FORMATION OF THAUMASITE IN AMMONIUM SALT SOLUTION BASED ON RAMAN SPECTROSCOPY AND THERMODYNAMIC ANALYSIS

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Cement-based materials sometimes encounter sulfate attack and ammonium salt environments during service, which can severely affect the long-term durability of these materials. In cement-based materials, the formation of thaumasite usually requires five conditions: sulfate, silicate, carbonate, and sufficient water and low temperature (<15°C). However, under other conditions, thaumasite can also form. To study the changing trend of thaumasite in an ammonium salt solution at ambient temperature (25°C), the formation process of thaumasite was studied by laser Raman spectroscopy and thermodynamic analysis. The reaction was accelerated in the presence of NH_4^+ ions at ambient temperature, and the presence of SO_4^{2-} anions enhanced this trend; this enhancement was even greater than that at low temperature. The change in the Gibbs free energy of formation of thaumasite in the presence versus absence of NH_4^+ ions was studied using thermodynamic methods, and the acceleration mechanism of the formation of thaumasite in the presence of NH_4^+ ions was explained.

Keywords: *thaumasite, ammonium salt, sulfate, Raman spectroscopy, thermodynamic analysis.*

ИССЛЕДОВАНИЕ ФОРМИРОВАНИЯ ТАУМАЗИТА В РАСТВОРЕ СОЛИ АММОНИЯ МЕТОДАМИ СПЕКТРОСКОПИИ КОМБИНАЦИОННОГО РАССЕЯНИЯ СВЕТА И ТЕРМОДИНАМИЧЕСКОГО АНАЛИЗА

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УДК 535.375.5

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(Поступила 24 сентября 2021))

Процесс образования таумазита изучен с помощью спектроскопии комбинационного рассеяния света и термодинамического анализа для выявления изменений таумазита в растворе соли аммония при температуре окружающей среды 25 °C. Показаны ускорение реакции в присутствии ионов NH_4^+ при температуре окружающей среды и усиление этой тенденции в присутствии анионов SO_4^{2-}. Это усиление больше, чем при низкой температуре. Изменение свободной энергии Гиббса образования таумазита в присутствии и в отсутствие ионов NH_4^+ изучено с использованием термодинамических методов. Объяснен механизм ускорения образования таумазита в присутствии ионов NH_4^+.

Ключевые слова: *таумазит, соль аммония, сульфат, спектроскопия комбинационного рассеяния света, термодинамический анализ.*

Introduction. Cement-based materials are the most common structural materials because of their excellent performance and low cost. These materials may often encounter many extreme environments during services, such as complex groundwater environments, seawater corrosion, and freeze-thaw cycles, which can

lead to severe degradation of their performance [1–3]. Cations in the complex environment of groundwater include mainly Mg^{2+}, Ca^{2+}, and ammonia nitrogen and anions include mainly SO_4^{2-}, Cl^-, and CO_3^{2-} [4]. Among them, ammonia nitrogen differs from the other ions because of its acidity and strong coordination; hence, its influence on the stability of compounds in cement-based materials is also different.

Cement-based materials are prepared by bonding sand and stone with cement to form cementitious materials, where the main chemical components of the cement include $3CaO \cdot SiO_2$, $2CaO \cdot SiO_2$, $3CaO \cdot Al_2O_3$, and $4CaO \cdot Al_2O_3\,Fe_2O_3$, among other compounds. After hydration of the cement, hydrated calcium silicate, hydrated calcium aluminate, $Ca(OH)_2$, and ettringite are formed, and the material gradually hardens due to the formation of these substances. There are many pores in these hardened cement-based materials and Ca^{2+}, SiO_3^{2-}, AlO_2^-, and OH^- ions in aqueous solution fill the pores and reach equilibrium with the solid phase. Based on the complex mixture of chemical ions in underground water, many reaction products are formed in cement-based materials, such as gypsum, ettringite, and thaumasite [5].

