

Influence of Hydrothermal Synthesis Conditions on the Formation of Calcium Silicate Hydrates: from Amorphous to Crystalline Phases

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Abstract: Hydrothermal treatment has been widely applied in the synthesis of well crystalline calcium silicate hydrate (CSH), such as tobermorite and xonotlite. However, both morphology and crystallinity of CSH are greatly affected by the conditions of hydrothermal treatment including siliceous materials, temperature increase rate and isothermal periods. In this study, the influence of hydrothermal conditions on the growth of nano-crystalline CSH was investigated based on XRD analysis. Results showed that siliceous materials with amorphous nature (*i.e.*, nano silica powder) are beneficial to synthesize pure amorphous CSH, while the use of more crystallized siliceous materials (*i.e.*, diatomite and quartz powder) leads to producing crystalline CSH. Results also indicate that the formation of tobermorite and xonotlite is greatly affected by the temperature rise rate during hydrothermal treatment.

Key words: hydrothermal synthesis; calcium silicate hydrate; amorphous; crystalline; XRD analysis; structural development

1 Introduction

Hydrothermal treatment has been widely employed in synthesizing calcium silicate hydrate (CSH, $C = CaO$, $S = SiO_2$, and $H = H_2O$). The reaction is usually based on $CaO-SiO_2-H_2O$ system with solid materials containing SiO_2 and CaO ^[1,2]. Water in hydrothermal synthesis acts as a medium which can depress the temperatures of solids and liquids, lower down its viscosity, break the crystal lattice of the substance and further improve the solubility of the ions^[3]. Finally, the hydrothermal product forms with increased grain size. Due to the presence of water, the transport of ions becomes much easier. Seeding and nucleation process is thus accelerated^[4]. In general, the formation of product is determined by one or several of the following factors: solubility of the materials (or ions), transporting rate of

ions, formation of complex substance, nucleation rate and growth of crystals. In this case, the crystallinity and morphology of hydrothermal products of the solid materials are dependent on the hydrothermal treatment conditions, such as Ca/Si molar ratios, isothermal temperatures, and water to solid ratios^[2,5,6].

Taylor^[7] has summarized the formation of crystalline calcium silicate hydrates under various conditions. The diagram was later modified by Meller^[8], as shown in Fig.1. Poorly ordered CSH is usually formed at a relatively low temperature ($< 120\text{ }^\circ\text{C}$), while more crystallized structures, such as 11 Å-tobbermorite, xonotlite and gyrolite, are usually stable at relatively higher temperature ($> 150\text{ }^\circ\text{C}$). Amorphous nature of CSH including C-S-H gel, C-S-H (I) and C-S-H (II), is a thermodynamic metastable phase (dash in C-S-H represents the non-stoichiometry of the substance). For C-S-H, a diffused peak at the d -spacing ranging from 0.27 to 0.31 nm can be observed and somehow a sharper one at 0.182 nm as determined by X-ray diffraction (XRD)^[5]. With the help of an atomic force microscope (AFM), one can observe that C-S-H is composed of fundamental spherical globules^[9]. In terms of crystallized calcium silicate hydrate, tobermorite ($Ca_5Si_6H_2O_{18}\cdot 4H_2O$) and xonotlite ($Ca_6Si_6O_{17}(OH)_2$) are the most popular

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products for the practical application attributed to their stabilized thermal properties and porous structure. The former one belongs to the family of phases with infinite chains of silicon tetrahedra between layers of Ca atoms. It includes riversideite, tobermorite and plombierite with interlayer distance of 9.6, 11.3 and 14.6 Å, respectively^[1]. Xonotlite is a natural mineral developed under the geothermal condition, but can also be synthesized when the starting materials with Ca/Si molar ratio of 1:1 are treated at 150- 400 °C^[10].

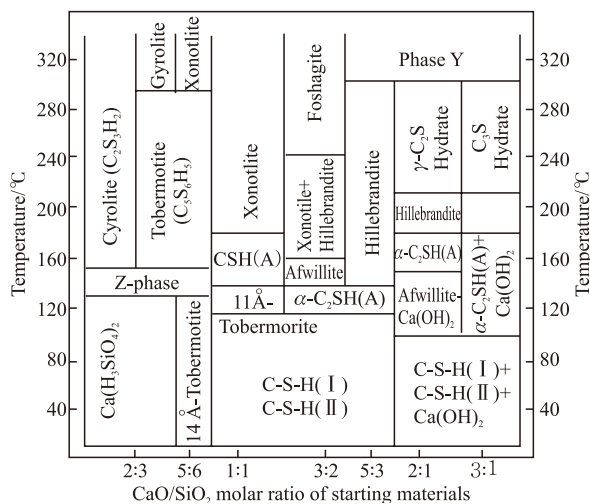


Fig.1 CaO-SiO₂-H₂O phases from 50 to 320 °C according to Taylor^[7] and Meller *et al*^[8]

Furthermore, it has also been reported that siliceous materials have great effect on the components of hydrothermal products^[11]. This is because the concentration of $[\text{SiO}_4]^{4-}$ in the solution is significant to the Ca/Si ratio in CSH solids^[12-14]. Jing *et al*^[15] synthesized tobermorite-based porous material from municipal incineration bottom ash at 180 °C for 12 hours. In that study, the solubility of silica was improved by NaOH solution. Different types of steel slags have also been used to produce calcium silicate hydrate^[16]. Besides, the morphology of CSH is sensitive to the stirring rate for a suspension slurry treatment. More porous surface of the particles could be formed at a stirring rate of 90 rpm than other rates as reported by Guan and his co-authors^[17]. Therefore, micro-porous spherical particles of xonotlite could be provided at a certain stirring speed during hydrothermal treatment^[18].

