm thick depending on its location. The second layer (outer layer) possessed faceted characters in its morphology. The XRD analysis of the layers indicated that they consisted of the metastable calcium aluminates hydroxide, $2CaO\cdot Al_2O_3\cdot 8H_2O$ and $4CaO\cdot Al_2O_3\cdot 13H_2O$. In the GLASS1 sample, the thickness of the first layer was thinner than that of the GLASS0 sample; it did not exceed 10 μm as noted in Fig. 5(B). With the CRYSTAL sample, the gelatinous layer was not formed and only the layer with the faceted phase was formed on the sample surface. The hydration reaction

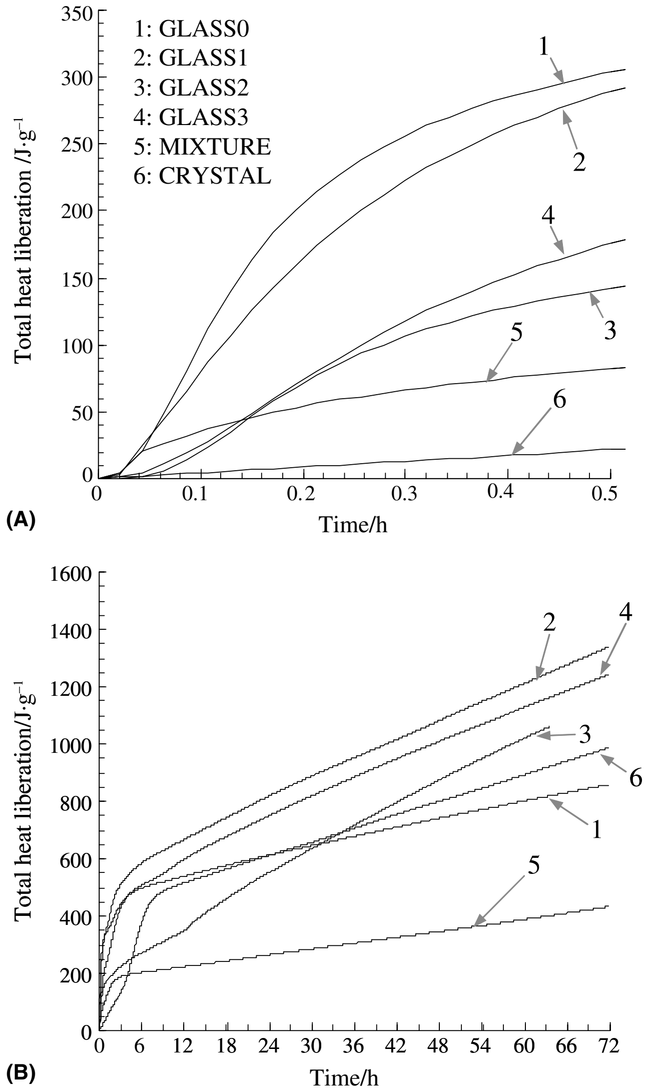

Fig. 4. The total heat liberation (THL) curve of the hydration of reactants, (A) within 30 min and (B) within 3 days.

is known to proceed in several steps: solvation, hydrate formation, followed by their precipitation [8]. As the atoms in the glass phase are generally of a higher chemical potential energy and less stable compared with those of the crystalline phase, it is expected that the solvation rate of the glassy phase into water will be faster than that of the crystalline phase. Table 4 shows the solvation rate of the reactants when in contact with water to within 2 s of hydration time. The faster solvation rate should, in turn, increase the initial rate of the hydration reaction and the degree of supersaturation of the hydrates formed. The particle size of hydrate precipitation from the homogeneous solution is known to depend on the degree of supersaturation [9]. Richards and Helmuth [10] showed that a dense calcium aluminate hydrate gel coating will form under conditions of high supersaturation. The size of the hydrates precipitated from the calcium aluminate glass, therefore, is expected to be

