

# Structural and Hydration Properties of Low Heat Portland Cement

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In order to study the structural and hydration properties of Low Heat Portland Cement (LHPC), X-ray powder diffraction (XPD) and quasi-elastic neutron scattering (QENS) experiments were performed. In the Rietveld refinement of LHPC, it was validated that the principal component of LHPC is  $\text{Ca}_2\text{SiO}_4$  of which structure has the monoclinic  $\beta$ -phase. The QENS experiments showed the hydration behavior of LHPC; three different stages (induction period, nucleation and growth period and diffusion-limited period) are clearly observed in the bound water index, *BWI*, as a function of hydration time. Moreover, the initial hydration process of LHPC could be described by a four-parameter equation based on the Avrami model.

Key words: low heat Portland cement, hydration, X-ray diffraction, Rietveld refinement, quasi-elastic neutron scattering

## 1. INTRODUCTION

Currently, Low Heat Portland Cement (LHPC) clinkers have occupied important positions in materials of huge buildings. The LHPC consists of several crystalline phases: dicalcium silicate ( $\text{Ca}_2\text{SiO}_4$ ), tricalcium silicate ( $\text{Ca}_3\text{SiO}_5$ ), tetracalcium aluminoferrite ( $\text{Ca}_4\text{Al}_2\text{Fe}_2\text{O}_{10}$ ) and gypsums. In particular, the  $\text{Ca}_2\text{SiO}_4$  is the most principal component of LHPC (more than 50 mass%) and the heat of hydration of  $\text{Ca}_2\text{SiO}_4$  is lower than that of other components. Although tricalcium aluminate ( $\text{Ca}_3\text{Al}_2\text{O}_6$ ), which has high heat of hydration, is a well-known component, its content should be slight in the LHPC. The important advantages of LHPC are to achieve the low heat of hydration and to suppress the self-contraction in concrete.

The compressive strength of the hardened LHPC may be strongly associated with the hydration properties of LHPC. Therefore, it is indispensable to study the structural and hydration properties of LHPC in detail, however it was very difficult owing to the complex composition mixed crystalline and amorphous phases of hydration products. Recently, quasi-elastic neutron scattering (QENS) technique has attracted much attention, because the QENS experiments provide us dynamical information of water molecules in materials. Even though cement clinkers have a lot of components, the hydration properties can be easily investigated from the point of view of the bound water in the hydrated cement. In fact, various investigators have begun to apply the QENS method to the  $\text{Ca}_3\text{SiO}_5$  sample [1-10], and the hydration process in three different stages (induction period, nucleation and growth period and diffusion-limited period) has been clearly observed.

Furthermore, a four-parameter equation based on the Avrami model:

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

has been suggested to explain the early hydration process of  $\text{Ca}_3\text{SiO}_5$ , where *BWI* stands for the bound water index, *k* is the nucleation and growth reaction rate, *n* is the exponent which characterizes the hydration process, *t<sub>i</sub>* is the induction time, *t* is the hydration time, *A* is the asymptotic value of *BWI* corresponded to nucleation and growth period that can be formed as  $t \rightarrow \infty$  [11]. Thus, it can be recognized that the QENS is particularly useful for evaluating the hydration rate of cement. We suggest that the QENS method should be sufficiently utilized for the LHPC, and to verify the four-parameter equation is needed.

In this work, crystal structure investigations of LHPC were carried out using X-ray powder diffraction (XPD). Subsequently, the hydration properties of LHPC were studied by QENS, and we will discuss about the initial hydration process of LHPC by the four-parameter equation.

## 2. EXPERIMENTAL

The powder sample of LHPC, which is made in Taiheiyo Cement Corporation, was characterized by X-ray diffractometer with Cu source (Rigaku Corporation, RAD-C). The obtained XPD pattern was analyzed by the Rietveld refinement program, RIETAN-2000 [12,13].

The hydration properties of LHPC were studied using the high-resolution pulsed cold neutron spectrometer, AGNES, belonging to Institute for Solid State Physics, University of Tokyo and installed at C3-1-1 port in the JRR-3M reactor of Japan Atomic Energy Agency (JAEA) [14,15]. The energy resolution is 120  $\mu\text{eV}$ , using PG002 monochromator ( $\lambda = 4.22 \text{ \AA}$ ). The LHPC clinkers were hydrated with light water ( $\text{H}_2\text{O}$ ) at 28°C in air. The  $\text{H}_2\text{O}$  to LHPC mass ratio was kept constant at 0.5. After mixing LHPC with  $\text{H}_2\text{O}$  for 2 minutes, the LHPC paste was spread on the thin Teflon sheet to suppress the reaction for a sample cell. The thickness of LHPC paste is about 0.5 mm. The product was wrapped in the aluminum foil, and then the rolled sample was put into a cylindrical aluminum cell of 14 mm in diameter and 50 mm in height.

