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Effect of C/S Ratio on Microstructure of Calcium Silicate Hydrates Synthesised By Solution Reaction Method

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Abstract. In this work, the calcium silicate hydrate was synthesized efficiently using the solution reaction of calcium nitrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$) and sodium nitrate ($\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$) at the C/S ratio of (0.8,1.2,1.5). The disciplinarian of C/S ratio with the calcium silicate hydrate was analyzed by XRD, SEM, IR, NMR. The experimental results showed that it could shorten the reaction time to 5 days, reduce the influence of the CO_2 in the air on the purity and ensure the quality of products controllable, when the calcium silicate hydrate was synthesized in nitrogen environment and with the ultrasonic dispersion; the d-spacing of (002),(101) and (200) decreased, the polymerization of silica tetrahedra of calcium silicate hydrate decreased 28.7%, the microstructure of calcium silicate hydrate varied from layer to irregular congeries and became denser as the C/S ratio increased from 0.8 to 1.5.

1. Introduction

The synthetic calcium silicate hydrate is regarded as a very promising new cement-based materials improver, but its performance is closely related to the synthesis process, research shows that the synthesis process, such as calcium-silicon ratio, reaction temperature, reaction time etc affects the composition and structure of calcium silicate hydrate [1, 9, 11]. Lv[1],He[2] synthesised the calcium silicate hydrate by the diatomite or fumed silica and calcium oxide and found that the polymerization of silicate tetrahedron of calcium silicate hydrate decreased as the calcium-silicon ratio increased. Zhao[14] synthesised the calcium silicate hydrate by solution reaction in the air and found that the microstructure of it transited from sheet to needle as the calcium-silicon ratio(1.0~1.7) increased. Zeng [10] synthesised the calcium silicate hydrate by silica and calcium oxide, found that its structure was more compact as the calcium-silicon ratio increased. calcium-silicon ratio affected synthesis of calcium silicate hydrate and its microstructure, previous studies more focused on hydrothermal synthesis of calcium silicate hydrate by calcium oxide and active silicon dioxide as raw material, but the process and product were complex, the minority synthesised the calcium silicate hydrate by solution reaction(7d) and investigated the effect of calcium-silicon ratio on the calcium silicate hydrate, with single testing method, longer synthetic cycle under air condition. Based on the related research, this paper synthesised the calcium silicate hydrate by solution reaction combined with ultrasonic instruments in the environment of nitrogen, in order to shorten the reaction time (5d), reduce the effect of CO_2 on the results and improve the controllability product quality etc. Combined with the XRD, SEM, IR, NMR test method to analyze the effect of products and calcium-silicon ratio on the microstructure of the calcium silicate hydrate, the relevant data can enrich the effect of calcium-silicon ratio on calcium silicate hydrate structure theories.



2. Raw Materials and Experimental Method

2.1. Raw Materials

The calcium silicate hydrate was synthesised by solution reaction with the analytically pure calcium nitrate($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$), sodium nitrate($\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$), sodium hydroxide(NaOH) and deionized water. Deionized water was prepared through the laboratory ultrapure water system.

2.2. Experimental Method

Take appropriate calcium nitrate and sodium nitrate, and then prepare 1mol/L solutions respectively. To set the calcium-silicon ratio of 0.8, 1.2, 1.5, take the volume of the solution and deionized water accurately. The deionized water, calcium nitrate solution and sodium silicate solution were added to the container sequentially, added 1~2 mL sodium hydroxide solution, adjusting the solution $\text{pH} > 12$, and then put into the water bath in 80°C , finally the mixed solution was dispersed by ultrasound instrument regularly. The synthetic calcium silicate hydrate named with CSH0.8, CSH1.2 and CSH1.5 respectively.

After the reaction was completed of, the products washed with deionized water and anhydrous alcohol (not less than 3 times), and then the products were dried in a vacuum desiccator (1~2d), finally the samples were analyzed using a variety of methods. The preparation of calcium silicate hydrate process was in figure 1.

