Development of an *in situ* X-ray diffraction system for hydrothermal reactions and its application to autoclaved aerated concrete formation

J. Kikuma,[a] M. Tsunashima, T. Ishikawa, and S. Matsuno
Analysis and Simulation Center, Asahi-KASEI Corporation, Shizuoka, Japan

A. Ogawa and K. Matsui
Asahi-KASEI Construction Materials Corporation, Ibaraki, Japan

An *in situ* time-resolved XRD system for hydrothermal reaction has been developed in order to investigate the phase evolution during autoclave process in autoclaved aerated concrete (AAC) formation. The system includes a novel autoclave cell for transmission XRD with thin beryllium windows, a two-dimensional photon-counting pixel array detector, and uses high energy X-rays from a synchrotron radiation source. The temperature and pressure inside the cell are extremely stable during hydrothermal reaction over the course of several hours. The system was utilized for the formation reaction of AAC. Phase evolution was clearly observed, including several intermediate phases, and detailed information on the structural changes during the hydrothermal reaction were obtained. © *2011 International Centre for Diffraction Data.* [DOI: 10.1154/1.3583565]

Key words: hydrothermal formation, tobermorite, steam pressure, real-time

I. INTRODUCTION

Autoclaved aerated concrete (AAC) is widely used as a building material because of its superior heat-insulation efficiency and fire resistance. A typical process for the AAC production includes hydrothermal treatment of a mixture of quartz sand, lime, cement, gypsum, and some other additives at high temperatures (typically, between 180 and 200 °C) under a saturated steam pressure, which results in the formation of crystalline calcium silicate hydrates, namely, tobermorite $(5CaO \cdot 6SiO_2 \cdot 5H_2O)$. Since both the quantity and quality of tobermorite formed in the AAC significantly affect the mechanical properties of AAC, understanding the mechanism of tobermorite formation during the hydrothermal treatment (i.e., autoclave process) is very important.

In situ XRD under hydrothermal condition has been considered to be a powerful tool for understanding the reaction in detail, and many *in situ* studies have been reported. Most of the reaction cells used in these studies were quite small, for example, capillary tubes or metal thin pipes. This is because such small cells make pressure sealing easier (Meller *et al.*, 2007; Christensen *et al.*, 2004; Norby, 2006). However, it is difficult to control water content in and around the sample in such small cells, even though it is one of the most important factors affecting the hydrothermal reaction conditions. It is also difficult to place the solid sample and the water (the source of steam) separately using these cells, although it is important in AAC production for the steam to be supplied constantly to the sample throughout the reaction. In addition, in some cases, peaks and/or background from the cell material interfere with the XRD data.

We have developed a relatively large-sized autoclave cell for *in situ* transmission XRD, which has sufficient space for the sample and the water reservoir (Kikuma *et al.*, 2009, 2010). The temperature and pressure in the cell can be con-trolled with high precision, and it is relatively easy to control water content in and around the sample. In addition, a two-dimensional pixel array detector was introduced to improve the time resolution. In this paper, we report the performance of *in situ* time-resolved XRD system and its application to AAC formation reaction.

II. AUTOCLAVE CELL

The autoclave cell is made of stainless steel, and consists of a rectangular parallelepiped main body (capacity: 35 cm^3) and a lid. The lower part of the cell can be used as a water reservoir. A sample piece is placed on top of the water reservoir using a mounting stand so that the sample does not contact with the water directly. Solid, slurry, and liquid samples can be measured using various types of sample holders. In hydrothermal reactions, the amount of the water in the sample must be controlled. For this reason, sample thickness should be thick enough so that the water in the sample may not be lost significantly during the sample preparation. Typical sample thickness for an AAC formation experiment is 3 mm.

Two beryllium windows (0.5 mm thick, 4 and 20 mm in diameter) are firmly welded on the center of each sidewall. Thus, no peak or background signal from the cell materials interferes in the data, as shown in Figure 1. Two thermocouples and a digital pressure sensor are inserted into the cell through the lid using compression pipe fittings. The main body and the lid are sealed by a heat-resistant rubber o-ring, and the cell reliably withstands the pressure of at least 1.2 MPa at 200 °C. The temperature of the cell is controlled by a copper heater block surrounded by a heat insulator. Since the windows are firmly welded on the cell body, the temperature and pressure inside the cell were found to be very stable during the *in situ* measurements for more than 12 h. Typically, the fluctuation of the temperature was about 0.1 °C, and the fluctuation of the steam pressure was about 0.005 MPa.

