

## Hydration Kinetics of Tricalcium Silicate Studied by Neutron Scattering

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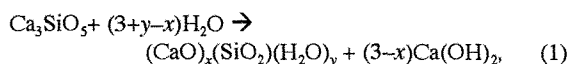
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The hydration kinetics of tricalcium silicate ( $\text{Ca}_3\text{SiO}_5$ ) has been studied by time-of-flight neutron powder diffraction (TOF-NPD) and time-of-flight small-angle neutron scattering (TOF-SANS). During the hydration process, the hydrated  $\text{Ca}_3\text{SiO}_5$  was quantified using the additional standard method with Si, and then we could obtain the time dependence of the hydration degree of  $\text{Ca}_3\text{SiO}_5$ . It was validated that the hydration of  $\text{Ca}_3\text{SiO}_5$  proceeds in three different stages: induction period, nucleation and growth period and diffusion-limited period. In the SANS experiments, the drastic variation in the SANS curve was observed over induction time ( $t_i \sim 6$  h). From these results, we point out that the hydration rate is strongly associated with the surface roughness of  $\text{Ca}_3\text{SiO}_5$  arising from the creation of hydration products. Furthermore, the four-parameter equation based on the Avrami model was applied to describe the hydration kinetics of  $\text{Ca}_3\text{SiO}_5$ . The  $n$ -value that characterizes the hydration process was estimated as  $\sim 2.6$ .

Key words: tricalcium silicate, hydration, neutron powder diffraction, small-angle neutron scattering

### 1. INTRODUCTION

Tricalcium silicate ( $\text{Ca}_3\text{SiO}_5$ ) is the most principal component of Ordinary Portland Cement (OPC) clinkers. The properties of hydrated  $\text{Ca}_3\text{SiO}_5$  may affect those of concrete such as high compressive strength and durability. The hydration process of  $\text{Ca}_3\text{SiO}_5$  can be represented as follows:



where first and second terms on the right-hand side of Eq. (1) indicate calcium silicate hydrate gel (C-S-H gel) and a calcium hydroxide ( $\text{Ca}(\text{OH})_2$ ), respectively. It is widely recognized that the hydration of  $\text{Ca}_3\text{SiO}_5$  proceeds in three different stages: induction period, nucleation and growth period and diffusion-limited period [1]. In the induction period, no creation of the hydration products occurs. After that, the hydration products appear and grow drastically. However, the hydration rate is gradually suppressed when the diffusion-limited kinetics begins at  $t_d$ .

In order to interpret the hydration kinetics of  $\text{Ca}_3\text{SiO}_5$ , many extensive studies have been performed by various authors [2–13]. Especially, for the early hydration process of  $\text{Ca}_3\text{SiO}_5$ , some investigators attempted to apply the Avrami model including three parameters ( $k$ ,  $t_i$  and  $n$ ):

$$X = 1 - \exp\left\{-[k(t - t_i)]^n\right\} \quad (2)$$

where  $X$  is the volume fraction of the transformed phase,  $k$  is the nucleation and growth reaction rate constant,  $t_i$  is the induction time,  $n$  is the exponent which characterizes the hydration process,  $t$  is the hydration time [2–5]. Although it seems that the Avrami model can fairly represent the hydration behavior of  $\text{Ca}_3\text{SiO}_5$ , the obtained  $n$ -value is considerably lower ( $< 2$ ) than would be expected, as suggested by Livingston [1]. On the other hand, the hydration kinetics of  $\text{Ca}_3\text{SiO}_5$  has been studied by quasi-elastic neutron scattering (QENS) [5–13]. The QENS experiment provides dynamical information of water molecules in the hydrated  $\text{Ca}_3\text{SiO}_5$ , that is, the bound water caused by the hydration can be directly observed. Recently, for the QENS data, a four-parameter equation:

$$BWI(t) - BWI(t_i) = A \left[ 1 - \exp\left\{-[k(t - t_i)]^n\right\} \right] \quad (3)$$

has been applied to the early hydration process of  $\text{Ca}_3\text{SiO}_5$ , where  $BWI$  stands for the bound water index,  $A$  is the asymptotic value of the amount of bound water that can be formed as  $t \rightarrow \infty$  [1]. Even though the physical factors that determine the  $A$ -value are still controversial, the  $n$ -value has been estimated as  $2 < n < 2.6$  [8]. This is consistent with nucleation and growth occurring in a three-dimensional pore space [1]. Thus, the validity of the four-parameter equation has been frequently discussed in order to understand the hydration kinetics of  $\text{Ca}_3\text{SiO}_5$ .

