

## Effect of Al<sup>3+</sup> on Tobermorite Crystallinity

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**Abstract:** The difference between the systems of CaO-SiO<sub>2</sub>-H<sub>2</sub>O and CaO-SiO<sub>2</sub>-Al(OH)<sub>3</sub>-H<sub>2</sub>O, was studied, especially the effect of Al<sup>3+</sup> on the crystallinity of tobermorite was focussed. As a result, in the system of CaO-SiO<sub>2</sub>-H<sub>2</sub>O, tobermorite formed early, however, with reaction time forward, tobermorite was replaced by xonotlite. So far as CaO-SiO<sub>2</sub>-Al(OH)<sub>3</sub>-H<sub>2</sub>O was concerned, hydrothermal reaction was carried out under the same condition as CaO-SiO<sub>2</sub>-H<sub>2</sub>O to study the morphological changes of tobermorite crystals. It was found that Al<sup>3+</sup> accelerated the crystal growth of tobermorite to some extent and was in favor of platy crystals. Moreover, with the Al<sup>3+</sup> content increasing in the starting material, the morphology of tobermorite did not change magnificently, but platy crystals became more and more eminent. As soon as the Al<sub>2</sub>O<sub>3</sub> content was over 15.6%, synthetic mineral greatly changed in structure and turned into hibschite different from 1.1 nm tobermorite. Obviously, xonotlite was not apt to form in the presence of Al<sup>3+</sup>.

**Key words:** calcium silicate hydrate; xonotlite; 1.1 nm tobermorite; hibschite

Tobermorite was one of the hydrous calcium silicate minerals, which was first discovered by Heddle at Tobermory in Scotland. Tobermorite was classified into three groups based on the basal spacing. Among them, 1.1 nm tobermorite was most easily synthesized by hydrothermal reaction using SiO<sub>2</sub> and CaO as starting materials and also known to be a main crystal phase of autoclaved lightweight concrete. For 1.1 nm tobermorite, many references were published. Kaori Sasaki studied the mechanochemistry of CaO-SiO<sub>2</sub>-H<sub>2</sub>O system [1]. Yasuo Arai investigated the effect of Mg(OH)<sub>2</sub>, Sr(OH)<sub>2</sub>, Al(OH)<sub>3</sub> and Fe(OH)<sub>2</sub> on crystal shape and xonotlite with tobermorite [2]. Following the phenomenon found out in 1964 that 1.1 nm tobermorite was decomposed through the action of CO<sub>2</sub> under moisture conditions into calcium carbonate (aragonite, vaterite or calcite and silica gel), Yasuhisa Ikeda indicated the structural change of silicate anions with carbonation [3], while Tamotsu Yasue clarified that the carbonation of 1.1 nm tobermorite from slag was controlled considerably comparing with that of silica stone-Ca(OH)<sub>2</sub>-AlCl<sub>3</sub> system [4]. This paper was further made to investigate the difference between CaO-SiO<sub>2</sub>-H<sub>2</sub>O and CaO-SiO<sub>2</sub>-Al(OH)<sub>3</sub>-H<sub>2</sub>O, the characteristics of synthetic minerals, and the best addition of Al<sup>3+</sup>, etc..

### 1 Experimental

Two experiments were carried out: the one was CaO-SiO<sub>2</sub>-H<sub>2</sub>O, and the other CaO-SiO<sub>2</sub>-Al(OH)<sub>3</sub>-H<sub>2</sub>O. To avoid the effect from impurities, starting materials were available from chemical agents, *i.e.*, calcium ma-

terial was supplied by CaO, siliceous material by quartz SiO<sub>2</sub>, and Al<sup>3+</sup> by Al(OH)<sub>3</sub>. Quartz was ground and passed 280 mesh. All materials were mixed in a mole ratio of CaO/SiO<sub>2</sub> of 0.8; and the mass of Al(OH)<sub>3</sub> was 3% mass of CaO and SiO<sub>2</sub>. Taken out 10 g of such mix, water was added until the mole ratio of water/solid set at 15:1. Then, the mix was emptied into autoclave of 2 000 ml. The reaction was held at 220°C for 5–10 h with 500 r/min agitation. Afterwards, the sample from the autoclave was filtered, and then reacted with 2 mol/L NaOH solution for 0.5 h. After the treatment, the selected sample was washed several times with deionized water. The washed and filtered sample was transferred to a beaker and dried at 150°C for 12 h for analysis. The additions of Al(OH)<sub>3</sub> were 3%, 5%, 8%, 10%, 15%, 20%, 30% and 50% in mass fraction, respectively.

