

THE EFFECTS OF RAPID CARBONIC ACID ON THE STRUCTURE OF THE MICROSTRUCTURE OF CALCIUM SILICATE

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Abstract: A possible method for carbon capture and storage is mineral carbonation of alkaline solid waste, such as used cement paste. By reusing the solid waste, environmental contamination may be decreased. One of the most common mineral phases that may be carbonated is calcium silicate hydrate (C-S-H). In this research, C-S-H with a C/S ratio of 1.50 was synthesized, and the effects of rapid carbonation on microstructure were examined. The Rietveld refinements (QXRD) was used to describe the carbonation products, while nuclear magnetic resonance, scanning electron microscopy, and nitrogen physisorption were each used to examine the microstructure. The findings show that carbonation causes the development of three distinct polymorphs of calcium carbonate as well as silica gel. Aragonite and vaterite have very low decomposition temperatures, whereas well-crystallized calcite decomposes at a greater temperature. Calcium carbonate starts to break down about 300 °C. Due to the stack of thick calcium carbonate, the average pore width drops from 10.33 nm to 6.69 nm, and the specific surface area decreases from 85.6 m²/g to 67.7 m²/g. In the interlayer of C-S-H, the Ca-O decalcifies, and the remaining silica tetrahedron protonates or connects with other silica tetrahedrons to create Q₃ or Q₄ with a higher degree of polymerization.

Key words: cement; nuclear magnetic resonance; carbonation; microstructure; calcium silicate hydrate

As the greenhouse effect has attracted more and more attention, CO₂ emission reduction and immobilization technology is an urgent need for sustainable development in China and the world [1]. Mineral carbonation is a permanent carbon fixation technology [2], where CO₂ reacts with minerals rich in calcium and magnesium to form stable carbonates. Huijgen et al. [3-4] believed that some solid wastes rich in calcium and magnesium can also be used as raw materials for carbonation and fixation of CO₂ minerals, mainly including steel slag, waste cement stone, coal fly ash, waste incinerator ash and some tailings from some metal smelting processes, etc. While solid waste fixes CO₂, it can also effectively prepare building material products with excellent performance or recycle precious metals and other high value-added products, which greatly reduces the cost [5-6].

Calcium silicate hydrate (CSH) is the main carbonizable component of many solid wastes, especially an important part of waste cement stone, accounting for about 2/3 of the mass of cement stone [7]. The changes in microstructure caused by C-S-H carbonization, such as changes in pore structure and silicon-oxygen tetrahedral structure, will have an important impact on the strength and durability of waste cement stone carbonized products. C-S-H with different calcium-silicon ratios will gradually decalcify to form calcium carbonate and silica gel in different crystal forms when exposed to air [8]. Morales research shows that C-S-H is carbonized in air for 2 weeks to form silica gel with high specific surface area, and calcium carbonate is aragonite and vaterite stacked to reduce porosity [9]. Black[10] found that the surface of C-S-H with different calcium-silicon ratios was carbonized to form calcium carbonate with different crystal forms.

The use of solid waste mineral carbonation to prepare building material products refers to carbonization under high CO₂ concentration and high CO₂ pressure, and the carbonization rate of C-S-H is greatly improved. It is of great significance to study the microstructural changes of CSH caused by high CO₂ concentration and carbonization under high pressure. Therefore, C-S-H with a calcium-silicon (C/S) ratio of 1.50 was synthesized, and carbonization was accelerated for 2 h under the conditions of CO₂ concentration of 99.9% and gas pressure of 0.2 MPa. The product type of accelerated carbonization was studied and the content of different crystal forms of calcium carbonate and amorphous phase was

quantitatively analyzed by QXRD (Rietveld full spectrum fitting), the change of pore structure was tested by N₂ adsorption method, and the solid high-resolution ²⁹Si MAS NMR. The effect of carbonization on the tetrahedral structure and degree of polymerization of C-S-H silicon-oxygen was analyzed.

1. Experiment.

1.1. Preparation.

Calcium silicate hydrate with a C/S ratio of 1.50 was synthesized from analytically pure calcium nitrate tetrahydrate (Ca(NO₃)₂·4H₂O), silicic acid nonahydrate (Na₂SiO₃·9H₂O), and sodium hydroxide (NaOH). Add the required calcium nitrate solution (1 mol/L) into the sodium silicate solution drop by drop according to the proportion, the water-solid ratio (the mass ratio of water to calcium nitrate tetrahydrate and sodium silicate nonahydrate) is 8, add NaOH to ensure the pH of the solution was greater than 13, and the resulting mixture was left at room temperature (25 °C) for 7 days until a colloid formed.