After about 20 minutes, the first QENS measurement of the hydrated LHPC was started on the AGNES. The QENS data were collected every 30 minutes for 14 h of hydration, and then every 1 h up to 3 days. Furthermore, the QENS spectra were measured every 3 h up to 5 days.

### 3. RESULTS AND DISCUSSION

Figure 1 shows the XPD pattern of LHPC. In the Rietveld refinement, five phases were assumed:  $\text{Ca}_2\text{SiO}_4$ ,  $\text{Ca}_3\text{SiO}_5$ ,  $\text{Ca}_4\text{Al}_2\text{Fe}_2\text{O}_{10}$  and two kinds of gypsums ( $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$  and  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ). The fairly good fit was obtained between the observed and calculated patterns;  $R_{\text{wp}} = 10.60\%$  and  $S = 2.3393$ , where  $R_{\text{wp}}$  and  $S$  are the reliability and goodness-of-fit, respectively. Although  $\text{Ca}_3\text{Al}_2\text{O}_6$  model was also examined, no appreciable improvement of  $R$  factors was achieved. The refined lattice parameters and mass fraction for each component are listed in Table 1. From this result, we could validate that the principal component in the LHPC is the  $\text{Ca}_2\text{SiO}_4$  and its crystal structure has the monotonic  $\beta$ -phase of space group symmetry  $P2_1/n$  [16-18]. In the second component, the  $\text{Ca}_3\text{SiO}_5$  occupies about 30 wt%. The whole mass fraction of gypsums included hydrogen atoms (H) is more than 15 wt%.

Figure 2 shows the time evolution of the QENS spectrum of the LHPC until 5 days of hydration at  $Q \sim 2 \text{ \AA}^{-1}$ , where  $Q$  is the momentum transfer. The QENS spectrum is extremely broad in the early hydration period, while the elastic peak at around  $E = 0 \text{ meV}$  is drastically grown in the later hydration period. This behavior can be safely interpreted as follows; the hydration process changes free water into  $-\text{OH}$  or water of crystallization [19-21]. We point out that the H atoms significantly contribute to the QENS intensity of the hydrated LHPC, because the incoherent scattering cross section of H ( $\sigma_{\text{inc}}[\text{H}] = 80.26(6) \text{ barn}$ ) is the largest among constituent atoms ( $\sigma_{\text{inc}}[\text{Ca}] = 0.05(3) \text{ barn}$ ,  $\sigma_{\text{inc}}[\text{Si}] = 0.004(8) \text{ barn}$ ,  $\sigma_{\text{inc}}[\text{O}] = 0.000(8) \text{ barn}$ ,  $\sigma_{\text{inc}}[\text{Al}] = 0.0082(7) \text{ barn}$ ,  $\sigma_{\text{inc}}[\text{Fe}] = 0.40(11) \text{ barn}$  and  $\sigma_{\text{inc}}[\text{S}] = 0.007(5) \text{ barn}$ ).

The signals of bound water (BW) and free water (FW) in the whole QENS spectrum were separated. In the first instance, the QENS intensities,  $I(Q, E)$ , were represented as follows:

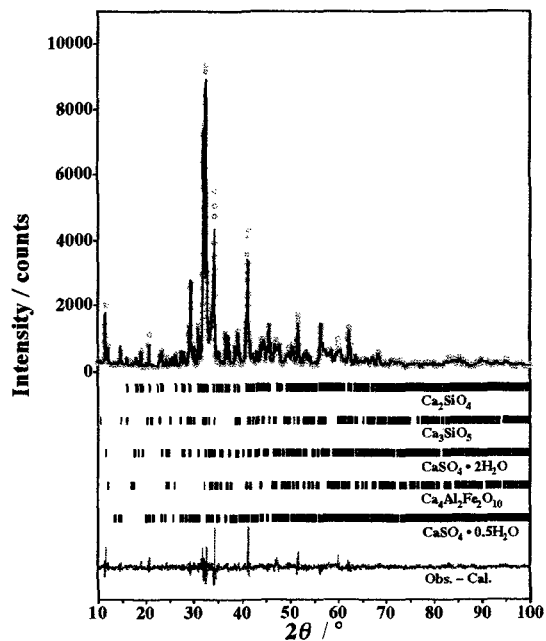


Fig. 1. Rietveld refinement pattern of Low Heat Portland Cement (LHPC) clinkers. The open symbols are observed X-ray diffraction intensities, and the solid line is a calculated one. The vertical marks below the profile indicate positions of Bragg reflections for five components: dicalcium silicate ( $\text{Ca}_2\text{SiO}_4$ ), tricalcium silicate ( $\text{Ca}_3\text{SiO}_5$ ), tetracalcium aluminoferrite ( $\text{Ca}_4\text{Al}_2\text{Fe}_2\text{O}_{10}$ ) and two kinds of gypsums ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  and  $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ ). The curve at the bottom is a difference between the observed and calculated intensities.

Table 1. Refined lattice parameters and mass fraction for each phase in the LHPC.

Component	Lattice parameters	Mass fraction
$\text{Ca}_2\text{SiO}_4$	$a = 5.4960(17) \text{ \AA}$ $b = 6.7532(20) \text{ \AA}$ $c = 9.3388(27) \text{ \AA}$ $\beta = 94.153(6)^\circ$	52 wt%
$\text{Ca}_3\text{SiO}_5$	$a = 12.2167(66) \text{ \AA}$ $b = 7.0556(24) \text{ \AA}$ $c = 9.2685(42) \text{ \AA}$ $\beta = 116.085(33)^\circ$	28 wt%
$\text{Ca}_4\text{Al}_2\text{Fe}_2\text{O}_{10}$	$a = 5.5389(35) \text{ \AA}$ $b = 14.5712(63) \text{ \AA}$ $c = 5.3464(25) \text{ \AA}$	3 wt%
$\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$	$a = 11.9862(72) \text{ \AA}$ $b = 6.9359(30) \text{ \AA}$ $c = 13.1053(69) \text{ \AA}$ $\beta = 89.464(42)^\circ$	9 wt%
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	$a = 5.7896(51) \text{ \AA}$ $b = 15.2071(67) \text{ \AA}$ $c = 6.6088(61) \text{ \AA}$ $\beta = 119.133(55)^\circ$	8 wt%

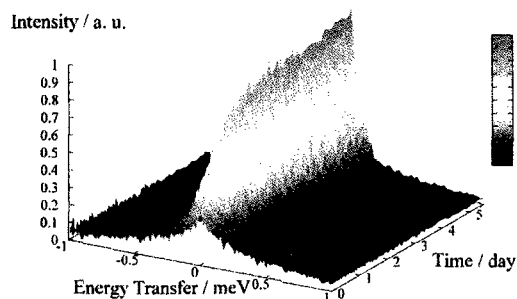


Fig. 2. Change of the quasi-elastic neutron scattering (QENS) spectrum of the LHPC at  $Q \sim 2 \text{ \AA}^{-1}$  for 5 days of hydration. The mass ratio of  $\text{H}_2\text{O}$  to LHPC is kept constant at 0.5. The energy resolution of the QENS spectrometer, AGNES, is  $120 \text{ \mu eV}$  for PG002 monochromator ( $\lambda = 4.22 \text{ \AA}$ ).

$$I(Q, E) = \{ (BW_0 + BW_1) \cdot \delta(Q, E) + FW_1 \cdot L(Q, E) \} \otimes R(Q, E) + BG, \quad (2)$$

where the first and second terms on the right-hand side indicate elastic and quasi-elastic scatterings for BW and FW, and  $BG$  is the constant background. The  $\delta(Q, E)$  and  $L(Q, E)$  are represented as a delta function and Lorentzian, respectively. Note that the  $BW_0$  corresponds to the component of gypsum in the LHPC and was employed as the constant value. The  $R(Q, E)$ , which is described by Gaussian, indicates the resolution function of the AGNES spectrometer. Its spectrum was carefully measured with a standard sample of vanadium. As shown in Figs. 3(a) and (b), the excellent fits between the observed and calculated patterns could be obtained for all QENS data. Eventually, the ratio of the signal from the  $BW_1$  of bound water to the total signal of water,  $BW_1 + FW_1$ , was defined as  $BWI (= BW_1 / (BW_1 + FW_1))$ , and calculated. The  $BWI$  as a function of  $t$  is shown in Fig. 4. The hydration process in three different stages, as mentioned in INTRODUCTION, could be clearly observed in our experiments using QENS. In the induction period, no hydration products are created up to  $\sim 0.1$  in day, as can be seen in the inset of Fig. 5. The consumption of FW is  $\sim 20\%$  after 1 day of hydration, and then the hydration rate decreases gradually.