This study aimed to investigate the structural development of CSH under varied hydrothermal conditions including siliceous materials, isothermal periods and temperature increase rates. The synthesis was carried out at the isothermal temperatures of 120 and 185 °C, respectively. Crystallinity and crystallite size of CSH were also discussed according to XRD analysis.

2 Experimental

2.1 Materials

Calcium silicate hydrate was prepared by hydrothermal synthesis method with stoichiometric amounts of calcium oxide (CaO) and siliceous materials (mainly containing SiO₂). The calcium oxide with 88.83 wt% CaO supplied by Shandong Company was calcined from limestone at about 800 °C. Its specific surface area by Blaine permeability test was 406 m²/kg. Three different types of siliceous materials were used for the synthesis, including nano-silica powder, quartz powder and diatomite powder, respectively. The nano-silica powder was reactive SiO₂ (China BlueStar Shenyang Chemical) with a BET specific area of 181 m²/g as reported by the producer. It was dried at 105 °C to remove the adsorbed water on the particle surface before use. Quartz powder with SiO₂ content of 99.09% was milled from α-quartz sand. Blaine permeability surface area was 521 m²/kg. The diatomite (Zhedong Diatomite Products Co., Ltd, Zhejiang) contained 89.64 wt% SiO₂ and 4.12 wt% Al₂O₃. The main crystalline phases were cristobalite and albite. Its BET specific surface area was 65 m²/g.

2.2 Synthesis of calcium silicate hydrate

Mixtures of calcium oxide and siliceous materials were treated in the autoclave (2 L, Weihai Chemical Machinery Co., Ltd., China). The water solid weight ratio was 10, and Ca/Si molar ratios of the starting materials of 1.0 and 0.83 were applied, respectively. The mixtures were treated as stirred suspensions (400 rpm) at varied curing temperatures (120 and 185 °C and isothermal periods (1 to 24 h). The suspensions were cooled to around 50 °C in 10 to 20 minutes before filtered. It was followed by oven drying at 80 °C to a constant weight (about 48 h). As mentioned, different siliceous materials including nano silica powder, diatomite and quartz powders were applied. Besides, two temperature rates, 0.75 and 1.7 °C/min, were applied when calcium oxide and quartz powder were used as source materials. It should be mentioned that tap water instead of distilled water was applied in the synthesis because the former can accelerate the formation of amorphous calcium silicate hydrate^[19].

The products were divided into three groups depending on the siliceous materials. Series 1 (S1) was prepared from the nano silica and calcium oxide. Those from series 2 (S2) were synthesized from the mixtures of diatomite and calcium oxide, and series 3 (S3) were

Table 1 Parameters of hydrothermal synthesis of calcium silicate hydrate (S1)

| Sample index | Materials | | | | Hydrothermal treatment | | |
|--------------|---------------------|----------------------|-------------|-----------------|------------------------|---------------------|---------------------------|
| | Siliceous materials | Calcareous materials | Ca/Si ratio | Water/solid/wt% | Temperature/°C | Isothermal period/h | Temperature rate/(°C/min) |
| NS10 | Nano silica | CaO | 1.0 | 10 | 120 | 10 | 1.7 |

Table 2 Parameters of hydrothermal synthesis of calcium silicate hydrate (S2)

| Powder index | Materials | | | | Hydrothermal curing | | |
|--------------|---------------------|----------------------|-------------|-----------------|---------------------|---------------------|---------------------------|
| | Siliceous materials | Calcareous materials | Ca/Si ratio | Water/solid/wt% | Temperature/°C | Isothermal period/h | Temperature rate/(°C/min) |
| D10 | Diatomite | CaO | 1.0 | 10 | 120 | 10 | 1.7 |
| D1 | Diatomite | CaO | 1.0 | 10 | 185 | 1 | 1.7 |
| D2 | Diatomite | CaO | 1.0 | 10 | 185 | 2 | 1.7 |
| D4 | Diatomite | CaO | 1.0 | 10 | 185 | 4 | 1.7 |
| D6 | Diatomite | CaO | 1.0 | 10 | 185 | 6 | 1.7 |