Thaumasite, which has the chemical formula $Ca_3[Si(OH)_6]CO_3SO_4 \cdot 12H_2O$ [6], is a mineral with a hexagonal structure and $P6_3$-type spatial structure (a = 11.030 Å and c = 10.396 Å) [7, 8]. Materials with similar structures mainly include ettringite $[Ca_6Al_2(OH)_{12}(SO_4)_3 \cdot 26H_2O]$ and bentorite $[Ca_6(Cr,Al)_2(SO_4)_3(OH)_{12} \cdot 26(H_2O)]$ [9]. Previous studies have shown that ettringite and thaumasite are widely formed in cement chemistry [10]. After sulfate attack of a cement-based material, many SO_4^{2-} anions react with it and form ettringite. If CO_2 or CO_3^{2-} anions are present in this solution system, especially at low temperatures, thaumasite can form [11, 12]. Ettringite and thaumasite have similar spatial structures; therefore, they have similar XRD diffraction peaks, which are easily confused in the detection process. According to the literature, in the presence of NH_4^+ ions, ettringite cannot exist stably and decomposes to gypsum [3], but Mileti et al. [13] found that the reaction products in cement-based materials were gypsum and ettringite in 10% $(NH_4)_2SO_4$ solution. In this study, the detection of ettringite was carried out using XRD, which led to a controversy regarding whether ettringite or thaumasite was formed in the presence of NH_4^+ ions.

Laser Raman analysis was demonstrated to be a better method of analyzing thaumasite, ettringite, and other hydration products in cement [14], in which thaumasite had three main spectral bands at 658, 990, and 1074 cm^{-1} and ettringite had two main bands at 990 and 1088 cm^{-1}. The three main spectral bands of thaumasite corresponded to $Si(OH)_6^{2-}$, SO_4^{2-}, and CO_3^{2-}. The peak that corresponded to SO_4^{2-} in thaumasite was the same as that of ettringite. Therefore, the other two main peaks of thaumasite can be used to distinguish it [15].

Two formation mechanisms have been identified in the formation process of thaumasite: conversion from ettringite to thaumasite [9, 16]. Luo et al. [17] showed that Mg^{2+} ions accelerated the formation of thaumasite more than Ca^{2+} ions and Na^+ ions; Li et al. [18, 19] reported that an increase in Cl^- anions can inhibit the formation of thaumasite, for which the main reason is that Cl^- can form $CaCl_2$ with Ca^{2+} ions and then react with hydrated calcium aluminate or ettringite in cement-based materials to form hydrated calcium chloroaluminate ($3CaO \cdot Al_2O_3 \cdot CaCl_2 \cdot 10H_2O$), and direct reaction in solution [20]. The direct formation of thaumasite in solution by Ca^{2+}, SiO_3^{2-}, SO_4^{2-}, and CO_3^{2-} ions has been related to the concentrations of relevant chemical ions. Xiao et al. [20] believed that adding $CaCl_2$ in this process could effectively accelerate the formation of thaumasite whereas SO_4^{2-} and CO_3^{2-} anions had little effect on the reaction rate of thaumasite formation. The reason was that more soluble Ca^{2+} ions were provided in the solution. However, $CaCl_2$ not only increased the concentration of Ca^{2+} ions in the solution but also increased the concentration of Cl^- anions. Therefore, the mechanism of the effect of Cl^- anion concentration on the formation of thaumasite was contradictory.

Thus, the effect of NH_4^+ ions on the stability of thaumasite was examined by studying the formation of ammonium salts (NH_4Cl and $(NH_4)_2SO_4$), which helped to explain the above differences. In this paper, to resolve the contradiction between the effects of Cl^- anions and OH^- on the formation of thaumasite, the effects of NaCl and NaOH on the stability of thaumasite were studied.