After standing, filter repeatedly with distilled water to wash away unreacted NO₃⁻ and Na⁺, and finally dry in a vacuum oven at 60 °C for 7 days to obtain the C-S-H sample. In the previous study, the author elaborated the calculation method of C/S and H/S in the obtained C-S-H in detail [11]. Due to the slight carbonization in the synthesis process, the C/S ratio was smaller than the theoretical design, and the obtained C-S-H was C_{1.27}SH_{0.76}.

1.2. Carbonization process

Stir 10g C-S-H and 1g water evenly, pour the mixture into a mold (20 mm×20 mm×100 mm), shape it under a pressure of 8 MPa, and keep the pressure for 30 s, and the obtained block is 20mm×20 mm×20 mm or so.

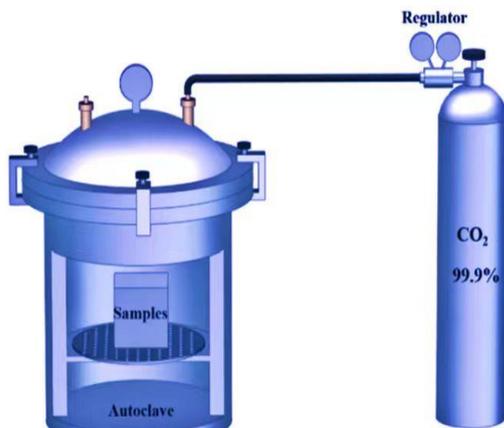


Fig. Schematic illustration of the equipment for accelerated carbonation.

Immediately after demoulding, the specimen was placed in a carbonization reactor to start the carbonization reaction, the CO₂ concentration was 99.9%, and the CO₂ pressure was 0.2 MPa.

After carbonization for 2h, the carbonization weight gain rate is 26.95%, and the carbonization rate is 69.9%. Characterization The phase analysis of the carbonized product was carried out using a German Bruker D8 Advance da Vinci (40 kV, 40 mA, step size 0.01°, scan time 0.5s) X-ray diffraction (XRD) instrument. In order to quantitatively calculate the content of the amorphous phase, 10% zinc oxide was added as an internal standard. Quantitative calculation of carbonization products was carried out with TOPAS 4.2, and the Rietveld refinement process included

factors such as X-ray source, background, instrument factor, and zero point error.

At the same time, the carbonized sample is thermally analyzed. The TG/DSC-MS system consists of a German NETZSCH STA449 F3 synchronous thermal analyzer and a NETZSCH QMS 403D mass spectrometer. The analyzer and the mass spectrometer are connected by a quartz glass capillary. The heating rate of thermal analysis was 10 °C/min, the electron energy of mass spectrometer ionization was 100 eV, the gas interface was single-step, the injection pressure was 0.1 MPa, and the working temperature was 300 °C. The microscopic morphology of the samples was observed with a FEI Quanta 450 scanning electron microscope.

The 3H-2000PS2 physical adsorption instrument was used to carry out the nitrogen adsorption-desorption test on the CSH samples. Before the experiment, the pretreatment was carried out at 80 °C, and the degassing time was 4h. Adsorption-desorption experiments were carried out at 77.3 K, and the specific surface area and pore size distribution of CSH before and after carbonization were calculated. The ²⁹Si MAS NMR spectrum was collected on an Agilent DD2-500 MHz nuclear magnetic resonance spectrometer, the resonance frequency of the silicon core was 99.2 MHz, hydrogen decoupling