Table 3 Parameters of hydrothermal synthesis of calcium silicate hydrate (S3)

| Powder index | Materials | | | | Hydrothermal curing | | |
|--------------|---------------------|----------------------|-------------|-----------------|---------------------|---------------------|---------------------------|
| | Siliceous materials | Calcareous materials | Ca/Si ratio | Water/solid/wt% | Temperature/°C | Isothermal period/h | Temperature rate/(°C/min) |
| Q1-10 | Quartz | CaO | 1.0 | 10 | 120 | 10 | 0.75 |
| Q1-1 | Quartz | CaO | 1.0 | 10 | 185 | 1 | 0.75 |
| Q1-2 | Quartz | CaO | 1.0 | 10 | 185 | 2 | 0.75 |
| Q1-4 | Quartz | CaO | 1.0 | 10 | 185 | 4 | 0.75 |
| Q1-24 | Quartz | CaO | 0.83 | 10 | 185 | 24 | 0.75 |
| Q2-10 | Quartz | CaO | 1.0 | 10 | 120 | 10 | 1.7 |
| Q2-2 | Quartz | CaO | 1.0 | 10 | 185 | 2 | 1.7 |
| Q2-4 | Quartz | CaO | 1.0 | 10 | 185 | 4 | 1.7 |
| Q2-6 | Quartz | CaO | 1.0 | 10 | 185 | 6 | 1.7 |
| Q2-24 | Quartz | CaO | 0.83 | 10 | 185 | 24 | 1.7 |

Note: Q1 denotes the products synthesized at the curing rate of 0.75 °C/min, and Q2 represents the curing rate of 1.7 °C/min.

the hydrothermal products of quartz powder and calcium oxide. More details of the hydrothermal treatment for calcium silicate hydrate are shown in Tables 1 to 3.

2.3 Microstructural characterization

The microstructural development of CSH under different hydrothermal synthesis conditions was characterized by X-ray diffraction (XRD, RigakuD/max-1200, Cu K α radiation, λ of K α_1 = 1.540 6 Å). The scanning rate was 2 °C/min with 2θ ranging from 5 to 70° and a step size of 0.02°.

Furthermore, crystallinity (η) and crystallite size of the phases were calculated from the XRD profiles. Normally, crystallinity is evaluated according to a reference sample which is 100% amorphous or 100% crystallized^[20]. However, it is suggested that quantitative analysis can also be conducted by a reference intensity ratio (RIR) using either internal or external standard methods by the application of MDI Jade (Ma-

terials Data Incorporated)^[17,21,22]. The crystallinity can be estimated based on the diffraction area and scattering area from the XRD profiles even if no reference sample is used. The expression is shown as follows:

$$\eta = \frac{A_{ic}}{A_{it}} \times 100\% = \frac{A_{ic}}{A_{ic} + A_{ia}} \times 100\% = 1 - \frac{A_{ia}}{A_{ic} + A_{ia}} \quad (1)$$

where A_{it} is the total area of all peaks, A_{ic} is the area of the crystalline diffraction peaks, and A_{ia} represents the area of scattering of amorphous phases. The background was subtracted before profile fitting. The area (in counts) is integration results of the peak intensity after profile fitting.

Scherrer equation^[23] is well known to evaluate the crystallite size or grain size of the nano crystalline bulk materials according to XRD profiles because the crystallite size can broaden the peaks. The expression is:

$$L = \frac{K\lambda}{\beta_{2\theta} \cos\theta} \quad (2)$$

where L is the average crystallite size, λ is the X-ray wavelength in nanometer (nm), $\beta_{2\theta}$ represents the peak width of the diffraction peak profile at FWHM of 2θ resulting from small crystallite size in radians, and K is a constant related to crystalline shape factor ranged from 0.62 to 2.08, between which 0.9 is usually used based on the assumption of the spherical crystals^[24]. In addition, the lattice microstrain may also affect the peak broadening^[25], but for powdered samples, it was not taken into account.

It should be mentioned that during the analysis of crystallinity and crystallite size, Pearson-VII function is used for XRD profile fitting. The background of the XRD profiles was subtracted before calculation. Estimated standard deviation (ESD) after profile fitting was between 10% and 15%.

3 Results and discussion

3.1 Influence of Siliceous materials

The main phases of hydrothermally synthesized products from mixtures of CaO and siliceous materials are shown in Fig.2. It can be seen that the peaks at 2θ of 28-32° and 50° were present in all XRD patterns, indicating the formation of CSH^[5]. However, the phases in the products obviously relied on the type of siliceous materials. When nano silica, a reactive silicate material was used in hydrothermal synthesis (Fig.2), mainly two peaks with d -spacing of 0.300 nm and 0.182 nm were present in NS10, demonstrating the formation of amorphous CSH^[5]. There also appeared a weak peak at d -spacing of 0.324 nm as an indication of dicalcium silicate hydrate (α -C₂SH, d -spacing of 0.324, 0.530, 0.421, 0.287, 0.250, 0.218, 0.176 8 nm). However, when diatomite and quartz powder were applied as siliceous materials, a mixture of crystalline phases was shown in the products. Apart from amorphous CSH and α -C₂SH, α -SiO₂ and Ca(OH)₂ which stemmed from the starting materials were still present, indicating the uncompleted reaction.