### 2 Results

#### 2.1 CaO-SiO<sub>2</sub>-H<sub>2</sub>O system

Through SEM, synthetic minerals, which were obtained by 6 h reaction in autoclave, included well-crystallized platy tobermorite — 1.1 nm tobermorite by XRD, with less fibrous xonotlite. When reaction time, however, was extended to 10 h, synthetic minerals, by means of SEM, consisted of a lot of fibrous xonotlite but less platy tobermorite. At the same time, the final minerals, from 3 h reaction in autoclave, essentially embraced heterogeneous colloid. Its composition, based on XRD, basically complied with C-S-H(I), mapped out by Kaori Sasaki [1].

## 2.2 CaO-SiO<sub>2</sub>-Al(OH)<sub>3</sub>-H<sub>2</sub>O system

When 3% of Al(OH)<sub>3</sub> in mass fraction was added, in the CaO-SiO<sub>2</sub>-Al(OH)<sub>3</sub>-H<sub>2</sub>O system, quartz didn't disappear in the reaction system until 6 h later by the results of XRD. SEM showed that the synthetic mineral was in the form of plate. The longer the reaction time lasted, the more eminent platy mineral presented. Basically, no fibrous mineral distributed.

Meanwhile, when 5% of Al(OH)<sub>3</sub> in mass fraction was added in the CaO-SiO<sub>2</sub>-Al(OH)<sub>3</sub>-H<sub>2</sub>O, platy mineral — tobermorite by SEM — was obtained. With the content of Al(OH)<sub>3</sub> going up, as in 8%, 10%, 15%, 20%, 30%, and 50% in mass fraction, the synthetic mineral turned up in plate, but more eminent was the platy mineral.

The synthetic mineral, following different content of Al(OH)<sub>3</sub>, had the composition shown in **table 1**.

**Table 1** Chemical analysis of synthetic mineral from different Al(OH)<sub>3</sub> contents. %

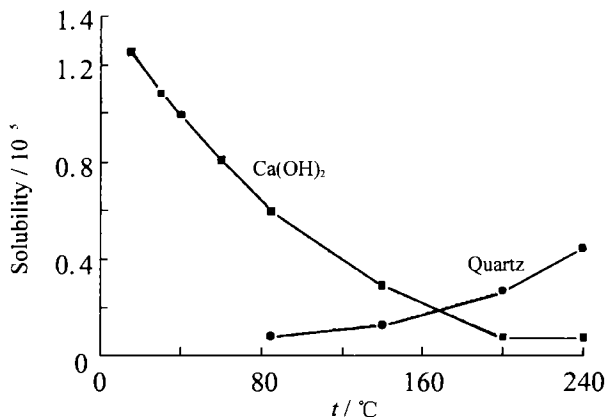
$W_{\text{Al(OH)}_3}$	$W_{\text{CaO}}$	$W_{\text{SiO}_2}$	$W_{\text{Al}_2\text{O}_3}$	$W_{\text{H}_2\text{O}}$
5	31.01	32.96	6.30	11.53
10	34.36	34.74	4.79	11.84
20	39.13	37.08	2.49	9.80
30	33.55	32.01	8.88	9.88
50	28.80	31.96	16.41	12.04

## 3 Analysis and Discussion

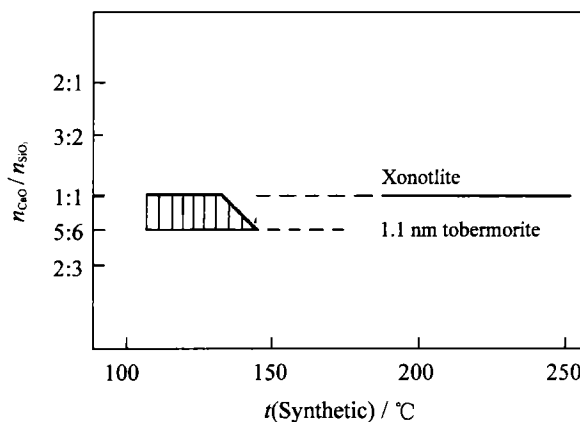
### 3.1 CaO-SiO<sub>2</sub>-H<sub>2</sub>O system