Materials and methods. Calcium oxide (CaO, AR, Xilong Chemical Co., Ltd.), sodium metasilicate nonahydrate ($Na_2SiO_3 \cdot 9H_2O$, AR; Sinopharm Chemical Reagent), anhydrous sodium sulfate (Na_2SO_4, AR; Sinopharm Chemical Reagent), anhydrous sodium carbonate (Na_2CO_3, AR; Tianjin FengChuan Chemical Reagent Technology), sucrose ($C_{12}H_{22}O_{11}$, AR; Xilong Chemical), sodium chloride (NaCl, AR; Sinopharm), ammonium chloride (NH_4Cl, AR; Sinopharm), ammonium sulfate ($(NH_4)_2SO_4$, AR, Sinopharm), calcium hydroxide (NaOH, AR; Chengdu Kelong Chemical Reagent Factory), and distilled water were the raw materials that were used in this study.

TABLE 1. Mix Proportions of Chemical Reactants

No.	CaO, mol	$Na_2SiO_3·9H_2O$, mol	Na_2SO_4, mol	Na_2CO_3, mol	NaCl, mol	NaOH, mol	$(NH_4)_2SO_4$, mol	NH_4Cl, mol	Sucrose, g	Water, g
N0	0.48	0.08	0.08	0.08	0	0	0	0	45.3	900.7
N1	0.48	0.08	0.08	0.08	0.08	0	0	0	45.3	900.7
N2	0.48	0.08	0.08	0.08	0	0.08	0	0	45.3	900.7
N3	0.48	0.08	0.08	0.08	0	0	0.08	0	45.3	900.7
N4	0.48	0.08	0.08	0.08	0	0	0	0.08	45.3	900.7

After accurately weighing the reactants according to the mix proportions of the raw materials (Table 1), they were dissolved in 5% sucrose solution, stirred with a magnetic stirrer for 0.5 h, and stored at 25°C. After 7 and 14 days, the samples were washed with absolute ethanol, filtered with a laboratory vacuum suction pump, and dried at 35°. A Finder One micro-area laser Raman spectrometer (Beijing Zolix) was adopted, with a resolution of ≤ 2 cm^{-1}, a laser light source wavelength of 540 nm, an integration time of 0.5 s, and a scanning interval of 50–1500 cm^{-1}.

Five milliliters of the supernatant were accurately obtained from the upper part of the solution that was cured for 14 days and diluted with water to 200 mL, and the conductivity of the solution was measured with a DDS-307A conductivity meter (Inesa Scientific Instrument). Then, a PHS-3C pH meter (Shanghai Yueping Scientific Instrument) was used to determine the pH of the solution.

Results and discussion. To study the effect of the addition of ammonium salt on the formation of thaumasite, experiments were designed to compare the effect of Cl^- by adding NaCl (N1), the effect of the enhancement of the alkali environment on the formation of thaumasite by adding NaOH (N2), and the effect of NH_4^+ by adding NH_4Cl (N3) and $(NH_4)_2SO_4$ (N4). Then, the effect of an ammonium salt environment on the stability of thaumasite was studied.

Ca^{2+}, SiO_3^{2-}, CO_3^{2-}, SO_4^{2-}, OH^-, and Cl^- ions were identified in the reaction solution system. In the Raman spectrum, the peaks at 660, 715 cm^{-1}, and approximately 1000 cm^{-1} corresponded to the vibration of $Si(OH)_6^2$ anions in thaumasite, CO_3^{2-} anions in calcite, and SO_4^{2-} anions in mainly thaumasite and dihydrate gypsum respectively; the peak at 1080 cm^{-1} corresponded mainly to the vibration of CO_3^{2-} anions of thaumasite and calcite; the peak at 380 cm^{-1} corresponded mainly to the vibration of OH^-; and the peaks at 150 and 280 cm^{-1} corresponded mainly to the vibration of calcite. As shown in Fig. 1a, after 7 days of chemical reaction, $Ca(OH)_2$ and calcite were detected in group N0 as the control group, and relatively weak vibrational bands of thaumasite were identified. In groups N3 and N4, after the addition of NH_4^+, not only $Ca(OH)_2$ and calcite bands were identified but also calcium silicate and gypsum bands; in addition, a relatively strong vibration band of thaumasite was detected, and the vibration band of thaumasite in N3 was stronger. The results showed that Cl^- and OH^- anions cannot promote the formation of thaumasite,