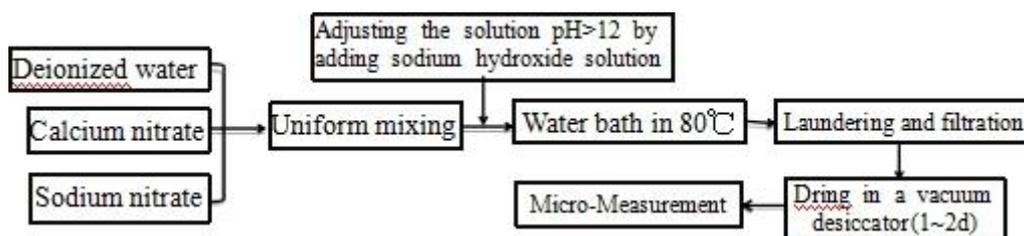


Figure 1. Process synthesis of Calcium Silicate Hydrate

3. Results and Analysis

3.1. XRD Analysis

To verify the effect of calcium-silicon ratio on the purity and structure of calcium silicate hydrate, the calcium silicate hydrate at different of calcium-silicon ratio (0.8, 1.2, 1.5) were analyzed by XRD firstly, and observed the mineral composition and corresponding purity of synthetic product, the XRD results are given in figure 2.

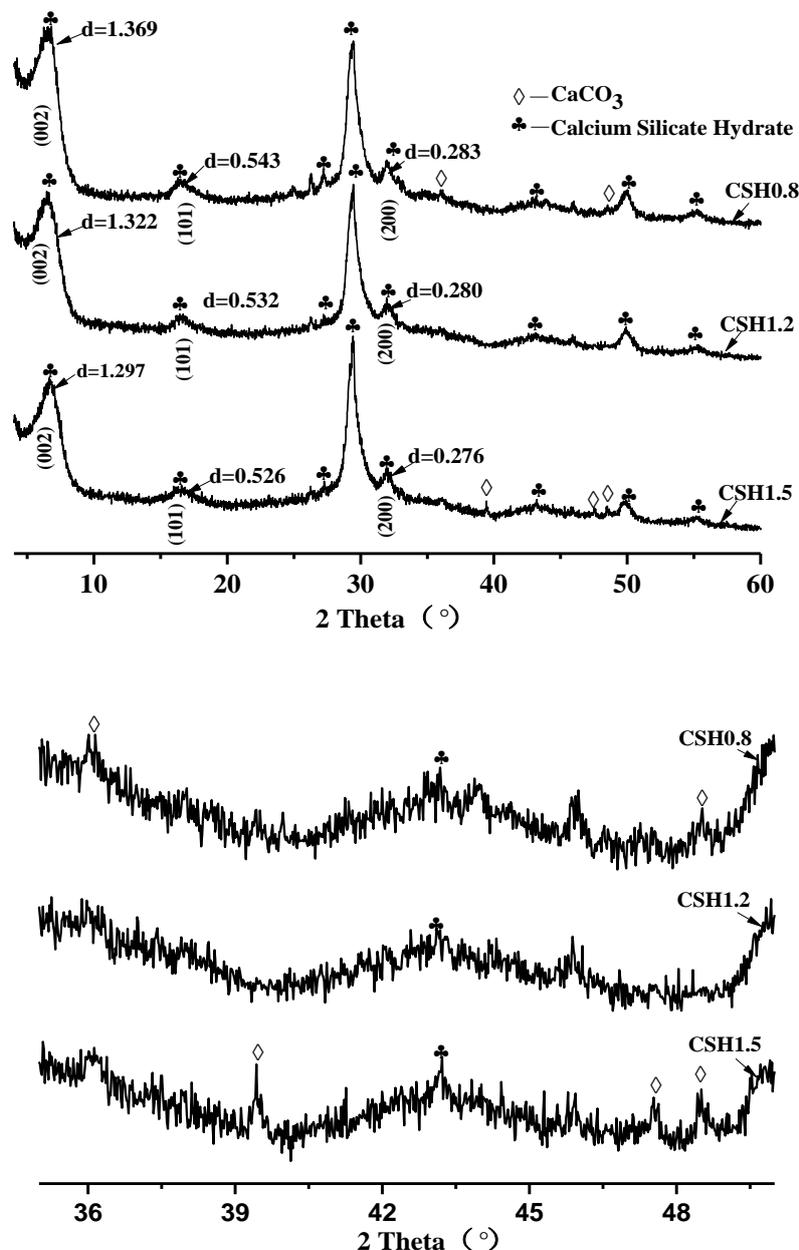


Figure 2. XRD patterns of Calcium Silicate Hydrate at different of C/S ratio.