Fig.3 shows the crystallite size and crystallinity of calcium silicate hydrate calculated according to Eqs. (1) and (2). In terms of series S1, it showed the lowest crystallinity (15.49%) and the smallest crystallite size (8.5 nm) because the main phase of NS was amorphous CSH. It demonstrates that the structure is poorly ordered and the product is nano-crystalline. With the use

of diatomite and quartz, the crystallinity of the products was higher than 80% attributed to the presence of crystalline phases. The crystallite size was above 40 nm, much higher than that of the S1 sample. Compared with the sample from S3 (sample Q2-10), the using of diatomite in hydrothermal synthesis accelerated the formation of CSH.

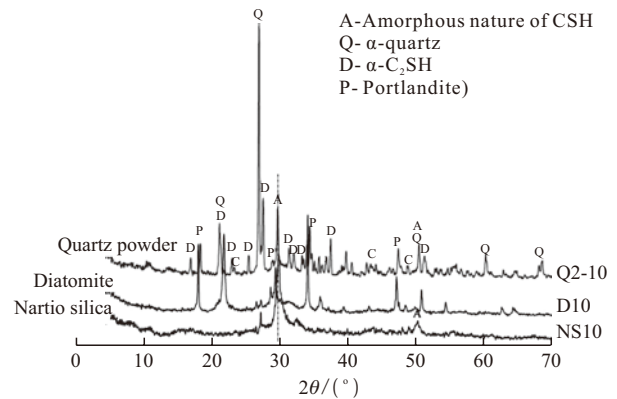


Fig.2 XRD patterns of the products synthesized from the mixture of CaO and different siliceous materials treated at 120 °C for 10 h with nano silica, diatomite, and quartz powder, respectively

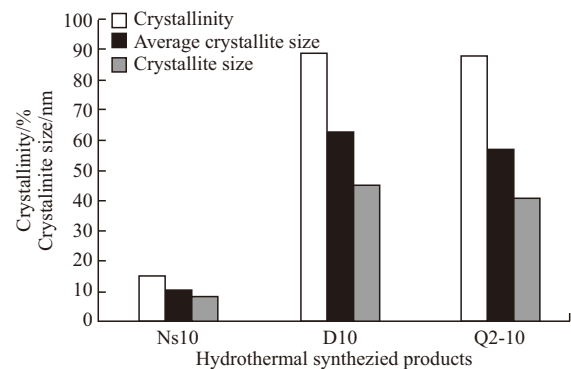


Fig.3 Crystallinity and crystallite size of calcium silicate hydrate at 120 °C for 10 h from calcium oxide and siliceous materials of nano silica (NS10), diatomite (D10), and quartz powder (Q2-10), respectively

Therefore, the formation of CSH is highly dependent on the reactivity of siliceous materials. It is in good agreement with the investigation conducted by Greenberg^[26] and Karatepe *et al*^[11] who pointed out that the dissolution rate of silica in a siliceous material is the rate limiting step for the formation of calcium silicate hydrate. The reactive SiO₂ is more beneficial to the formation of amorphous CSH because of its huge surface area and presence surface Si-OH groups. Those hydrogen groups on the surface of nano silica particles will provide numerous condensation sites^[27], resulting in the rapid consumption of Ca(OH)₂ in the suspension. It is also shown that the diatomite is more reactive than quartz powder due to its porous structure, thereby to

produce more CSH.

3.2 Isothermal periods

The formation of CSH is also known to be dependent on the isothermal period^[28]. In this section, the influence of treatment period on the formation of CSH was studied by using diatomite and quartz powders as siliceous materials (S2 and S3), respectively. Results are shown in Figs.4 to 6. For S2, the main products were amorphous CSH and tobermorite (Fig.4(a)). The appearance of tobermorite was ascribed to the presence of peak at 1.13 nm. Calcite was also detected in all samples which was caused by carbonation during drying process. With respect to the curing periods, the dominant phase of the sample treated for 1 h (Sample D1) was amorphous CSH for the most intensive peak at d -spacing of 0.302 nm ($2\theta=29.2^\circ$). The crystallinity of the sample was 72% (Fig.5). As the reaction proceeded, the peak intensity at 2θ of 29.2° (d -spacing of 0.302 nm) greatly decreased. Instead, the intensity of peaks orientated at 0.308 nm (220) and 0.298 nm (222) which represent the formation of tobermorite increased. Consequently, the crystallinity was up to 90.6% for 6 h treatment (Sample D6). It is worthy of noting that there was a slight increment of the peak intensity at 0.113 nm (002) which is the most representative peak of tobermorite. The high intensity of peaks orientated in (220), (222) and (040), but low in (002) indicates that ($hk0$) spacing resulted from growth of structure along ab direction^[19]. For the growth of c direction which requires more order parallel to c -axis than other directions^[28], longer treatment is required. It is also interesting that xonotlite was not observed in all samples of S2 as the typical peak at d -spacing of 0.424 nm was absent. The main reason is that the presence of Al in diatomite will participate in the hydrothermal reaction to maintain the tobermorite structure by developing Al-substituted tobermorite^[19]. Therefore, diatomite is a suitable siliceous material to synthesize pure tobermorite.

