

Formation of Autoclaved Aerated Concrete Studied by *In Situ* X-ray Diffraction under Hydrothermal Condition

Autoclaved aerated concrete (AAC) is a porous concrete material having the features of both lightweight (density of about 0.5 g/cm³) and mechanical strength. Because of its porous structure, AAC also has superior properties in terms of high heat insulation and fire resistance. Therefore AAC has been one of the most industrially important building materials in the world. About 2.5 million m³ of AAC is manufactured every year in Japan, and 18 million m³ in Europe. Typically, AAC is produced by hydrothermal treatment of mixtures of quartz sand, lime, cement, gypsum and aluminum powder in a temperature range of 180 - 200°C. During the hydrothermal treatment, platy-shaped tobermorite crystals (5CaO·6SiO₂·5H₂O) are formed as a major component of AAC (Fig. 1). It is known that the crystallinity of tobermorite largely affects the physical properties of AAC.

The formation mechanism of tobermorite has not been understood thoroughly owing to the difficulty in investigating under the hydrothermal reaction atmosphere, i.e., an autoclave process. The conventional *ex situ* approach, conducted by terminating the reaction in the middle of the autoclave process, includes ambiguity caused by the temperature dependence of solubility, unfavorable reactions during the cooling process, a variation among different pieces used as samples at different reaction stages, and so on. Thus, *in situ* observation of the reaction has been highly desirable. We have developed a system for high-performance *in situ* transmission XRD under hydrothermal conditions, using high-energy X-rays in combination with an originally designed autoclave cell [1]. Here, we report phase transformations during the AAC formation process investigated by *in situ* XRD.

In situ XRD was carried out at BL19B2 beamline, using an X-ray energy of 30 keV. A pre-cured mixture solid (quartz sand, lime, cement, gypsum and water), together with distilled water as a steam source, was set in the autoclave cell. The temperature was elevated from 100 to 190°C with a ramping rate of 1°C/min., then held at 190°C for 6 h. During this process, the XRD measurements were conducted at intervals of either 15 or 30 min.

Figure 2 shows a series of XRD patterns obtained during the autoclave process. Several constituents related to tobermorite formation are identified. The intensities of the major peaks are plotted in Fig. 3, together with the temperature and pressure inside the cell. Both the temperature and pressure were very

stable throughout the experiment.

There are several advantages for an *in situ* experiment compared with *ex situ* approaches. One is the ability to detect a small change in the course of reaction. In this study, we were able to observe the intensity change of 'non-crystalline' calcium silicate hydrate (C-S-H), which is formed by a reaction of dissolved quartz with dissolved Ca(OH)₂, and well-known as a precursor of tobermorite [2]. Generally, with an *ex situ* type of experiment, it is difficult to determine the amount of non-crystalline materials during a reaction process because the intensity of the amorphous halo could be affected by the background intensity, which could vary among different pieces of the sample or by sample preparation. In an *in situ* experiment, however, the same portion of the sample is continuously measured throughout the experiment. This allows one to detect a slight change in the amorphous intensity. The intensity change at the C-S-H amorphous halo region (3.43 nm⁻¹) is plotted together in Fig. 3 (no background subtracted). The intensity reaches a maximum at around 150 min, which is the same time at which there is a drastic decrease in the amount of portlandite and the beginning of the tobermorite formation. Then, the intensity decreases as the formation of tobermorite proceeds.

Another advantage is the ability to investigate the reaction pathways directly. Two pathways of tobermorite formation are observed in this study. The first is a formation via non-crystalline C-S-H (formula (1)), as described above.

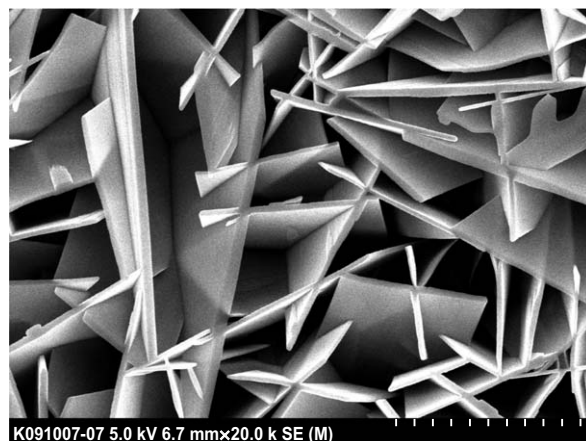
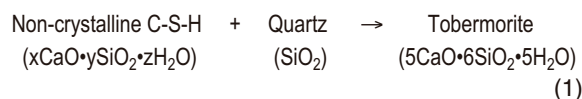


Fig. 1. SEM image of platy crystals of tobermorite. (Scale: one division corresponds to 0.2 μm.)