In this work, time-of-flight neutron powder diffraction (TOF-NPD) experiments have been carried out using the hydrated  $\text{Ca}_3\text{SiO}_5$  with heavy water ( $\text{D}_2\text{O}$ ). In particular, we focus on the consumption of  $\text{Ca}_3\text{SiO}_5$  during the hydration process and evaluated the  $n$ - and  $A$ -values on the four-parameter equation through the quantitative analysis of the hydrated  $\text{Ca}_3\text{SiO}_5$ . Simultaneously, the variation of surface roughness on  $\text{Ca}_3\text{SiO}_5$  particles due to the creation of hydration products was observed by time-of-flight small-angle neutron scattering (TOF-SANS).

## 2. EXPERIMENTAL

The crystal structure of polycrystalline  $\text{Ca}_3\text{SiO}_5$  made in Taiheiyo Consultant Co., Ltd. has been refined on the basis of the triclinic phase, as reported elsewhere [4]. The hydration properties of  $\text{Ca}_3\text{SiO}_5$  were studied by TOF-NPD. The neutron powder diffractometer, Vega, is installed at the pulsed neutron source of Neutron Science Laboratory (KENS) in High Energy Accelerator Research Organization (KEK) [14], and its resolution ( $\Delta d/d$ ) is about 0.2%. In order to quantify the mass of the hydrated  $\text{Ca}_3\text{SiO}_5$  during hydration process, we applied the standard addition method with Si. The detailed sample preparation is illustrated in Fig. 1. The mass of Si,  $M_{\text{Si}}$ , was carefully measured as 0.3432 g, and then the Si was put into a small vanadium capsule to separate from  $\text{Ca}_3\text{SiO}_5$  paste. In the hydration of  $\text{Ca}_3\text{SiO}_5$  at 23°C, we substituted heavy water ( $\text{D}_2\text{O}$ ) for light one ( $\text{H}_2\text{O}$ ) because of suppressing the large incoherent scattering of H atoms. After mixing  $\text{Ca}_3\text{SiO}_5$  with  $\text{D}_2\text{O}$  for 3 minutes in argon gas, the mixture was loaded into a cylindrical vanadium cell. Here, the  $\text{D}_2\text{O}$  to  $\text{Ca}_3\text{SiO}_5$  mass ratio ( $\text{D}_2\text{O}/\text{Ca}_3\text{SiO}_5$ ) is 0.5. Finally, the cylindrical vanadium cell of  $\text{Ca}_3\text{SiO}_5$  paste including the small capsule with Si was put into another large cylindrical vanadium cell filled with argon gas.

After about 15 minutes of hydration, the first NPD measurement of the hydrated  $\text{Ca}_3\text{SiO}_5$  was started on Vega. The NPD data were collected every 30 minutes for 1 day. Furthermore, NPD experiments were carried out using the same sample after 2 weeks, ~ 1 month and ~ 2 months. The Rietveld analysis program, RIETAN-2001T, developed for Vega and Sirius was utilized in the multi-phase Rietveld refinements [15–18]. In this program, standard deviations in all structure parameters are estimated by the conventional method.

TOF-SANS data of the hydrated  $\text{Ca}_3\text{SiO}_5$  with  $\text{D}_2\text{O}$  at 23°C were collected every 2 h for 1 day on the small/wide-angle neutron diffractometer, SWAN, installed at KEK-KENS [19]. The  $\text{D}_2\text{O}/\text{Ca}_3\text{SiO}_5$  was fixed to be 0.5.

## 3. RESULTS

Figure 2 shows the variation of NPD pattern of the hydrated  $\text{Ca}_3\text{SiO}_5$  with  $\text{D}_2\text{O}$ . Several Bragg reflections are drastically growing during the hydration process. It is easily expected that these Bragg peaks correspond to  $\text{Ca}(\text{OD})_2$ , as can be seen in Eq. (1). Note that a couple of Bragg peaks indexed as asterisks (\*) indicate the standard sample of Si.