Differently, when quartz powder was used as the siliceous material (series S3), in Fig.4(b) where a low temperature rate was applied ($0.75^\circ\text{C}/\text{min}$), the products in sample Q1-1 (1 h isothermal treatment) were blends of α -C₂SH, amorphous CSH, more ordered calcium silicate hydrate and α -SiO₂. As the isothermal period increased to 2 h (Q1-2), the main phases were amorphous CSH and more ordered C-S-H (I). Besides, SiO₂ was continuously consumed causing decreased peak intensity. For 4 h treatment (sample Q1-4), SiO₂ disappeared, and the product consisted of tobermorite (d -spacing of 0.113, 0.548, 0.353, 0.308, 0.298, 0.282

and 0.184 nm) and xonotlite (d -spacing of 0.855, 0.424, 0.324, 0.308, 0.282, 0.225 and 0.203 nm). It should be mentioned that the main difference between tobermorite and xonotlite is the presence of a defining tobermorite peak at 0.298 nm (222)^[28]. Both tobermorite and xonotlite were still present in sample Q1-24 when the synthesis extended to 24 h. The most intensive

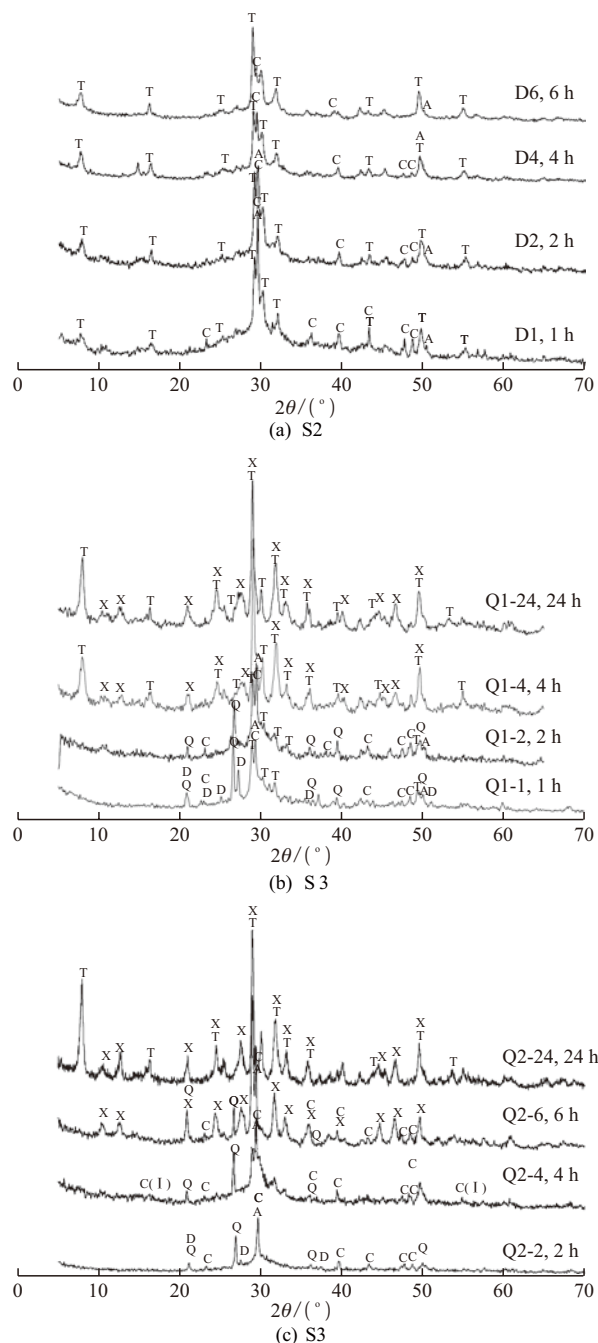


Fig.4 XRD patterns of products synthesized at 185°C with different isothermal periods: (a) siliceous materials of diatomite with curing rates of $1.7^\circ\text{C}/\text{min}$; (b) siliceous materials of quartz with curing rates of $0.75^\circ\text{C}/\text{min}$; (c) siliceous materials of quartz with curing rates of $1.7^\circ\text{C}/\text{min}$ (A-Amorphous nature of CSH, Q- α -quartz, D- α -C₂SH, P- Portlandite, T-tobermorite, X-xonotlite, C-Calcite)

peak was at 0.308 nm rather than at 1.13 nm resulting from the appearance of xonotlite. It can be seen that the crystallinity increased from 50% to 97% when the isothermal period went from 1 up to 4 h and followed by a stable value. The products were well crystallized.