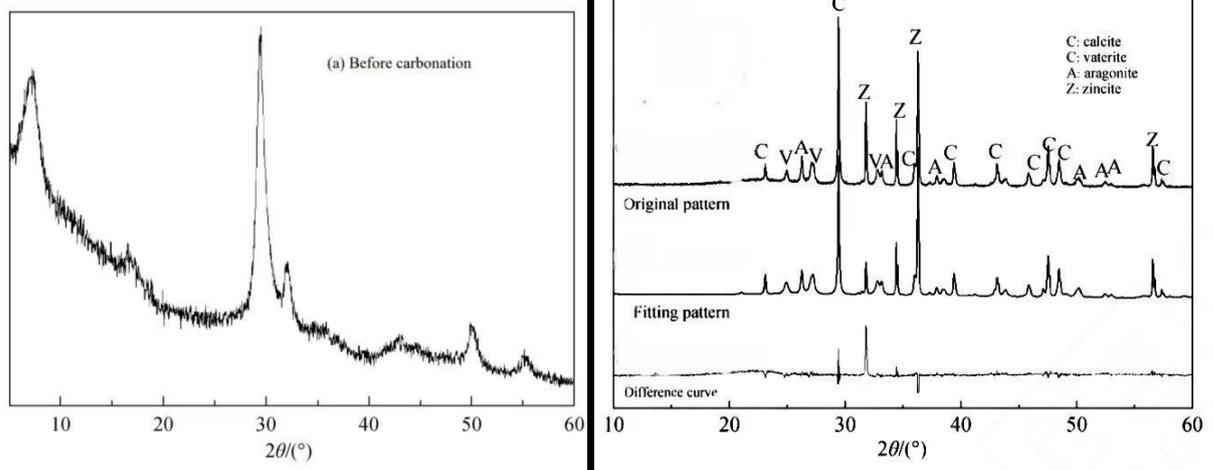
technology was used, the rotation speed was 5 kHz, the p/4 pulse width of 2.8 ms, 300 accumulations and 240s cycle delay time. The chemical shift reference standard is tetramethylsilane (TMS).

2. Results and discussion

2.1 Phase Quantitative Analysis

Figure 1 is the XRD spectrum of CSH before and after carbonization. It can be seen from Figure 1a that diffuse diffraction peaks appeared at 29°, 32°, and 50°, indicating that CSH gels similar to cement hydration products were synthesized [12]. Figure 1b shows the XRD spectrum of CSH after carbonization for 2h, including the original XRD spectrum, refined fitting spectrum and residual. It can be seen from Figure 1b that the carbonization products include calcium carbonate of three different crystal forms: calcite, aragonite, and vaterite. Import the crystal structure file (shown in Table 1) into TOPAS 4.2 software for quantitative analysis of the phases. Calcite, aragonite, and vaterite The mass fractions of aragonite, vaterite and amorphous phase are 34.0%, 18.7%, 17.1% and 30.2%, respectively. No diffraction peak of SiO₂ was found in the XRD spectrum, indicating that SiO₂ crystals were not formed after carbonization of CSH but a gel was formed. At the same time, the carbonized products were analyzed by TG/DSC-MS (Fig. 2). Figure 2a is the TG-DSC curve and Figure 2b is the separation of the thermal decomposition gas products.

Variation curve of sub-strength with temperature. From the TG curve, it can be seen that there is a slow mass loss in the range of 60-300 °C, and the DSC curve produces an endothermic peak at around 100 °C. The mass loss in this range is caused by the dehydration of calcium silicate hydrate and silica gel. At the same time, the ion flux of pyrolysis gas H₂O reached its peak at 100.9 °C. The decomposition temperature of calcium carbonate formed under accelerated carbonization conditions is relatively low, and it begins to decompose at about 300 °C. Correspondingly, two endothermic peaks can be seen in the DSC curve. Figure 3 is the SEM photos of C-S-H before and after carbonization. Figure 3a says the ion current curves of CO₂ reached their peaks at 523.0 and 757.9 °C. The mass loss in different temperature ranges in the range of 300-800 °C is caused by the decomposition of calcium carbonate in different crystal forms. Morandeu et al. [12] believed that aragonite and vaterite have lower decomposition temperatures, while well-crystallized calcite decomposes in the range of 750–900°C. Therefore, the endothermic peak at 524.6 °C in this experiment represents the temperature of aragonite and vaterite. Decomposition, the endothermic peak at 753.6°C represents the decomposition of calcite.



(a) Before carbonation **(b) After carbonation**
Fig. 1. XRD patterns of CSH before and after accelerated carbonization

The mass loss caused by CaCO₃ decomposition is 28.9%, indicating that the CaCO₃ content is 65.7%. Calcium carbonate content calculated by thermogravimetric method is 4.1% smaller than that obtained by Rietveld full spectrum fitting. The TG method is a test method that can accurately determine the content of calcium carbonate, but different crystal forms of calcium carbonate have overlapping areas during the decomposition process, and the content of each phase cannot be distinguished. Rietveld full-spectrum fitting can measure the content of each phase, but in order to

determine the content of the amorphous phase, 10% ZnO is added as an internal standard, and whether the mixing process is uniform will affect the result.