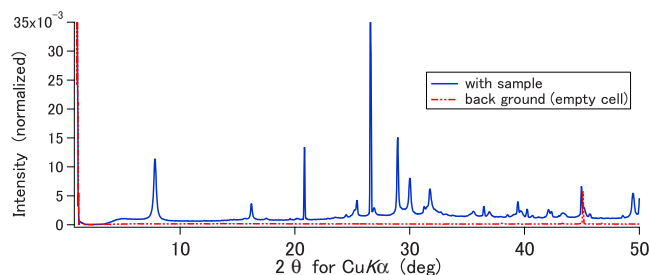[a]Author to whom correspondence should be addressed. Electronic mail: kikuma.jb@om.asahi-kasei.co.jp

Figure 1. (Color online) Typical XRD pattern obtained by the original autoclave cell (solid line). Dash-dotted line shows the pattern for the empty cell indicating low background and no interference peak except for one around $45°2\theta$ (from Be windows).

Figure 3. Stuck of time-resolved XRD patterns. Temperature was elevated from 100 to 190 °C and held at 190 °C for 6 h. (T, tobermorite; P, portlandite; Q, quartz; MS, calcium aluminate monosulfate; KA, katoite; HE, hydroxylellestadite.)

III. *IN SITU* XRD MEASUREMENT

XRD measurements were carried out at the BL19B2 beamline of SPring-8, using an X-ray energy of 30 keV. The X-ray energy was selected so that the transmittance of the X-rays through the sample would be around 50%.

A two-dimensional pixel array detector, either Pilatus-2M or Pilatus-100K (Dectris), was placed downstream with a sample-to-detector distance of about 750 mm. In the latter case, the detector area (34 mm width and 84 mm height) was not large enough to measure the entire diffraction angle range of interest; three images were acquired for each measurement by moving the detector along the vertical direction such that some part of each image was overlapped. Three images were then connected seamlessly to obtain a long rectangular-shaped image. Examples of the images obtained by two detectors are shown in Figure 2. For the Pilatus-100K, time resolution (measurement cycle) would be in the order of minutes including the time for moving the detector. With the Pilatus-2M, on the other hand, time resolution can be in the order of seconds or less than 1 s.

IV. APPLICATION TO AAC FORMATION REACTION
A. Materials and sample preparation

The *in situ* measurement system was applied to the AAC formation reaction under autoclave conditions. The starting material was a mixture of 54.4 wt % crushed natural quartz sand, 4.7 wt % quicklime (Kawai Sekkai), 38.9 wt % ce-

ment, and 2.0 wt % gypsum (Wako: research grade) with a Ca/Si molar ratio of 0.53. It was mixed in the presence of water at 50 °C for several minutes using a motor-driven blade stirrer. Water-to-solid ratio was 0.75:1 by weight. The mixture slurry was poured into a plastic beaker and kept at 60 °C for more than 12 h to produce a precured cake. The precured cake was cut into a piece of size 6×18 mm^2 and thickness 3.0 mm, just before the *in situ* measurement was conducted.

B. *In situ* XRD measurements

The autoclave cell with a sample and water inside was set in the copper heater block. First, the temperature was elevated to 100 °C with a ramping rate of 2 °C/min. The temperature was held at 100 °C for 15 min. During this period, the cell was evacuated for a few seconds, and about 95% of the air was removed from the cell. After the steam pressure was built up again at 100 °C, the first XRD measurement was conducted. After 15 min, the temperature was elevated again from 100 to 190 °C with a ramping rate of 1 °C/min, and then held at 190 °C for 6 h. During this process, the XRD measurements were conducted using Pilatus-100K. Image data were sector averaged to produce one-dimensional diffraction patterns. For convenience, the diffraction angles for 30 keV photon energy are converted to the equivalent for a Cu $K\alpha$ source and shown the figures in this paper.