Based on both XRD and SEM, CaO-SiO<sub>2</sub>-H<sub>2</sub>O, at the same temperature and pressure, produced platy tobermorite at first. With reaction time lasting, tobermorite was replaced with xonotlite. The factors, attributed such a result, was explained as follows.

At the beginning of hydrated reaction, the solubility of CaO was larger than that of SiO<sub>2</sub> in a large-scale way (**figure 1**). Consequently, the mole ratio of CaO/SiO<sub>2</sub> stood high, and C-S-H colloid or semi-colloid was formed with a higher mole ratio of CaO/SiO<sub>2</sub>. As shown in figure 1, with reaction time up gradually, both temperature and pressure in the autoclave rose simultaneously, and the solubility of SiO<sub>2</sub> overweighed that of CaO. As a result, the mole ratio of CaO/SiO<sub>2</sub> turned lower, and tobermorite, with a lower mole ratio of CaO/SiO<sub>2</sub>, appeared. Meanwhile, based on synthetic temperatures for both tobermorite and xonotlite as shown in **figure 2**, when the mole ratio of CaO/SiO<sub>2</sub> closed at 5:6, and temperature fluctuated from 175 to 190°C, tobermorite crystallized, while the mole ratio of CaO/SiO<sub>2</sub> ended at 1:1, and temperature kept constant over 200°C,



**Figure 1** Solubilities of both quartz SiO<sub>2</sub> and CaO at various temperatures.



**Figure 2** Synthetic temperatures of both tobermorite and xonotlite.

xonotlite was formed. Therefore, it was easily concluded that tobermorite formed in a lower temperature range while xonotlite, on the contrary, showed up in a high temperature range. Elevated temperature, in this experiment, was held at 220°C, and it was a range where xonotlite was produced. This was why tobermorite, following the higher and higher elevated temperature, was replaced with xonotlite.

### 3.2 CaO-SiO<sub>2</sub>-Al(OH)<sub>3</sub>-H<sub>2</sub>O system

**Figure 3** showed the infrared spectra of the mineral in the system of CaO-SiO<sub>2</sub>-Al(OH)<sub>3</sub>-H<sub>2</sub>O with Al(OH)<sub>3</sub> mass fraction of 3%. As seen, a part of Al<sup>3+</sup> took over some structure of synthetic mineral. In other words, Al<sup>3+</sup>, in the reaction of both CaO and SiO<sub>2</sub>, dispersed in Si-O structure, or substituted part of Si<sup>4+</sup> owing to the addition of Al(OH)<sub>3</sub> [4].

Based on XRD for the addition of Al(OH)<sub>3</sub> 5%, 8%, 10%, 15%, 20%, 30%, and 50% in mass fraction respectively, some conclusions were drawn as follows.

(1) When Al(OH)<sub>3</sub> of 10% in mass fraction was added, another mineral by XRD, hydrated calcium aluminum silicate, showed relatively strong diffraction peak,

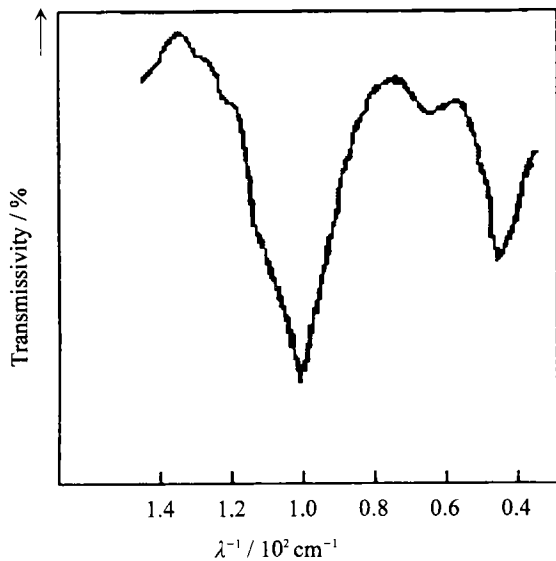


Figure 3 Infrared spectra for synthetic mineral in the system of  $\text{CaO-SiO}_2\text{-Al(OH)}_3\text{-H}_2\text{O}$  with 3%  $\text{Al(OH)}_3$  in mass fraction.

although, no other else minerals but tobermorite presented while the addition of  $\text{Al(OH)}_3$  closed at 5%–8% in mass fraction.