In order to evaluate the kinetics of LHPC in the early hydration period ( $< 1$  day of hydration), we applied the four-parameter equation of Eq. (1) to the  $BWI$ . 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 [1,11]. The hydration of LHPC 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 least-squares fit, the  $n$ - and  $t_i$ -values were kept constant at 2.88 and 0.1 in day, respectively. Especially, the  $n$ -value was estimated from the results of small angle

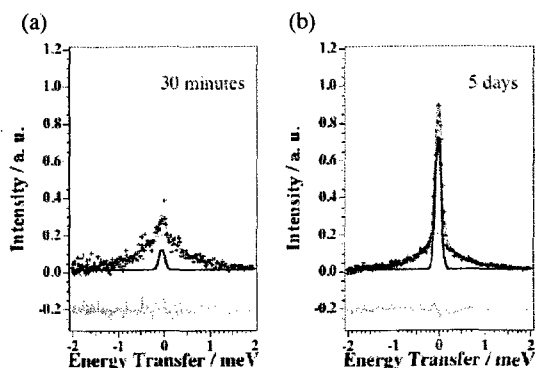


Fig. 3. QENS spectra of the hydrated LHPC for 30 minutes (a) and 5 days (b) of hydration, respectively. The plus marks are observed QENS intensities, and the gray solid line is a calculated one. The gray curve at the bottom is a difference between the observed and calculated intensities. The components of bound water (BW) and free water (FW) are described as gray broken and black solid lines, respectively.

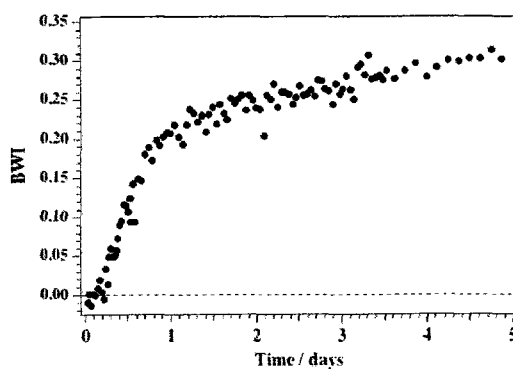


Fig. 4. Bound water index,  $BWI$ , of the hydrated LHPC as a function of hydration time.

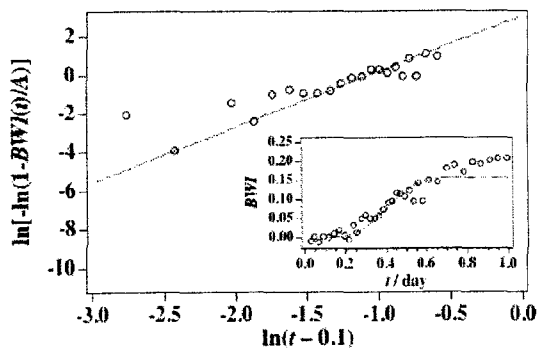


Fig. 5. A plot of the logarithmic form for the  $BWI$  of the hydrated LHPC. The inset shows the time dependence of  $BWI$  for 1 day.

neutron scattering experiments, which will be reported elsewhere. Figure 5 shows a plot of the logarithmic form of Eq. (1). The straight line fit to this data was obtained under 0.6 in day. Consequently, the  $k$ - and  $A$ -values were estimated to be  $2.9 \text{ day}^{-1}$  and 0.16, respectively. After 0.6 in day, the  $BWI$  of the logarithmic form deviated from the calculated straight line. This implies that the hydration stage gradually shifts from the nucleation and growth period to the diffusion-limited period.

Furthermore, in the present work, it was found that the hydration behavior of LHPC is really similar to that of  $\text{Ca}_3\text{SiO}_5$ ; both of them show the reduction in the hydration rate over  $\sim 1$  day of hydration [22,23]. In general, the reactivity of  $\text{Ca}_3\text{SiO}_5$  is higher than that of  $\text{Ca}_2\text{SiO}_4$ . Even though the main component of LHPC is  $\text{Ca}_2\text{SiO}_4$ , the initial hydration properties of LHPC probably depends on those of  $\text{Ca}_3\text{SiO}_5$ .