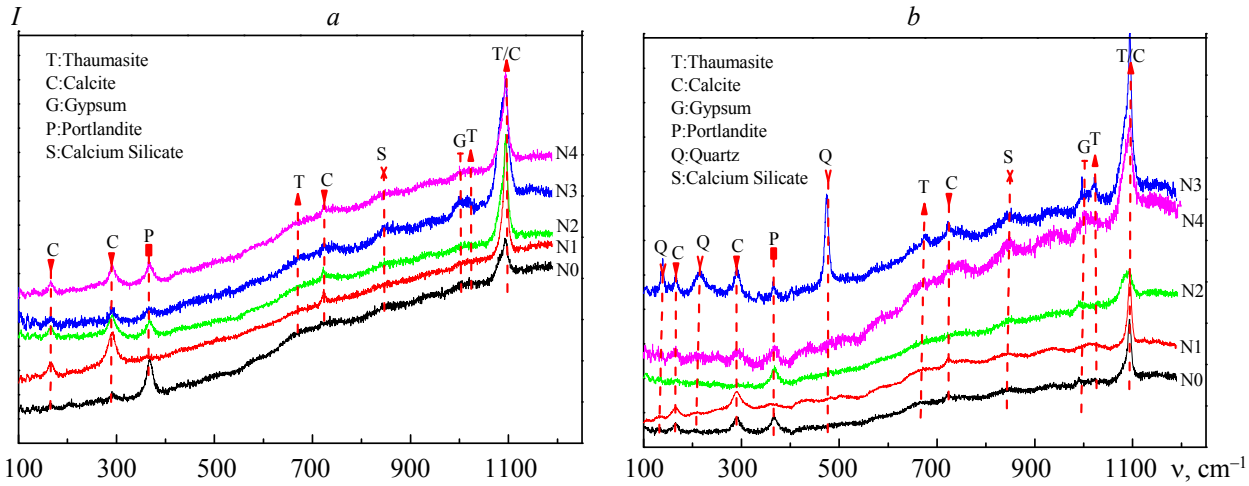


Fig. 1. Raman spectra of reaction products that were formed in the solution after reaction for (a) 7 and (b) 14 days.

whereas NH_4^+ ions can promote the formation of thaumasite, and more importantly, sulfate anions can promote the formation of thaumasite more than Cl^- anions.

However, as the spectral band of thaumasite that was formed by various chemical reactions was never obvious, the reaction products after 14 days of chemical reaction were analyzed, and the results were shown in Fig. 1b. Figure 1b shows that the bands of the chemical reaction that occurred in the solution that was cured for 14 days were stronger. According to N4, at 660 cm^{-1}, the vibration band of the reaction product, namely, $Si(OH)_6^{2-}$ anions, in the solution with added NH_4Cl, was stronger, the vibration band of gypsum and thaumasite at 1000 cm^{-1} was split, and the vibration band of silicate at 850 cm^{-1} was more obvious. In the solution with $(NH_4)_2SO_4$, not only the spectral bands of the above products but also the spectral band of SiO_2 were observed.

After 14 days of curing, two samples of the solution were stored for 1 week, one at ambient temperature and the other at low temperature (2°C). By comparing the changes in the reaction products between the two samples, the effects of a low-temperature environment on the formation of thaumasite in the presence of ammonium salt were studied, and the results were shown in Fig. 2. Figure 2 shows that after curing, the bands of calcium hydroxide, calcite, and calcium silicate were all formed in the spectra at ambient temperature and low temperature (2°C), and the bands of thaumasite were also formed. Comparing the reaction products, the spectral band of thaumasite was stronger at ambient temperature. At the same time, calcium hydroxide and calcium silicate were substantially precipitated. This showed that thaumasite easily formed at low temperatures. However, compared with Fig. 1b, the vibration band of the thaumasite that formed after curing in the ammonium sulfate solution for 14 days was sharper than that of the thaumasite at low temperature. This showed that the promotional effect of ammonium sulfate on the formation of thaumasite was stronger than that at low temperatures.