When a higher curing rate (1.7 °C/min) was applied (S3), however, the proceeding of CSH development was somehow different (Fig.4(c)). For 2h treatment, the main phases in Q2-2 were amorphous CSH and unreacted SiO₂. It can be seen that there was a small amount of α -C₂SH. When the isothermal treatment increased to 4 h (sample Q2-4), amorphous CSH transformed into more ordered C-S-H (I) which was a precursor of xonotlite. It is noted that SiO₂ was still present in the product but α -C₂SH was absent. As the reaction proceeded, in sample Q2-6 (6h), the main SiO₂ peak at 0.334 nm decreased, whilst xonotlite formed as demonstrated by the marked peaks at 0.308 nm (320), 0.421 nm (400), 0.282 nm (322) and 0.184 nm (040). However, tobermorite was not present due to the lack of the defining peak at 0.298 nm. It can be inferred from the XRD pattern that the growth of xonotlite is preferred to orientate in *ab* direction similar to the development of tobermorite. When the treatment was extended to 24 h (sample Q2-24), the product was a mixture of tobermorite and xonotlite. The crystallinity of the products increased as the reaction proceeded (Fig.5). It increased from 40% to 90% when the isothermal period increased from 2 to 6 h and followed by a slight increase.

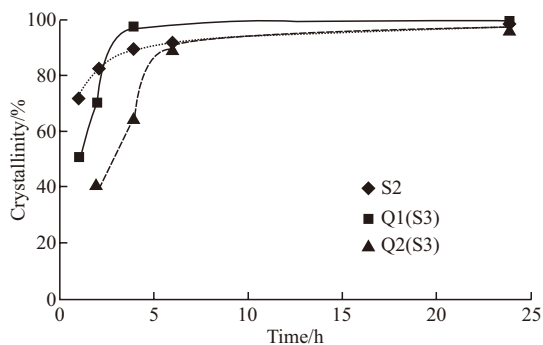


Fig.5 Crystallinity of calcium silicate hydrate of Series S2 and S3 at different curing time (Q1 represents the curing rate of 0.75 °C/min and Q2 indicates the curing rate of 1.7 °C/min)

The results show that during the hydrothermal reaction, α -C₂SH together with a small amount of amorphous CSH firstly appears due to the higher solubility of Ca(OH)₂ than SiO₂. As the reaction proceeds, the dissolution of SiO₂ continues and will further react with α -C₂SH to form CSH with a lower Ca/Si ratio. The disordered CSH transforms into more ordered structure,

such as C-S-H (I) which is a precursor of tobermorite and/or xonotlite as a result of the extended isothermal period or increased isothermal temperature. Finally, well crystallized structure is developed. Results also show that the use of diatomite can maintain tobermorite structure during the hydrothermal synthesis. It is interesting that there is a slight difference from previous studies that xonotlite is usually transformed from tobermorite structure^[28]. In this study, on the contrary, xonotlite can be directly formed from C-S-H(I) at a short period of treatment (4 h), and followed by the formation of tobermorite if a longer period of treatment was applied. Furthermore, the decrease of SiO₂ crystallite size from 43 nm (Q2-2) to 33 nm (Q2-4) demonstrates the dissolved process during hydrothermal reaction, which is in agreement with Greenberg's study^[26].

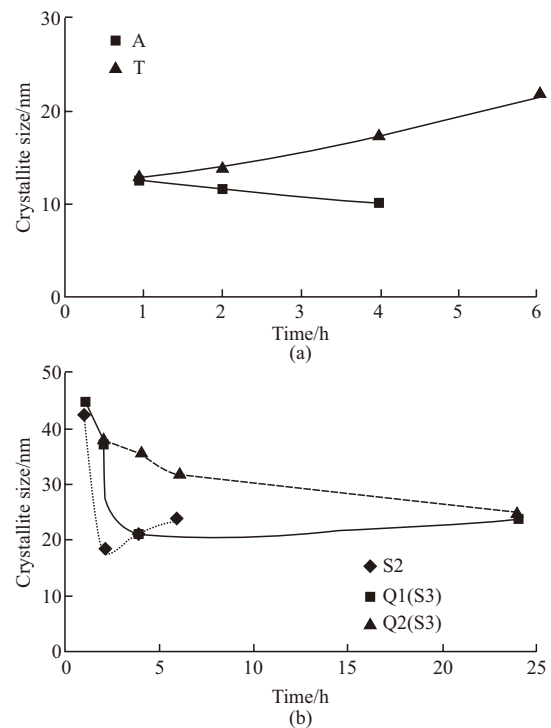


Fig.6 Influence of curing time on the crystallite size of hydrothermal synthesized products at 185 °C: (a) crystallite size of different phases of samples from mixture of CaO and diatomite (A- amorphous CSH, T- Tobermorite); (b) average crystallite size of calcium silicate hydrate from series S2 and S3

It can be seen from Fig.6(a) that the crystallites size of amorphous CSH was around 10 nm, and a slight decrease was observed when isothermal period increased from 1 to 4 h. For a longer treatment period, the crystallite size of tobermorite gradually increased from 13.1 to 21.5 nm owing to the growth in *ab* direction as mentioned previously.