By figure 2, the dispersion diffraction peaks at (7° and 17° nearby) and condyloma characteristics peaks at (29° and 31° nearby) in the XRD patterns showed that the synthesis of calcium silicate hydrate were materials with the crystalline and amorphous, the figure 2 (left) in $35\text{--}50^\circ$ was amplified of the figure 2 (right). When the calcium-silicon ratio were 0.8 and 1.5, there was a small amount of CaCO_3 characteristic peaks in XRD patterns, there was no CaCO_3 characteristic peaks when the calcium-silicon ratio was 1.2; When the calcium-silicon ratio was 1.5, the CaCO_3 characteristic peak was more than compared to 1.2, this was because the high calcium-silicon ratio could accelerate the early carbide of calcium silicate hydrate, those were consistent with the research conclusion of Chang [19]. Besides, The figure 2 also showed that when the calcium-silicon ratio increased from 0.8 to 1.5, the d-spacing of (002) decreased by 0.072 nm, the d-spacing of (101) decreased by 0.007 nm, the d-spacing of (200) decreased by 0.007 nm, the d-spacing of (002) changed greatly compared to the d-spacing of (101) and (200), this might be the low angle diffraction peak was more sensitive than the

high angle diffraction peak to the change of calcium-silicon ratio. With the increase of calcium-silicon ratio, the d-spacing of (002), (101) and (200) decreased, thus were identical with the research conclusion of He [2, 14], Kim [15] and Foley [17], namely with the increase of calcium-silicon ratio, the d-spacing of calcium silicate hydrate decreased.

3.2. IR Analysis

The characteristic groups (Q^1 , Q^2) of calcium silicate hydrate in the analysis of IR had specific wavenumber range (see table 1), when the structure of calcium silicate hydrate changed, its specific wavenumber would shift. The polymerization degree of silica tetrahedra of three different calcium silicate hydrate samples were analyzed by IR analysis method, in order to further clarify the effect of calcium-silicon ratio on the structural parameters of the samples.

Table 1. Formatting sections, subsections and subsubsections.

Groups	O-Si-O	Si-O-Si	Si-O(Q^2)	O-Ca-O	H ₂ O	-OH
Wavenumber/cm ⁻¹	450 around	650 around	970 around	1445 around	1640 around	3440 around

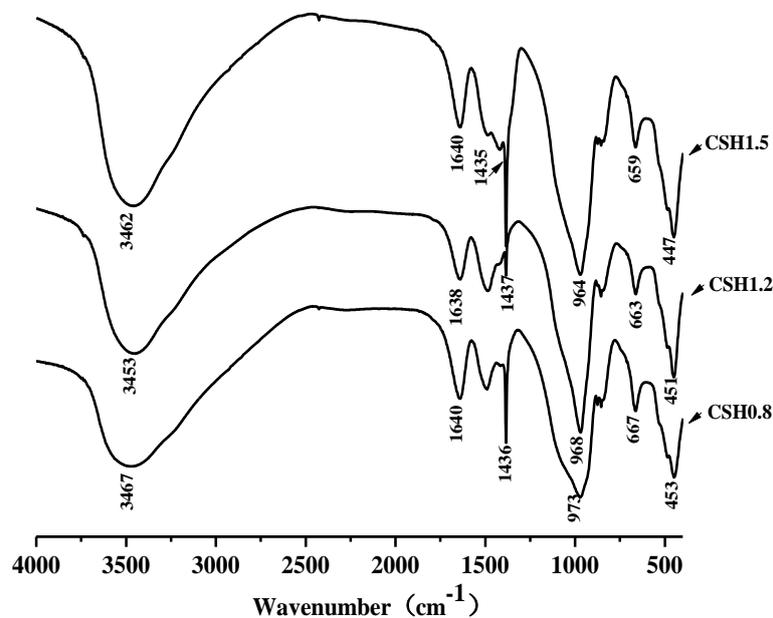


Figure 3. Infrared patterns of Calcium Silicate Hydrate at different of C/S ratio.

By figure 3, the characteristic vibration peaks position of the three kinds of calcium silicate hydrate samples were similar, and corresponding to various groups within the scope of wavenumber range, it showed that the characteristic group of the three kinds of calcium silicate hydrate by the solution reaction were basically the same. In figure 3, 970cm⁻¹, 450cm⁻¹ characteristic peaks were on behalf of Si-O-Si(Q^1) bending vibration and Si-O(Q^2) elastic vibration respectively[2]. Based on previous studies, the change of characteristic peaks position in the infrared spectrum represented the change of polymerization degree of silica tetrahedra of calcium silicate hydrate. When the calcium-silicon ratio increased from 0.8 to 1.5, the Si-O-Si(Q^1) vibration wavenumber position from 453cm⁻¹ to 447cm⁻¹, and Si-O(Q^2) vibration wavenumber position from 973cm⁻¹ to 964cm⁻¹, the position of characteristic peaks shifted to low wavenumber, showing that the polymerization degree of silica tetrahedra of calcium silicate hydrate decreased with the increase of calcium-silicon ratio, and thus were identical with the research conclusion of Yu [3], Wang [6], Yang [4], Beaudoin [16, 17], namely with the increase of calcium-silicon ratio, the polymerization degree of silica tetrahedra of calcium silicate hydrate decreased. Besides the 1436cm⁻¹, 1435cm⁻¹, 1437cm⁻¹ showed the vibration of O-Ca-O, and