C. *In situ* time-resolved XRD data set and phase evolution

Figure 3 shows the time-resolved XRD data set during the AAC formation reaction. Several constituents involved in the reaction are clearly observed. The time dependences of peak intensities of major constituents are plotted in Figure 4.

Calcium aluminate monosulfate (MS : $3CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 14H_2O$) was observed at the beginning of the autoclave cycle (100 °C), and decreased with increasing temperature, then completely diminished at around 50 min. Portlandite ($Ca(OH)_2$) remained constant at the beginning and started to decrease after 70 min, and eventually disappeared completely. Quartz decreased slowly from the beginning, the decreasing rate became a little faster in the middle and then became slower again towards the end.
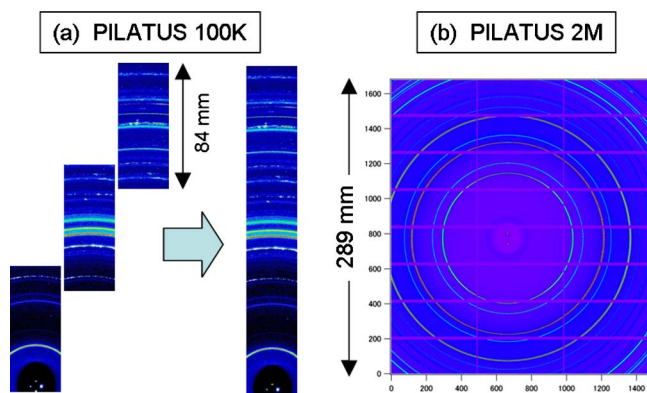

Figure 2. (Color online) Examples of image data obtained by (a) Pilatus-100K and (b) Pilatus-2M. Time resolution for (a) would be several minutes and that for (b) can be less than 1 s.
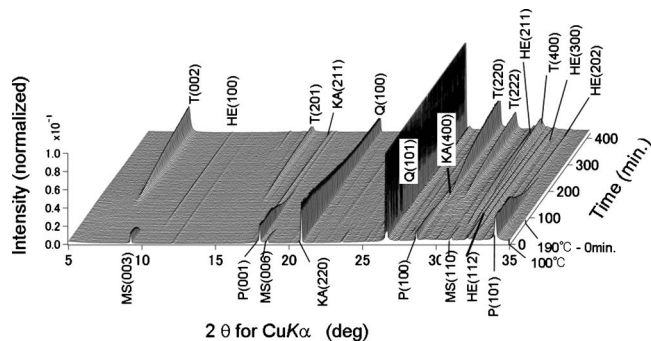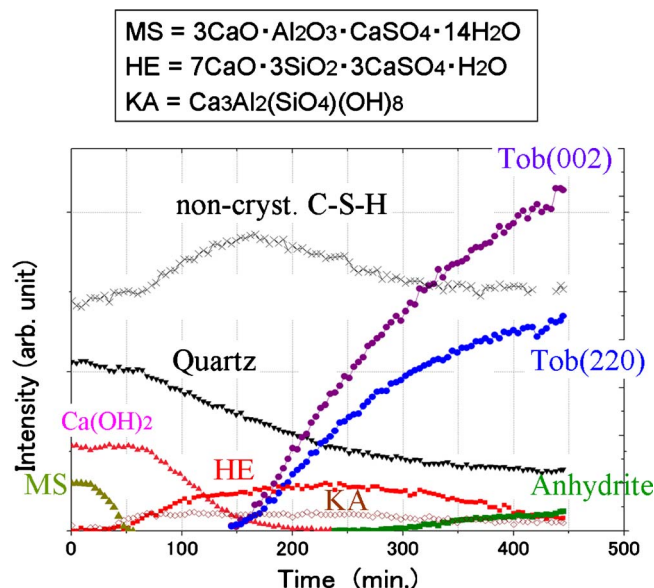
Development of an *in situ* X-ray diffraction system for hydrothermal...