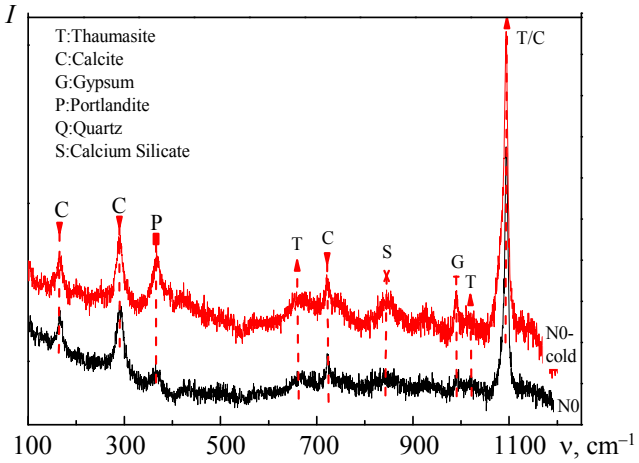


Fig. 2. Raman spectroscopic analysis of thaumasite at two temperatures.

Conductivity and pH changes in the solution. To study the relevant changes in the solution, the conductivity and pH of the solution in the process were studied, and the overall changes in the solution were evaluated based on these two parameters. The results were shown in Fig. 3. According to Fig. 3, when NaCl (N1), $(NH_4)_2SO_4$ (N3), and NH_4Cl (N4) were added to the solution, the changes in pH in the solution were not obvious, and the pH of the solution with added NaOH (N2) was slightly higher than those of the other solutions. When NaCl, NaOH, and NH_4Cl were added to the solution, the conductivity of the solution with $(NH_4)_2SO_4$ was much lower than those of the other solutions. This showed that the chemical reactions in the solution occurred in an alkaline environment, the amount of CaO that was added to the system was excessive, the addition of NH_4^+ ions did not change the alkalinity of the solution, and the solution remained alkaline. When $(NH_4)_2SO_4$ was added to the solution, the conductivity of the solution decreased gradually. The conductivity of the solution had the following relationship with the ion concentration in the solution:

$$\Lambda_m = \Lambda_m^0 + KC^{1/2},\ \Lambda_m^0 = \nu_+\lambda_+ + \nu_-\lambda_- . \quad (1)$$

This variation is referred to as Kohlrausch's law [21]. Λ_m^0 denotes the limiting molar conductivity; K is a constant; C is the concentration of ions in the solution; λ_+ and λ_- are the limiting molar conductivities of the cations and anions, respectively; and ν_+ and ν_- are the numbers of cations and anions, respectively, per formula unit of electrolyte.

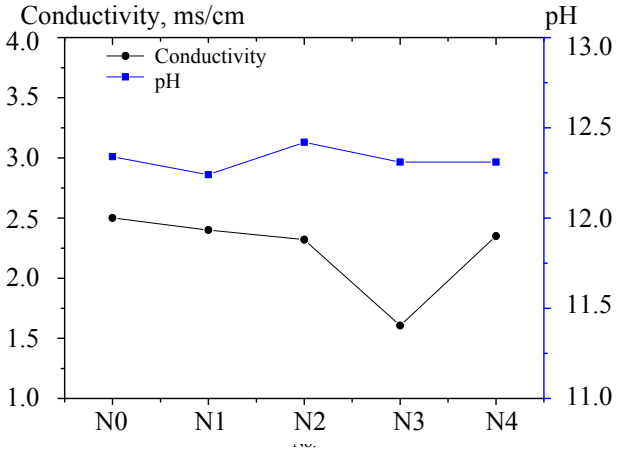


Fig. 3. Conductivity and pH values of the solution that was cured for 14 days.