there were no obvious change of the wavenumber position from CSH0.8 to CSH1.5, but the peak intensity of CSH1.2 was weak, showing that the reactants could generate calcium silicate hydrate furthest. In figure 3, the vibration of H₂O peak was near 1640cm⁻¹, this because it could not remove the interlayer water in the calcium silicate hydrate structure at 60 °C under the condition of vacuum drying.

3.3. ²⁹Si NMR Analysis

²⁹Si NMR was by measuring element chemical shift responding to element environment change. He[7], Feng [12] thought that chemical shift indicated the change of the polymerization degree of silica tetrahedra of calcium silicate hydrate, The average molecular chain length (degree of polymerization) could be calculated by ²⁹Si NMR. In the silicate minerals, the common ²⁹Si atoms chemical environment was used by Qⁿ, n=(0~4) showed the number of bridging oxygen in the silicate tetrahedron. The polymerization methods of silicon atom corresponded to different chemical shift range, and then the ²⁹Si NMR test could indicate four polymerization status in the silicate tetrahedron, table 2 listed each state chemical shift range [12].

Table 2. The ²⁹Si NMR Chemical shift of the structure unite of Qⁿ.

Types of Si-O-X	Symbol	Range/ppm
Monomer	Q ⁰	-68~-76
Dimer& chain end groups	Q ¹	-76~-82
Chain middle groups	Q ²	-82~-88
Layers & branched chain	Q ³	-88~-98
Three-dimensional networks	Q ⁴	-98~-129