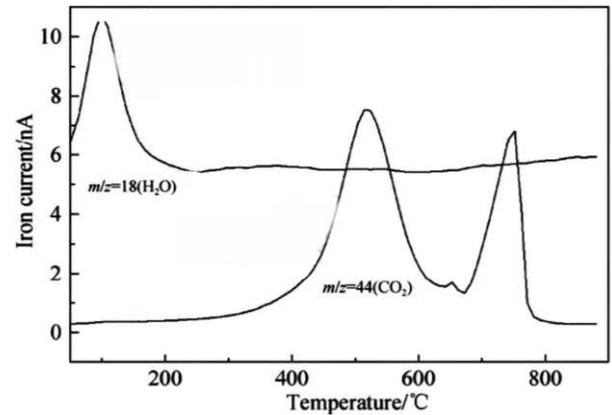
Crystal structure parameter

Mineral	COD ID	a/nm	b/nm	c/nm	$\alpha/(\circ)$	$\beta/(\circ)$	$\gamma/(\circ)$
Calcite	4502443	4.97577	4.97577	16.99207	90	90	120
Aragonite	2100187	4.96183	7.96914	5.742852	90	90	90
Vaterite	3000000	8.4721	7.1575	4.1265	90	90	90
Zinc oxide	1011258	3.22	3.22	5.2	90	90	120

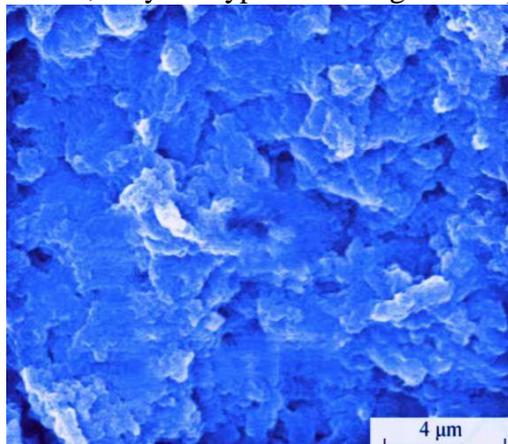
Fig. 2 TG-DSC-MS curves of CSH after carbonation

2.2. Morphological analysis.

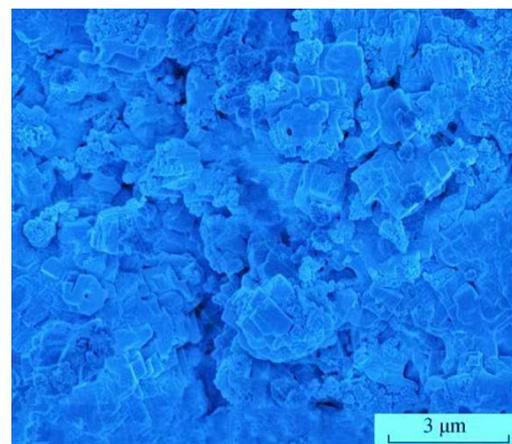
Figure 3 is the SEM photos of C-S-H before and after carbonization. Figure 3a says the synthesized C-S-H is an amorphous material with rough surface. Although it is different from the fibrous, network-like, and needle-rod-like C-S-H in [13], the synthesized C-S-H is a porous, high-specific surface area gel substance. After 2 h of accelerated carbonization (Fig. 3b), the calcium carbonate crystals with smooth surface were piled up with gel-like substances in the middle.



C-S-H forms three different crystal forms of calcium carbonate during accelerated carbonization, although the typical morphologies of calcite, aragonite, and vaterite reported in the literature are rectangular, needle-rod, and elliptical, respectively. But in the SEM photos after accelerated carbonization, only the typical rectangular shape of calcium carbonate can be seen.