Before commencing multi-phase Rietveld analyses for

all NPD data of the hydrated  $\text{Ca}_3\text{SiO}_5$ , structure parameters of Si were refined on the basis of the cubic model; the lattice parameter,  $a$ , was estimated as 5.42963(6) Å. In the subsequent profile refinements, the lattice parameters, atomic coordinates and profile parameters were fixed at the same values obtained from the Rietveld analyses of Si in addition to  $\text{Ca}_3\text{SiO}_5$ .

The multi-phase Rietveld analyses of the hydrated  $\text{Ca}_3\text{SiO}_5$  were carried out assuming three phases: unhydrated  $\text{Ca}_3\text{SiO}_5$ ,  $\text{Ca}(\text{OD})_2$  and Si. Figure 3 shows the final Rietveld refinement pattern of the hydrated  $\text{Ca}_3\text{SiO}_5$  for 2 months of hydration. The fairly good fit was obtained between calculated and observed patterns ( $R_{\text{wp}} = 3.12\%$  and  $S = 1.3463$ , where  $R_{\text{wp}}$  and  $S$  are the reliability factor and goodness-of-fit, respectively). The crystal structure of  $\text{Ca}(\text{OD})_2$  based on the trigonal phase (space group:  $P\bar{3}m1$ ) were used as a starting model; the lattice parameters of  $\text{Ca}(\text{OD})_2$  are  $a = 3.59218(7)$  Å and  $c = 4.9009(2)$  Å, and the atomic coordinates of  $\text{Ca}(\text{OD})_2$  are  $\text{Ca}(0, 0, 0)$ ,  $\text{D}(1/3, 2/3, 0.5835(16))$  and  $\text{O}(1/3, 2/3, 0.7697(12))$ .

The results of multi-phase Rietveld refinements gave us the ratio of mass fraction for three phases. We could calculate the mass for each phase as follows:

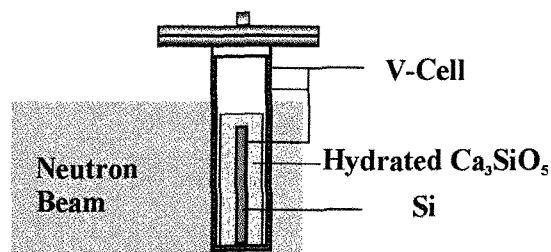


Fig. 1. Schematic illustration of the sample cell in neutron powder diffraction experiments of the hydrated  $\text{Ca}_3\text{SiO}_5$ . The Si is utilized as a standard material in the additional standard method, being covered with vanadium film to separate from the  $\text{Ca}_3\text{SiO}_5$  paste.

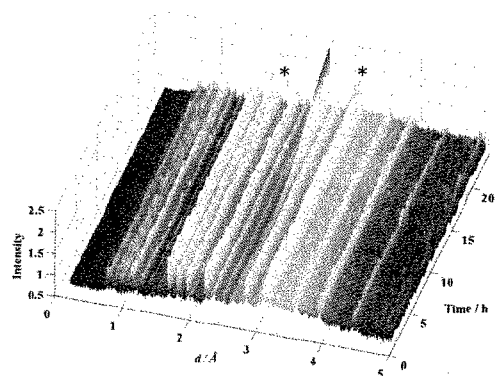


Fig. 2. Change of the neutron powder diffraction pattern of the hydrated  $\text{Ca}_3\text{SiO}_5$  with  $\text{D}_2\text{O}$  at 23°C for 1 day. The Bragg reflection of  $\text{Ca}(\text{OD})_2$  is drastically growing at around 2.6 Å. A couple of peaks indexed as asterisks (\*) indicate Si, which is utilized as a standard material in the additional standard method.

$$M_{Ca_3SiO_5} = \frac{\omega_{Ca_3SiO_5}}{\omega_{Si}} \times M_{Si}, \quad M_{Ca(OD)_2} = \frac{\omega_{Ca(OD)_2}}{\omega_{Si}} \times M_{Si} \quad (4a, 4b)$$

where  $M$  and  $\omega$  indicate the mass and the mass fraction for each component, respectively. Figure 4 shows the time dependence of mass for unhydrated  $Ca_3SiO_5$ ,  $Ca(OD)_2$  and Si. The induction period clearly appears under 10 h of hydration due to no sign of  $Ca(OD)_2$  phase. The mass of the unhydrated  $Ca_3SiO_5$  in the induction period was determined to be 1.602 g. Consequently, the degree of hydration,  $x(t)$ , was quantified from the following equation:  $x(t) = (1.602 - M_{Ca_3SiO_5}(t)) / 1.602$ , as shown in Fig. 5. The mole ratio of  $Ca(OD)_2$  to hydrated  $Ca_3SiO_5$  for ~ 1 month of hydration was estimated as ~ 1.6. This is consistent with the hydration formula of  $Ca_3SiO_5$ :  $Ca_3SiO_5 + 3.90H_2O \rightarrow (CaO)_{1.68}(SiO_2)(H_2O)_{2.58} + 1.32Ca(OH)_2$ , reported by Fujii and Kondo [20].