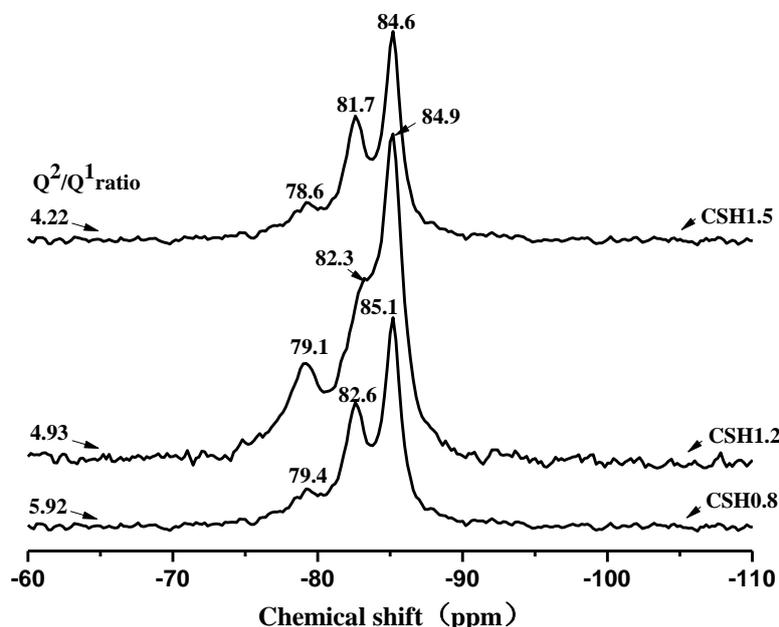


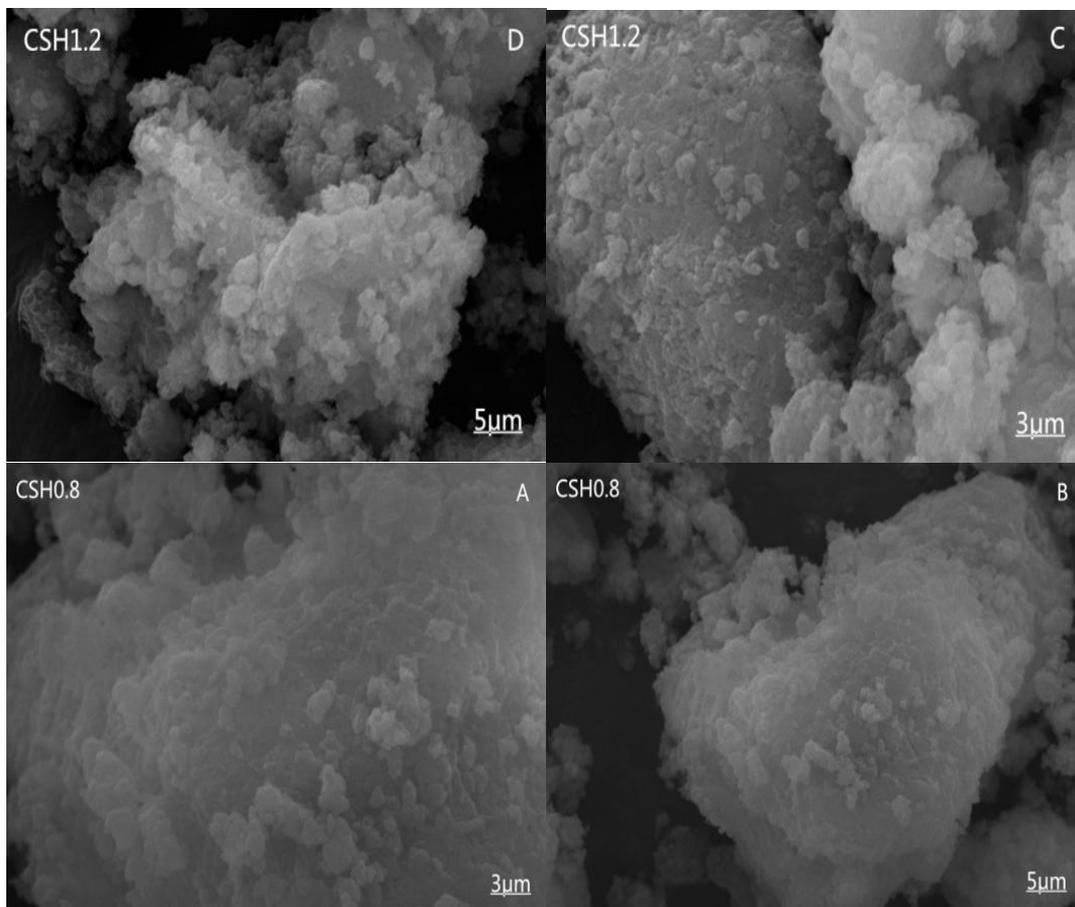
Figure 4. NMR patterns of Calcium Silicate Hydrate at different of C/S ratio.

The figure 4 showed that the characteristic peaks Q¹(-79ppm), Q²_{BT}(-82ppm), Q²_{PT}(-85ppm) were similar in three kinds of calcium silicate hydrate, there were no obvious Q⁰, Q³ and Q⁴ characteristic peaks, indicating that the silicate tetrahedron polymerized long chain polymers mainly without few branched chain in three kinds of calcium silicate hydrate by solution reaction. Three samples of characteristic peaks Q² included two shoulder peaks (Q²_{BT}, Q²_{PT}), indicating that there were two different vibration forms in the silicate tetrahedron.

In figure 4, along with the increase of the calcium-silicon ratio, the characteristic peaks Q^1 (-79ppm), Q^2_{BT} (-82ppm), Q^2_{PT} (-85ppm) in three kinds of calcium silicate hydrate samples CSH0.8, CSH1.2, CSH1.5 shifted to positive wavenumber position slightly. The ^{29}Si NMR tests showed that when calcium-silicon ratio was 0.8, Q^2/Q^1 was 5.92; when calcium-silicon ratio increased to 1.5, Q^2/Q^1 was 4.22, the ratio of Q^2/Q^1 decreased by 28.7%. Thus it could be seen with the increase of calcium-silicon ratio, the ratio of Q^2/Q^1 decreased and the characteristic peaks of Q^1 , Q^2 shifted to positive wavenumber position slightly, indicating that the polymerization degree of silica tetrahedra decreased. The conclusion was in agreement with Feng [12], Lv [1], Kim [15] and He [2, 13] et al.

3.4. SEM Analysis

Calcium-silicon ratio had an effect on micro-morphology and microstructure of calcium silicate hydrate. Taylor [20] found that the morphology of calcium silicate hydrate included four basic forms network-like large particles or iso-diameter particles, fibrous and layer. Figure 5 was the SEM pictures of CSH0.8, CSH1.2, CSH1.5 under 10000 times and 20000 times.