(a) Before carbonation

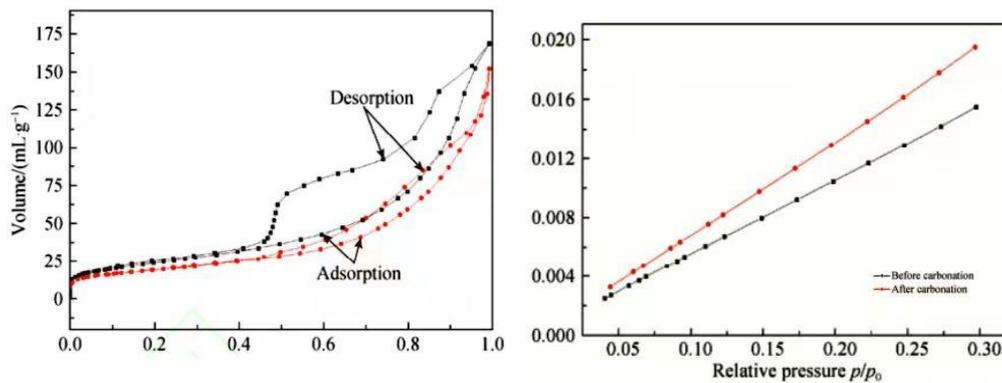


(b) After carbonation

Fig. 3 SEM photographs of CSH before and after accelerated carbonization accelerated carbonation

2.3. N₂ adsorption analysis

In order to study the effect of accelerated carbonization on the specific surface area and pore structure of C-S-H, the N₂ adsorption-desorption test was carried out on the samples, and the results are shown in Figure 4. The synthesized C-S-H exhibits a type IV adsorption-desorption curve (Fig. 4a) and has an H₂ type "hysteresis loop" caused by capillary condensation, indicating that C-S-H has an irregular pore shape and pore size distribution. After accelerated carbonization of C-S-H for 2h, the total adsorption capacity decreased, and the total pore volume. The volume decreased from 0.31 mL/g to 0.26 mL/g. In the low-pressure part (p/p₀=0~0.3), the gas adsorption amount increases almost linearly, which is caused by micropore absorption.



(a) Nitrogen adsorption-desorption isotherm (b) Multipoint Brunauer-Emmett-Teller (BET) graphs

Fig. 4 Nitrogen adsorption-desorption analysis of CSH before and after carbonization before and after carbonation

Figure 4b is the multi-point BET diagram of the sample. According to the slope and intercept of the straight line, the specific surface area S_{BET} and adsorption constant C_{BET} of the sample can be obtained as shown in the picture. As shown in 4b, the carbonization reaction reduces the pore volume in all ranges, and the accelerated carbonization for 2h reduces the average pore diameter of the sample from 10.33 nm to 6.69 nm. Silica gel is a porous substance with high specific surface area [14], and the adsorption constant C_{BET} after carbonization increased from 112.6 to 178.5, indicating that silica gel has stronger adsorption capacity than C-S-H.

The decrease in total pore volume and average pore diameter is due to the accumulation of a large amount of densely structured calcium carbonate. At the same time, the close packing of calcium carbonate makes the overall specific surface area S_{BET} of the carbonized products decrease from 85.6 m^2/g to 67.7 m^2/g . This is contrary to the results of Morales [15], who placed C-S-H powder in CO_2 saturated water for carbonization, but this experiment was carbonized under the condition of low water-solid ratio.

2.4. Structural change of silicon-oxygen tetrahedron.

In NMR analysis, the chemical environment of Si is represented by Q^n show. Q^1 represents a silicon-oxygen tetrahedron connected to only one silicon-oxygen tetrahedron, characterize the silicon-oxygen tetrahedron at the end of the linear chain in the dimer or polymer; Q^2 represents a silicon-oxygen tetrahedron connected with 2 silicon-oxygen tetrahedra, characterizing Siloxane tetrahedron in the middle of a linear chain; Q^3 represents the Silicon-oxygen tetrahedrons connected by faces, with chain branches, double-chain polymer structure or layered structure; Q^4 means to form a three-dimensional network with four silicon-oxygen tetrahedrons network structure. C-S-H has a distinct layered structure due to its composition, it is difficult to have an accurate structural model due to the complexity of the structure and structure. Currently, the most common

The generally accepted model is the 14-E tobermorite structure proposed by Taylor and the Jennite structure [16]. Both structures contain silicon-oxygen tetrahedral bulk polymerized structural layer and intermediate Ca-O layer. Research shows that in Some silicon-oxygen tetrahedrons in C-S-H are tilted, rotated, missing, etc. Only Q^1 and Q^2 exist in the silicon-oxygen tetrahedron in C-S-H [17].