3.3 Temperature increase rate

Different temperature increase rates, 0.75 °C/

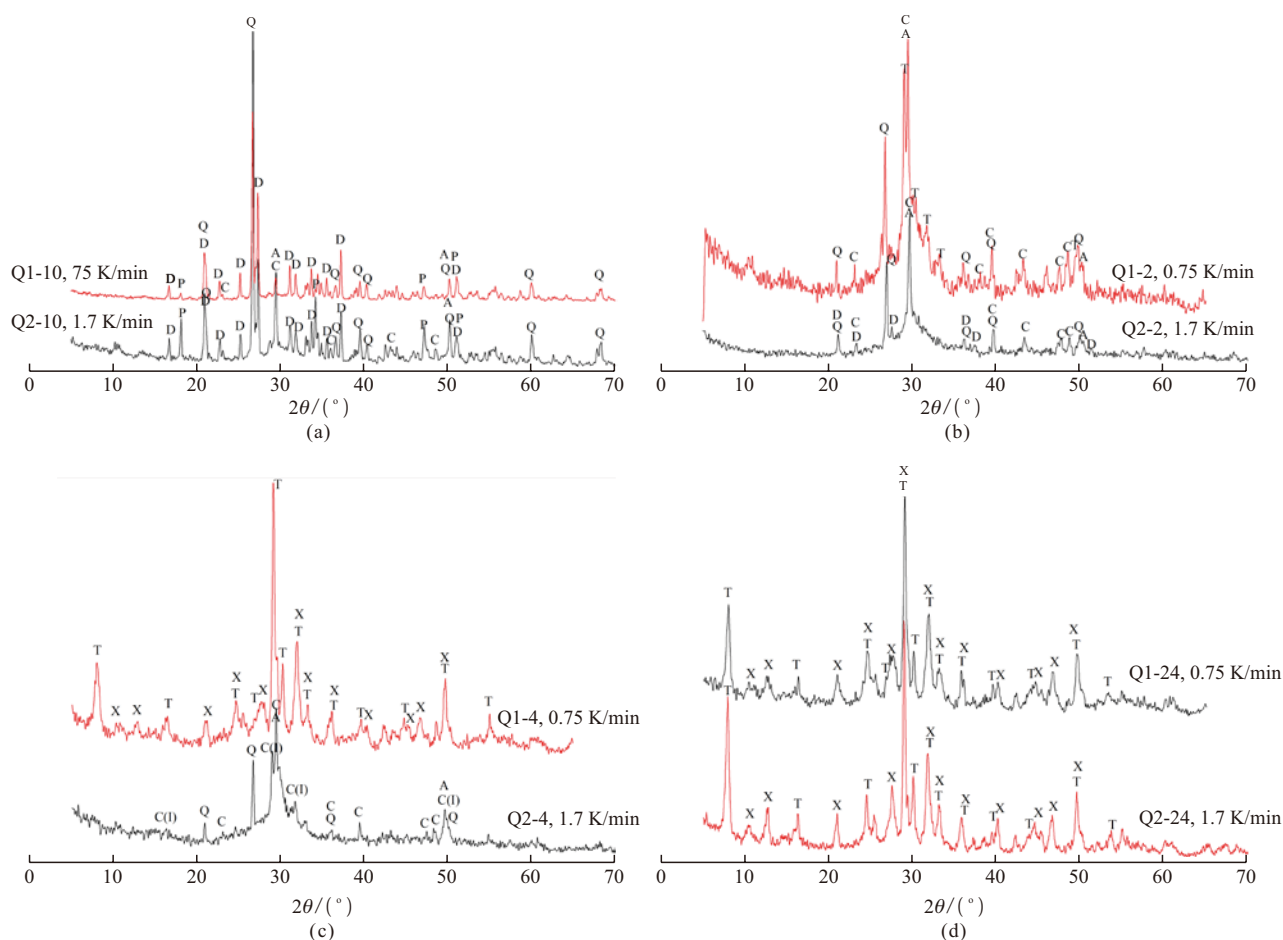


Fig.7 XRD patterns of the products synthesized with the curing rates of 0.75 °C/min and 1.7 °C/min respectively: (a) 120 °C for 10 h; (b) 185 °C for 2 h; (c) 185 °C for 4 h; (d) 185 °C for 24 h: (A-Amorphous nature of CSH, Q- α -quartz, D- α -C₂SH, P- Portlandite, C(I)- C-S-H(I), T- Tobermorite, X- xonotlite, C- Calcite)

Table 4 Crystallite size of the nanocrystals of the products synthesized with the curing rates of 0.75 °C/min (Q1) and 1.7 °C/min (Q2) for series S3 samples

| Powder samples | Crystallinity/% | Crystallite size/nm | | | | | | |
|----------------|-----------------|---------------------|------------------|---------------|----------|-----------------------------|-------------|-----------|
| | | Average | SiO ₂ | Amorphous CSH | C-S-H(I) | α -C ₂ SH | Tobermorite | Xonotlite |
| Q1-10 | 94.30 | 58.0 | 47.5 | 66.4 | - | 58.6 | - | - |
| Q2-10 | 88.07 | 57.0 | 61.4 | 41.2 | - | 42.9 | - | - |
| Q1-2 | 70.06 | 37.6 | 33.1 | 34.5 | 15.4 | - | - | - |
| Q2-2 | 39.61 | 38.2 | 43.1 | 30.0 | - | - | - | - |
| Q1-4 | 96.75 | 21.1 | - | - | - | - | 20.8 | 23.5 |
| Q2-4 | 65.77 | 35.6 | 33.1 | 9.2 | 17.8 | - | - | - |
| Q1-24 | 98.78 | 23.7 | - | - | - | - | 22.3 | 21.9 |
| Q2-24 | 97.24 | 25.0 | - | - | - | - | 25.1 | 25.2 |