(2) Main diffraction peaks, related to tobermorite, were clearly indicated until the addition of  $\text{Al(OH)}_3$  reached 20% in mass fraction. This meant that  $\text{Al}^{3+}$ , when addition of  $\text{Al(OH)}_3$  was less than 20% in mass fraction, partly took the place of  $\text{Si}^{4+}$ , and impeded into the crystal structure of tobermorite, but did not result in the morphological change of tobermorite into hibschite.

(3) When the addition of  $\text{Al(OH)}_3$  was up to or over 30% in mass fraction, 1.1 nm tobermorite basically disappeared in XRD, and main diffraction peaks were controlled by hibschite.  $\text{Al}^{3+}$  thoroughly changed the structure of tobermorite, and the newly crystallized mineral (hibschite) possessed a kind of structure different from 1.1 nm tobermorite. Consequently, the optimum addition of  $\text{Al(OH)}_3$ , accelerating the crystallinity of tobermorite but not resulting in change of its structure, was limited to 30% in terms of  $\text{Al(OH)}_3$  in mass fraction.

Besides, as shown in table 1, the more  $\text{Al(OH)}_3$  was added, the less  $\text{Al}^{3+}$  was involved in the structure of tobermorite. However, when the addition exceeded 20%, more  $\text{Al}^{3+}$  came into the structure of tobermorite.

### 3.3 Comparison of $\text{CaO-SiO}_2\text{-H}_2\text{O}$ with $\text{CaO-SiO}_2\text{-Al(OH)}_3\text{-H}_2\text{O}$

As shown aforesaid, two systems,  $\text{CaO-SiO}_2\text{-H}_2\text{O}$

and  $\text{CaO-SiO}_2\text{-Al(OH)}_3\text{-H}_2\text{O}$ , differed from each other in mineral formation. The former consisted of xonotlite and tobermorite, while the latter includes residual quartz and platy tobermorite. Such a conclusion was summarized in figure 4.

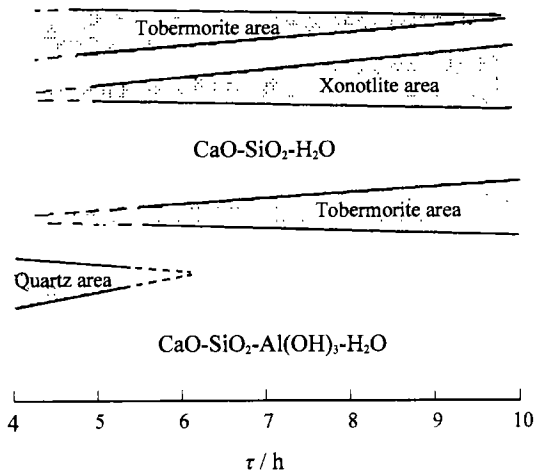


Figure 4 Phases in the reacted sample in different systems through different reaction time with 3%  $\text{Al(OH)}_3$  in mass fraction.

## 4 Conclusions

(1) Considering the synthetic reaction of  $\text{CaO-SiO}_2\text{-H}_2\text{O}$ , tobermorite crystallized early and followed xonotlite. With reaction time lasting, more xonotlite was available, although, tobermorite run on the contrary as for crystallinity.

(2) The presence of  $\text{Al}^{3+}$  interfered in the formation of fibrous xonotlite, but favored the crystallinity of platy tobermorite.

(3) The addition of  $\text{Al(OH)}_3$ , facilitating the crystallinity of tobermorite, was optimum limited in 30% in terms of  $\text{Al(OH)}_3$  in mass fraction.

## References

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