^{29}Si MAS NMR was used to analyze the change of silicon-oxygen tetrahedral structure before and after C-S-H carbonization, and Gauss fitting was performed on the spectral lines with PEAKFIT 4.12, as shown in Figure 6. It can be seen from Figure 6a that there are only two silicon structural units with different structures in C-S-H, and the peak positions are as follows. The peaks around -80.65 , -86.24 and -90.96 are assigned to Q^1 respectively and Q^2 structures, which are similar to the structure of C-S-H in hydrated cement [18]. After accelerated carbonization (Fig. 6b), the characteristic peak intensities of Q^1 and Q^2 decrease, and the characteristic peak intensities of Q^3 and Q^4 increase. The absorption peak at -112.3 is Q^4 connected with four silicon-oxygen tetrahedrons, the absorption peak at -102.94

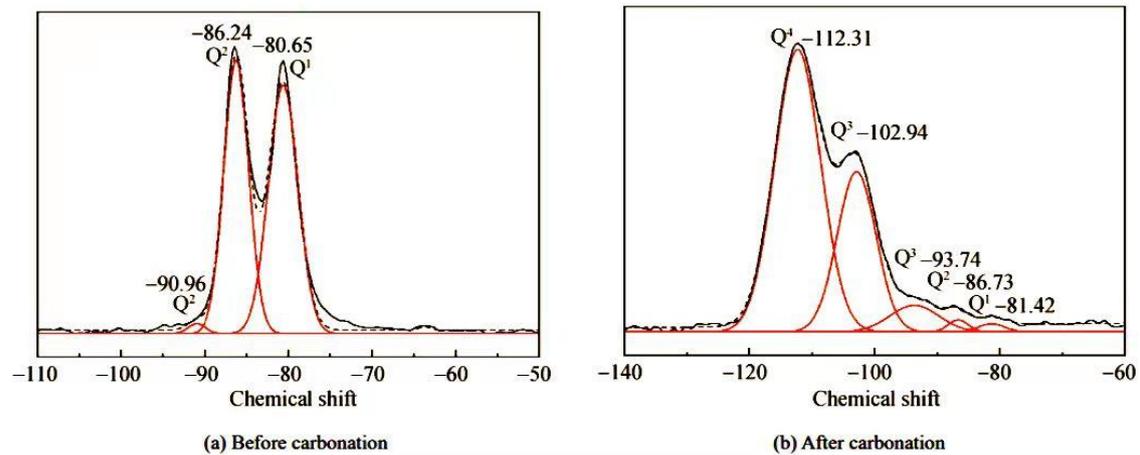


Fig.6 29Si NMR spectrum of CSH before and after carbonation

Q³ connects with 3 silicon-oxygen tetrahedrons and 1 hydroxyl group; the absorption peak at -86.73 is Q², which connects with 2 silicon-oxygen tetrahedrons and 2 Ca²⁺; the absorption peak at -86.73 is Q¹. The Ca-O layer between the two silicon-oxygen chains of C-S-H is removed and reacts with CO₂ to form calcium carbonate. The siliconoxygen tetrahedrons that lost Ca are protonated or linked with neighboring silicon-oxygen tetrahedra, forming Q³ and Q⁴ structures with higher degrees of polymerization. The characteristic peak at -112.3 indicates that the carbonization product is silica gel, not SiO₂. The research results of Matsushita [19] also showed that when the carbonization rate of C-S-H is less than 20%, it will not cause shrinkage. When the carbonization rate is higher than 25%, the chain structure of CSH will be destroyed and cause shrinkage.

3. Conclusion.

Calcium silicate hydrate with a calcium-silicon ratio of 1.50 was synthesized. After compression molding under a pressure of 8 MPa, the carbonization mass increase rate was 26.95% and the carbonization rate was 69.9% after accelerated carbonization under 99.9% CO₂ and a pressure of 0.2 MPa for 2h.

1) After C-S-H accelerated carbonization, three different crystal forms of calcium carbonate and silica gel were formed. The mass percentages of calcite, aragonite, vaterite and amorphous silica were 34.0%, 18.7%, 17.1% and 30.2%, respectively. Calcium carbonate begins to decompose at about 300 °C, aragonite and ball graupel, Calcite has a lower decomposition temperature, and calcite with good crystallization has a higher decomposition temperature.

2) The silica gel formed after C-S-H carbonization has high adsorption capacity, but the average pore size decreases from 10.33 nm to 6.69 nm, and the specific surface area decreases from 85.6 m²/g to 67.7 m²/g, which is due to the dense structure of calcium carbonate caused by accumulation;

3) The Ca-O layer between the C-S-H double-layer silicon-oxygen chains is gradually removed to react with CO₂, and the silicon-oxygen tetrahedron is protonated or linked with the adjacent silicon-oxygen tetrahedron, forming Q³ and Q⁴ structures with a higher degree of polymerization.

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