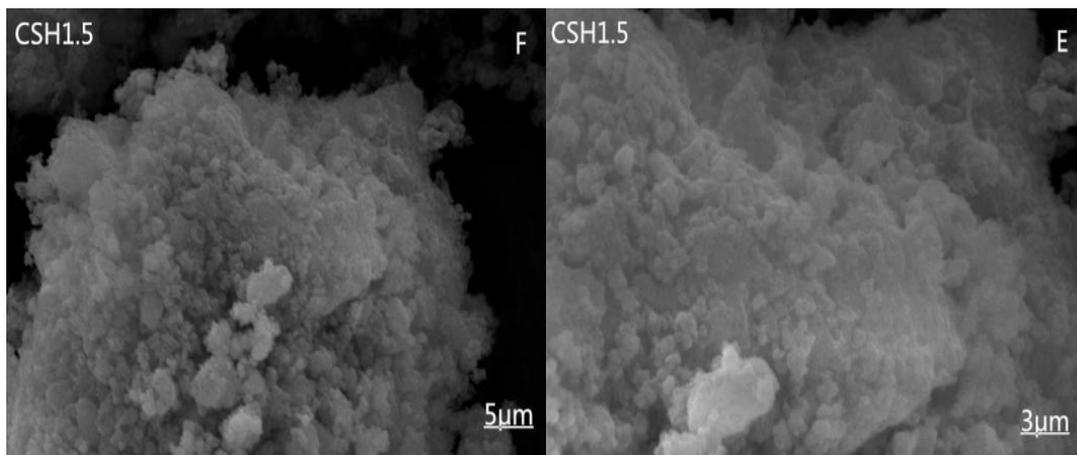


Figure 5. SEM patterns of Calcium Silicate Hydrate at different of C/S ratio.

By figure 5, the three samples CSH0.8, CSH1.2, CSH1.5 were gel state structure by random material. Under 10000 times, when the calcium-silicon ratio was 0.8, the morphology of calcium silicate hydrate was layer attached to a small number of irregular congeries; When the calcium-silicon ratio was 1.2, the morphology of calcium silicate hydrate was layer attached to a number of irregular congeries; When the calcium-silicon ratio was 1.5, the morphology of calcium silicate hydrate was irregular congeries primarily, the layer morphology disappeared nearly, and the structure more compact. Zeng [10] found that the calcium silicate hydrate by hydrothermal synthesis was random gel material, its structure was more compact with the increase of calcium-silicon ratio, Shi [9], Zhao [15] found that the morphology of calcium silicate hydrate changed from layer to honeycomb stacked by particles gradually.

Under 20000 times, the calcium silicate hydrate presented similar laws with the increase of calcium-silicon ratio (0.8~1.5). When the calcium-silicon ratio was 0.8, the morphology of calcium silicate hydrate was layer with few irregular congeries attached; When the calcium-silicon ratio was 1.2, the irregular congeries on the surface of calcium silicate hydrate increased and the layer morphology disappeared gradually; When the calcium-silicon ratio was 1.5, the morphology of calcium silicate hydrate was irregular congeries mainly with more compact structure.

4. Conclusions

(1) The calcium silicate hydrate was a material including crystalline and amorphous at the same time with high purity, it could be synthesised by solution method with calcium nitrate, sodium nitrate, sodium hydroxide and deionized water, with the increase of calcium-silicon ratio, the d-spacing of calcium silicate hydrate decreased.

(2) The calcium-silicon ratio had an effect on the polymerization degree of silica tetrahedra, with the increase of calcium-silicon ratio(0.8~1.2), the characteristic peaks (450cm^{-1} , 970cm^{-1}) shifted to low wavenumber position in IR, showing that the polymerization degree of silica tetrahedra decreased with the calcium-silicon ratio than increased.

(3) The calcium-silicon ratio influenced on polymerization methods of silica tetrahedra, with the increase of calcium-silicon ratio(0.8~1.2), the ratio of Q^2/Q^1 reduced, the characteristic peaks Q^1 and Q^2 shifted to positive wavenumber position slightly, when the calcium-silicon ratio increased from 0.8 to 1.5, the ratio of Q^2/Q^1 decreased by 28.7%.

(4) The calcium-silicon ratio impact on calcium silicate hydrate micro-morphology, with the increase of calcium-silicon ratio (0.8~1.5), the morphology of calcium silicate hydrate changed from layer to irregular congeries with more compact structure.

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