Figure 6 shows SANS spectra of the hydrated  $Ca_3SiO_5$  with  $D_2O$  up to ~ 2 months of hydration. The slope of SANS curve is lowest at early hydration times. The SANS spectrum drastically changes over 6 h of hydration. It is most likely that the variation of SANS spectrum reflects that of the surface roughness arising from the creation of hydration products, as suggested by Thomas et al. [7].

### 5. DISCUSSION

The four-parameter equation of Eq. (3) was employed to evaluate the hydration kinetics of  $Ca_3SiO_5$  in the nucleation and growth period. The logarithmic form of Eq. (3) can be written in the form

$$\ln \left[ -\ln \left( 1 - \frac{x(t)}{A} \right) \right] = n \ln(t - t_i) + \ln k. \quad (5)$$

Figure 7 shows a plot of the logarithmic form (Avrami plot) for  $x(t)$ . It is noteworthy that the  $t_i$  is determined to be 6 h from the results of SANS experiments. In preliminary least-squares fits using Eq. (5), the  $A$ -value tended to converge at around 0.34, therefore it was fixed as 0.34 in the subsequent analyses. As can be seen in Fig. 7, the straight line fit to this data was obtained. Consequently, the  $n$ - and  $k$ -values were estimated as 2.6 and  $0.05 \text{ h}^{-1}$ , respectively. The  $n$ - and  $A$ -values obtained from our experiments are in agreement with that reported by FitzGerald et al. [8].

It is widely recognized that the  $n$ -value reflects the nature of phase transformation through the three parameters:  $P$ ,  $S$  and  $Q$ , where  $P$  is the dimensionality for growth product,  $S$  is the type of growth,  $Q$  is the nucleation rate [1,5]. The hydration of  $Ca_3SiO_5$  may show the interfacial growth ( $S = 1$ ) and the site-saturated nucleation ( $Q = 0$ ) in the nucleation and growth period, that is,  $n \sim P$ . In the NPD patterns, the Bragg peaks of  $Ca(OD)_2$  are appreciably sharp; this may mean that the crystalline  $Ca(OD)_2$  has three-dimensional nucleation and growth. Presumably, the  $n$ -value indicated the fractal nucleation and growth mainly depends on the growth form of C-S-H gel such as tobermorite and jennite [21-23].

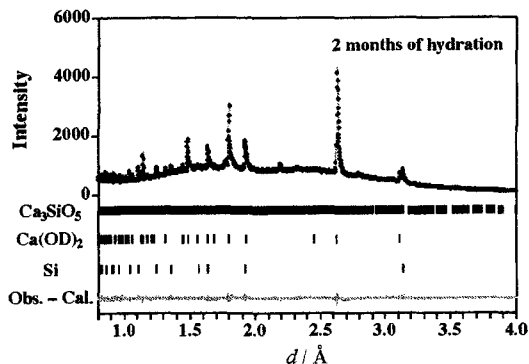


Fig. 3. Rietveld refinement pattern of the hydrated  $Ca_3SiO_5$  with  $D_2O$  at  $23^\circ C$  for ~ 2 months of hydration. The plus marks are observed neutron diffraction intensities, and the solid line is a calculated one. The vertical marks below the profile indicate positions of Bragg reflections. The curve at the bottom is a difference between observed and calculated intensities.

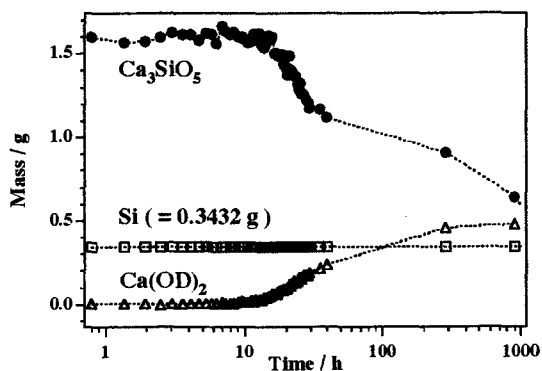


Fig. 4. Hydration time dependences of mass for three components: unhydrated  $Ca_3SiO_5$ ,  $Ca(OD)_2$  and Si. The mass of Si was fixed to be 0.3432 g.