min and 1.7 °C/min, were used in the CaO-SiO₂-H₂O system when quartz powder was applied as the siliceous material. Results are shown in Fig.7 and Table 4. From XRD profiles (Fig.7), it can be seen that a higher amount of CSH was produced at the lower temperature increase rate. This is attributed to the longer period for reaction in the whole hydrothermal synthesis process. Specifically, when the mixtures were treated at 120 °C (Fig.7(a)), the main products consisted of amorphous

CSH and α -C₂SH. Even though α -SiO₂ and Ca(OH)₂ were still present in these samples, their peak intensity was much lower in the sample treated at 0.75 °C/min (Q1-10) than at 1.7 °C/min (Q2-10), especially that peaks of portlandite were not pronounced in the former sample. The crystallite size in Q1-10 was related to the CSH in both amorphous and crystalline nature, while in Q2-10 it was dependent on α -SiO₂ (Table 4), despite that the two samples showed quite similar sizes.

As the temperature increased to 185 °C, the main phases in Q1-2 were amorphous CSH and more ordered C-S-H (I) (d-spacing of 0.307, 0.183, 0.167, 0.280, and 0.850 nm). The crystallite size of C-S-H (I) was only 15 nm, indicating low crystallinity. If the temperature increase rate was 1.7 °C/min, amorphous CSH was a primary phase in Q2-2. A small amount of α -C₂SH was also present due to a weak peak at 0.327 nm. The reason was that it took only two hours to increase temperature from 20 to 185 °C which was about two hours shorter than using the rate of 0.75 °C/min. Worth noting is that the crystallite size of α -SiO₂ was smaller in the sample treated at 0.75 °C/min, which is an indication of a higher amount of consumption. As the isothermal period increased to 4 h (Fig.7(c)), a mixture of tobermorite and xonotlite was in Q1-4 with temperature increase rate of 0.75 °C/min. The average crystallite size was about 20 nm. Whereas at a higher rate (1.7 °C/min), in Q2-4, the main components were amorphous CSH, more ordered C-S-H(I) and SiO₂. The dominant phase of the crystallite size was SiO₂, which was around 33 nm. Thus, a lower temperature increase rate accelerated the formation of tobermorite and xonotlite attributing to the longer reaction time in total. However, with a longer isothermal period, *i.e.*, 24 h, the effect of temperature increase rate on hydrothermal products was not obvious. The main components in both samples were tobermorite and xonotlite. Their crystallite sizes were between 22 and 25 nm (Table 4). It should be mentioned that the diffraction peak at d-spacing of 1.13 nm was more pronounced in Q2-24 than in Q1-24. It confirmed that tobermorite, compared to xonotlite, was more likely to be formed when the materials were treated at a shorter isothermal period but at a higher temperature increase rate.

4 Conclusions

In this study, the influence of hydrothermal conditions, including siliceous materials, isothermal period and curing rate, on the formation of calcium silicate hydrate was investigated. It is found that the development of calcium silicate hydrate is greatly dependent on the reactivity of SiO₂. Single phase of amorphous CSH with low crystallinity is formed at 120 °C when the reactive SiO₂ (*i.e.* nano silica powder) is used for the synthesis. Crystallized siliceous materials are more beneficial to the formation of crystalline calcium silicate hydrate attributing to the lower solubility of silicate anions. For instance, dicalcium silicate hydrate is

mainly the dominant phase when synthesized at 120 °C. At a higher temperature, compared to the quartz powder, diatomite is effective for the development of tobermorite structure, while quartz powder can accelerate the formation of xonotlite. The structure of calcium silicate hydrate is also affected by the temperature increase rate. For the same isothermal period, crystallized structure is more easily provided by a lower rate with more SiO₂ consumed than at a higher increase rate. The lower temperature increase rate, 0.75 °C/min in this study, improves the transformation of tobermorite structures from amorphous CSH, while 1.75 °C/min accelerates the development of xonotlite.

In terms of the formation of calcium silicate hydrate, dicalcium silicate hydrate initially forms due to the low solubility of SiO₂ but high solubility of Ca(OH)₂. As the reaction proceeds, more silicates are dissolved into ions and further coordinated into the silicate chain of C₂SH to form amorphous CSH with low Ca/Si. The continuous reaction will lead to the transformation of amorphous phase into more ordered structure, such as C-S-H (I) which is the precursor of tobermorite and/or xonotlite. Finally, stable structure composed by tobermorite and xonotlite is formed after a long curing period. In this study, it is also found that both tobermorite and xonotlite show a preferred orientation at 0.308 nm (*hk0*). Crystallinity of the calcium silicate hydrate ranges between 9% and 99%, and the crystallite size is approximated at 10 to 50 nm.

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