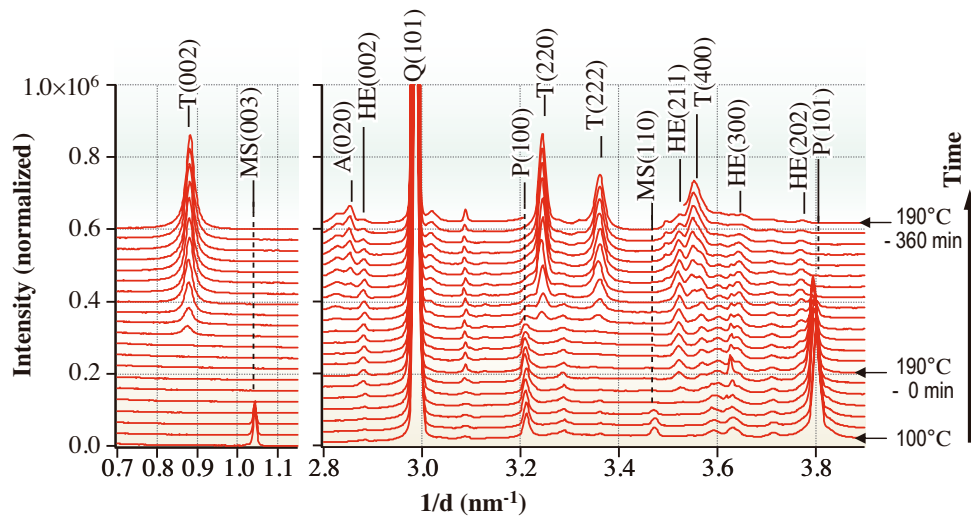


Fig. 2. Stack of *in situ* XRD patterns obtained during the autoclave process. The reaction under the autoclave proceeds from bottom to top. T: tobermorite, P: Ca(OH)₂, Q: quartz, MS: monosulfate-14, HE: hydroxyllellstadite, A: anhydrite. [1]

The second pathway is that with hydroxyllellstadite (HE : Ca₁₀(SiO₄)₃(SO₄)₃(OH)₂) as a calcium source. HE is an intermediate material formed with sulfur released from monosulfate-14 (MS: Ca₄Al₂O₆(SO₄)·14H₂O), as indicated in Fig. 3. In a model system using high-purity reagents, it has been reported that HE reacts with dissolved quartz to form tobermorite and anhydrite [3] (formula (2)).

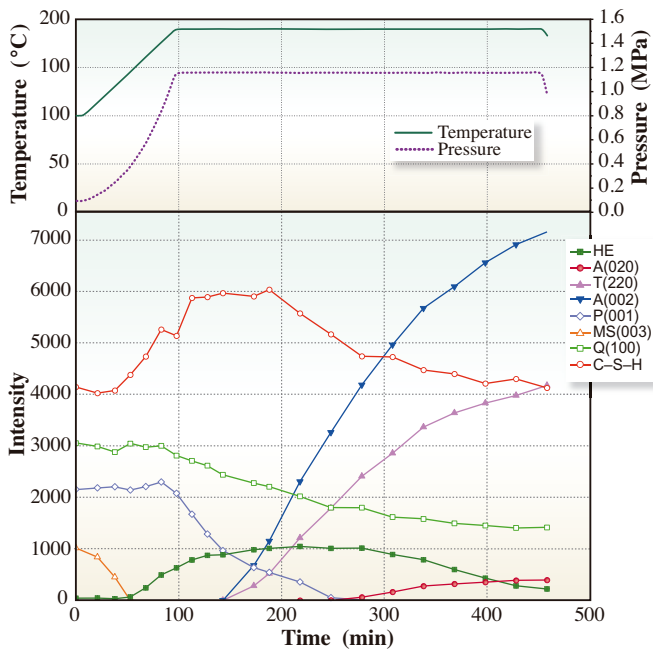
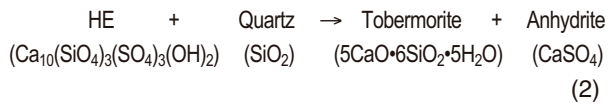


Fig. 3. Top: Time dependence of the temperature and the pressure inside the cell during the autoclave process. Bottom: Time dependence of the intensities of the major constituents during the autoclave process. [1]

Figure 3 shows the decrease in the amount of HE, and the increase in the amount of anhydrite occurs simultaneously. This is considered to be strong evidence of the occurrence of the tobermorite formation via HE in a real manufacturing process. It should be pointed out that the amount of non-crystalline C-S-H starts to decrease much earlier than that of HE, suggesting the difference in reactivity between these two intermediate materials.

The newly developed autoclave cell, combined with high-energy transmission XRD, can be used for *in situ* analyses of hydrothermal reactions. By using a CCD or a photon-counting pixel array detector, it is possible to conduct much faster measurements, which enables the discussion of the reaction kinetics.

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References

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