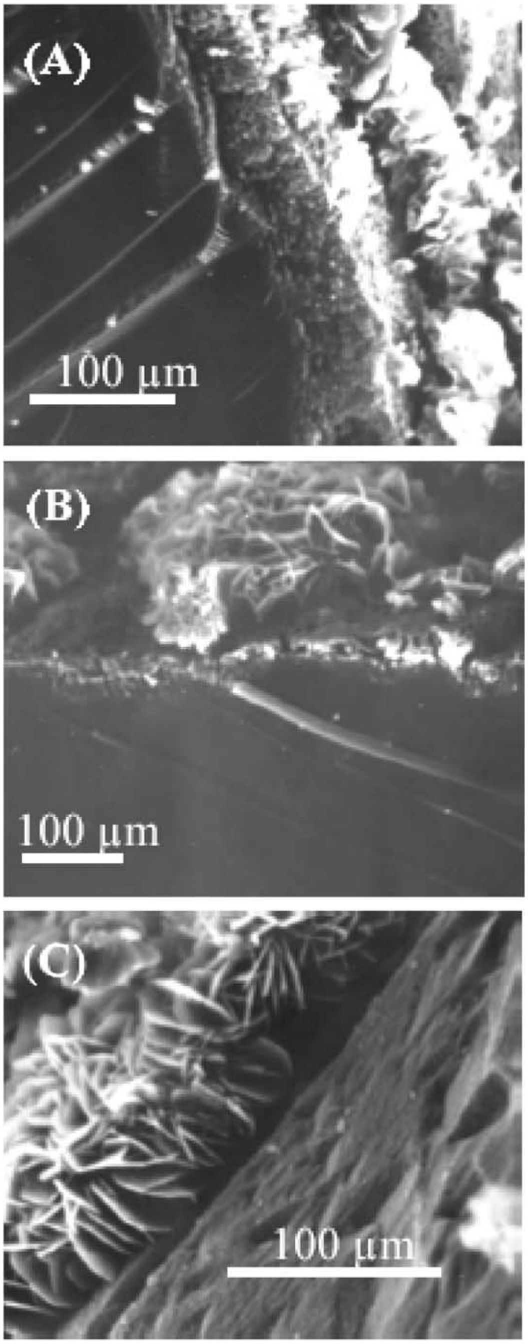

Fig. 5. SEM images of cross section of reactants hydrated for 30 min of hydration, (A) GLASS0; (B) GLASS1; and (C) CRYSTAL.

Table 4
Solvation rate of reactants on initial contact with water

	CRYSTAL	MIXTURE	GLASS0	GLASS1	GLASS2	GLASS3
Solvation rate (J h^{-1} g^{-1})	40.9	144.0	410.0	274.3	145.9	94.7

smaller than that of crystalline phase. In other words, the rapid solvation of GLASS0 must have led to a highly supersaturated solution and a precipitation of colloidal size hydrates on the surface of the particle, i.e., a gelatinous hydrate layer. The gelatinous layer was only observed with the glassy samples, GLASS0 and GLASS1, possibly due to their high solvation rates.

The presence of the gelatinous layer coated on the surface of the GLASS0 sample is expected to reduce the rate of the hydration reaction since the layer acts as a barrier for the mass transfer of the reaction. Fukuhara et al. [11] have shown that the hydration reaction of $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ is controlled by diffusion through the gelatinous hydrate layer. In the samples with more permeable hydrate layers, such as the faceted layer on the CRYSTAL sample, on the other hand, the hydration reaction at the second stage should proceed at higher rates. From these discussions, it is believed that the gelatinous hydrates formed during the first hydration stage of GLASS0 hindered further hydration; therefore the THL of GLASS0 up to three days became lower than that of the others. In addition, the relatively weak second peak is believed to have resulted from the retarding effect of the hydrated layer formed at the first hydration stage. At later stages, the extent of the hydration of crystalline $C_{12}A_7$ may have become greater than the glassy $C_{12}A_7$, as reported elsewhere [7].

In this study, the hydration reaction rates of glass samples to which silica was added—i.e., the GLASS1, GLASS2 and GLASS3 samples—were lower than that of the GLASS0 sample. The samples with the added silica reduced the thickness of the gelatinous hydrate layer formed. The addition of silica seemed to stabilize the network of calcium aluminate glass, reducing their solvation rate. Atomistic modeling of samples with a silica addition will be discussed in a forthcoming paper.

4. Conclusion

In this study, the effects of crystallinity and the addition of silica on the kinetics of the hydration reaction of calcium aluminate were investigated by measuring heat liberation rate during the reaction. The crystallinity of the sample was controlled by changing the cooling rate of the sample after the synthesis reaction: furnace cooling, air cooling and quenching into liquid nitrogen. It was observed that the hydration reaction of the samples occurs in two stages, and that the rate of heat liberated in the first stage was much larger than that of the second stage. After the first stage, layers of hydrates were formed on the sample whose characteristics depended on the crystallinity of the sample. In the glass sample, layers of gelatinous and faceted phases were formed. With the crystalline sample, on the other hand, only the layer with the faceted phase was formed. This difference in the hydrated layer structure was observed to influence the long-term kinetics of the hydration reaction as they act as a barrier for mass transfer. The addition of silica, on the other hand, decreased the reaction rate.

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