## 5. CONCLUSION

The structural and hydration properties of LHPC were studied by XPD and QENS, respectively. In the Rietveld refinement of LHPC, it was revealed that  $\text{Ca}_2\text{SiO}_4$  is a major component and has the monoclinic  $\beta$ -phase on the basis of  $P2_1/n$  space group symmetry. The QENS experiments with the hydrated LHPC showed the time dependence of  $BWI$ ; three different periods (induction period, nucleation and growth period and diffusion-limited period) were clearly observed. The four-parameter equation could fairly represent the initial hydration process of LHPC. The  $k$ - and  $A$ -values were estimated to be  $2.9 \text{ day}^{-1}$  and 0.16 when the  $n$ - and  $t_f$ -values were kept constant at 2.88 and 0.1 in day.

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## REFERENCES

- [1] R. Berliner, M. Popovici, K. W. Herwig, M. Berliner, H. M. Jennings, J. J. Thomas, *Cem. Concr. Res.*, 28 (2), 231 (1998).
- [2] H. Inoue, Y. Kiyonagi, Y. Sakamoto, *Nippon-Gensiryoku-Gakkaishi*, 22 (3), 189 (1980) [in Japanese].
- [3] J. J. Thomas, S. A. FitzGerald, D. A. Neumann, R. A. Livingston, *J. Am. Ceram. Soc.*, 84 (8), 1811 (2001).
- [4] S. A. FitzGerald, D. A. Neumann, J. J. Rush, D. P. Bentz, R. A. Livingston, *Chem. Mater.*, 10, 397 (1998).
- [5] S. A. FitzGerald, J. J. Thomas, D. A. Neumann, R. A. Livingston, *Cem. Concr. Res.*, 32, 409 (2002).
- [6] E. Fratini, S. -H. Chen, P. Baglioni, J. C. Cook, J. R. D. Copley, *Phys. Rev. E*, 65, 10201 (2002).
- [7] E. Fratini, S. -H. Chen, P. Baglioni, J. C. Cook, J. R. D. Copley, *Phys. Rev. E*, 65, 10201 (2001).
- [8] E. Fratini, S. -H. Chen, P. Baglioni, M. -C. Bellissent-Funel, *J. Phys. Chem. B*, 106, 158 (2002).
- [9] A. J. Allen, J. C. McLaughlin, D. A. Neumann, R. A. Livingston, *J. Mater. Res.*, 19, 3242 (2004).
- [10] V. K. Peterson, D. A. Neumann, R. A. Livingston, *J. Phys. Chem. B*, 109, 14449 (2005).
- [11] R. A. Livingston, *Cem. Concr. Res.*, 30, 1853 (2000).
- [12] H. M. Rietveld, *J. Appl. Crystallogr.*, 2, 65 (1969).
- [13] F. Izumi, T. Ikeda, *Mater. Sci. Forum*, 321-324, 198 (2000).
- [14] T. Kajitani, K. Shibata, S. Ikeda, M. Kohgi, H. Yoshizawa, K. Nemoto, K. Suzuki, *Physica B*, 213-214, 872 (1995).
- [15] O. Yamamuro, Y. Inamura, Y. Kawamura, S. Watanabe, T. Asami, H. Yoshizawa, Activity Report of Neutron Science Laboratory, Institute for Solid State Physics, University of Tokyo, 12, 12 (2005).
- [16] W. G. Mumme, R. J. Hill, G. B. Wye, E. R. Segnit, *N. Jb. Miner. Abh.*, 169, 35 (1995).
- [17] W. Mumme, L. Cranswick, B. Chakoumakos, *N. Jb. Miner. Abh.*, 170, 171 (1996).
- [18] R. Berliner, C. Ball, P. B. West, *Cem. Concr. Res.*, 27, 551 (1997).
- [19] J. J. Chen, J. J. Thomas, H. F. W. Taylor, H. M. Jennings, *Cem. Concr. Res.*, 34, 1499 (2004).
- [20] E. Bonaccorsi, S. Merlino, H. F. W. Taylor, *Cem. Concr. Res.*, 34, 1481 (2004).
- [21] A. Nonat, *Cem. Concr. Res.*, 34, 1521 (2004).
- [22] K. Mori, K. Yatsuyanagi, K. Oishi, T. Fukunaga, T. Kamiyama, T. Ishigaki, A. Hoshikawa, S. Harjo, K. Iwase, K. Itoh, M. Kawai, *J. Neu. Res.*, 13 (1-3), 163 (2005).
- [23] K. Mori, T. Sato, T. Fukunaga, K. Oishi, K. Kimura, K. Iwase, M. Sugiyama, K. Itoh, F. Shikanai, T. Wuernisha, M. Yonemura, D. Sulistyanintyas, I. Tsukushi, S. Takata, T. Otomo, T. Kamiyama, M. Kawai, *Physica B*, in press.

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