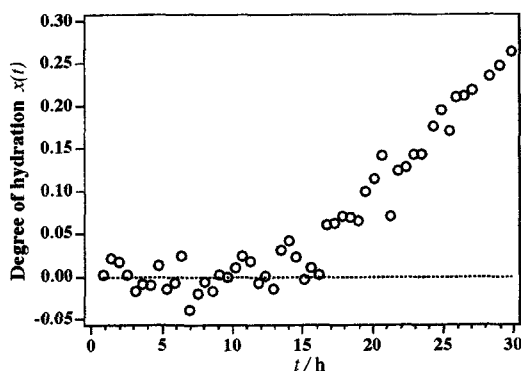


Fig. 5. Degree of hydration for  $Ca_3SiO_5$  as a function of hydration time,  $t$ .

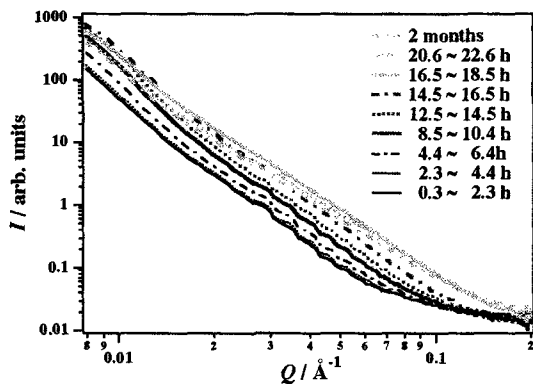


Fig. 6. SANS spectra of the hydrated  $\text{Ca}_3\text{SiO}_5$  with  $\text{D}_2\text{O}$  at  $23^\circ\text{C}$  up to  $\sim 2$  months of hydration. The mass ratio of  $\text{D}_2\text{O}$  to  $\text{Ca}_3\text{SiO}_5$  is fixed to be 0.5.

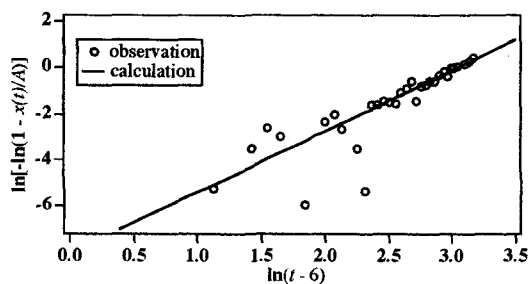


Fig. 7. A plot of the logarithmic form based on the four-parameter equation. The induction time,  $t_i$ , was determined to be 6 h from the results of SANS experiments.

## 6. CONCLUSION

The hydration properties of  $\text{Ca}_3\text{SiO}_5$  have been studied by TOF-NPD and TOF-SANS. The mass of the hydrated  $\text{Ca}_3\text{SiO}_5$  during the hydration process was quantified by the additional standard method with Si, and then we could obtain the hydration degree of  $\text{Ca}_3\text{SiO}_5$  as a function of  $t$ . Furthermore, SANS experiments showed the drastic variation in the SANS curve over induction time ( $t_i \sim 6$  h). The results obtained from TOF-NPD and TOF-SANS experiments lead to the important conclusion that the hydration rate is strongly associated with the surface roughness of  $\text{Ca}_3\text{SiO}_5$  arising from the creation of hydration products. The four-parameter equation based on the Avrami model was applied to describe the hydration kinetics of  $\text{Ca}_3\text{SiO}_5$ . The  $n$ -value that characterizes the hydration process was estimated as 2.6, being consistent with the results reported by various investigators [1,8].

## ACKNOWLEDGEMENTS

We wish to acknowledge Mr. S. Sudo of Taiheiyo Consultant Co. Ltd. for the help in the preparation of sample. This work was supported by a Grant-in-Aid for Creative Scientific Research from the Ministry of

Education, Science, Sports and Culture, Japan.

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(Received January 31, 2006; Accepted June 2, 2006)