MS = 3CaO·Al₂O₃·CaSO₄·14H₂O
HE = 7CaO·3SiO₂·3CaSO₄·H₂O
KA = Ca₃Al₂(SiO₄)(OH)₈

Figure 4. (Color online) Time dependence of peak intensities for the major constituents during the autoclave process.

Katoite $[KA:Ca_3Al_2(SiO_4)_{3-x}(OH)_{4x}]$ and $x=1.5$ to 3.0, a kind of hydrogarnet, was observed at around 35 min (135 °C). Then observation of hydroxylellestadite (HE: $7CaO\cdot3SiO_2\cdot3CaSO_4\cdot H_2O$) started at around 50 min, almost the same time as MS diminished. The fact that these two intermediate materials are formed right after the decomposition of MS suggests that the Al and SO_4 ions released from MS are used as sources for KA and HE, respectively.

Tobermorite was observed starting at around 150 min (60 min after the temperature reached 190 °C) and increased until the end of the autoclave cycle. It is well known that the noncrystalline calcium silicate hydrate (hereafter, C–S–H) is a precursor for tobermorite. In this system, we were able to evaluate the amount of C–S–H by monitoring the baseline intensity change due to the C–S–H amorphous halo. The intensity is plotted in Figure 4. It is clear that the tobermorite started to be observed at the same time as C–S–H started to diminish. It is interesting to note that tobermorite amount still keeps increasing even after the intensity of C–S–H leveled off, at around 300 min. It should also be noted that another intermediate phase, HE, started to decrease around 300 min. At the same time, anhydrite started to be observed.

It was previously reported by Sakiyama *et al.* (2000) that HE reacts with dissolved quartz to form tobermorite and anhydrite. Thus, it is strongly suggested that this reaction occurred in this system. In other words, tobermorite was formed via two different pathways, via C–S–H and via HE.

V. CONCLUDING REMARKS

Taking advantage of very stable temperature and pressure inside the cell under hydrothermal condition, it is possible to extract much detailed information from the time-resolved XRD data set, such as changes in d-spacings, composition change in solid solutions, and information on reaction kinetics, which helped to clarify the reaction mechanism. This system is a powerful tool for the investigation of a wide variety of hydrothermal systems.

ACKNOWLEDGMENTS

Christensen, A. N., Jensen, T. R., and Hanson, J. C. (**2004**). "Formation of ettringite, $Ca_6Al_2(SO_4)_3(OH)_{12}$-26H₂O, AFt, and monosulfate, $Ca_4Al_2O_6(SO_4)$-14H₂O, AFm-14, in hydrothermal hydration of portland cement and of calcium aluminum oxide-calcium sulfate dihydrate mixtures studied by in-situ synchrotron x-ray powder diffraction," J. Solid State Chem. **177**, 1944–1951.

Kikuma, J., Tsunashima, M., Ishikawa, T., Matsuno, S., Ogawa, A., Matsui, K., and Sato, M. (**2009**). "Hydrothermal formation of tobermorite studied by in-situ X-ray diffraction under autoclave condition," J. Synchrotron Radiat. **16**, 683–686.

Kikuma, J., Tsunashima, M., Ishikawa, T., Matsuno, S., Ogawa, A., Matsui, K., and Sato, M. (**2010**). "In-situ X-ray diffraction under hydrothermal condition using synchrotron radiation and its application to tobermorite formation reaction," Bunseki Kagaku **59**, 287–292.

Meller, N., Hall, C., Kyritsis, K., and Giriat, G. (**2007**). "Synthesis of cement based CaO−Al₂O₃−SiO₂−H₂O (CASH) hydroceramics at 200 and 250 °C: Ex-situ and in-situ diffraction," Cement Concr. Res. **37**, 823–833.

Norby, P. (**2006**). "In-situ XRD as a tool to understanding zeolite crystallization," Curr. Opin. Colloid Interface Sci. **11**, 118–125.

Sakiyama, M., Oshio, Y., and Mitsuda, T. (**2000**). "Influence of gypsum on the hydrothermal reaction of lime-quartz system and on the strength of autoclaved calcium silicate product," J. Soc. Inorg. Mater. Jpn. **7**, 685–691.