In the comparative test, the conductivity changed only minimally when NaCl, NaOH, and NH_4Cl were added to the solution: Na^+ ($\nu_+ = 1$, $\lambda_+ = 5.01$ ms/m^3), Cl^- ($\nu_- = 1$, $\lambda_- = 7.63$ ms/m^3), OH^- ($\nu_- = 1$, $\lambda_- = 19.8$ ms/m^3), and NH_4^+($\nu_+ = 1$, $\lambda_+ = 7.37$ ms/m^3). In contrast, the conductivity decreased substantially when SO_4^{2-}($\nu_- = 2$, $\lambda_+ = 16$ ms/m^3) was added. According to Eq. (1), $(NH_4)_2SO_4$ had a large limiting conductivity, but according to the test, it had a small conductivity. Therefore, the ion concentration in the solution gradually decreased owing to the addition of $(NH_4)_2SO_4$. Thus, more ions precipitated and separated from the solution system.

Thermodynamic factors in the reaction of thaumasite. The raw materials were CaO, Na_2SiO_3, Na_2SO_4, and Na_2CO_3. These compounds were dissolved in water and formed free ions. The reaction was expressed as follows:

$$3CaO + SiO_3^{2-} + SO_4^{2-} + CO_3^{2-} + 18H_2O \rightarrow Ca_3\left[Si(OH)_6 \cdot 12H_2O\right]CO_3SO_4 + 6OH^- \quad (2)$$

According to Eq. (2), the Gibbs chemical free energy of the chemical reaction was calculated. According to the data in Langer's Chemistry Manual and studies from the literature [22–24], the Gibbs chemical free energy of thaumasite at 298 K was calculated as follows:

$$\Delta_r G_m^{\Theta}\left(Ca_3\left[Si(OH)_6 \cdot 12H_2O\right]CO_3SO_4\right) = -210.43 \text{ kJ/mol}. \quad (3)$$

Therefore, the Gibbs free energy of the chemical reaction in this process was negative; thus, the reaction in Eq. (2) occurred spontaneously.

When NH_4^+ was present in the solution, owing to the alkalinity of the chemical system, it was transformed into NH_3(aq), and it could also be smelled during the experiment. In the Raman spectrum, the vibration peak at 715 cm^{-1} showed that calcite was formed in the reaction. The peak at 660 cm^{-1} proved that $Si(OH)_6^{2-}$ was produced in the reaction process, namely, that thaumasite was formed in the reaction. The vibrational peak at 1000 cm^{-1} indicated that a sulfate solid material was formed, and this peak was split, thereby indicating that the sulfate corresponded to different chemical environments. Owing to the presence of sulfate in thaumasite, dihydrate gypsum was also formed in the reaction.

Based on the above analysis, the chemical reaction can be expressed as follows:

$$3CaO + 2NH_4^+ + SiO_3^{2-} + SO_4^{2-} + CO_3^{2-} + 16H_2O \rightarrow Ca_3\left[Si(OH)_6 \cdot 12H_2O\right]CO_3SO_4 + 4OH^- + 2NH_3^- \quad (4)$$

According to the data in [22–24], the Gibbs chemical free energy of thaumasite at 298 K was calculated as follows:

$$\Delta r G_m^{\Theta}\left(Ca_3\left[Si(OH)_6 \cdot 12H_2O\right]CO_3SO_4\right) = -245.9 \text{ kJ/mol}. \quad (5)$$

At the same time, Ca^{2+}, SiO_3^{2-}, SO_4^{2-}, and CO_3^{2-} ions were present in the system, and the following chemical reactions also occurred in the system [25]:

$$Ca^{2+} + SiO_3^{2-} \rightarrow CaSiO_3 \quad (6)$$

$$Ca^{2+} + SO_4^{2-} + 2H_2O \rightarrow CaSO_4 \cdot 2H_2O \quad (7)$$

$$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3 \quad (8)$$

Some of the silicic acid, namely, H_4SiO_4, in the solution was polymerized. The molecular weight of the silicate anion increased gradually in the concentrated solution, and the silicate anion was converted among

various polymers [26], which finally formed quartz. Therefore, the analysis showed that $CaSiO_3$, gypsum, calcite, and quartz were gradually formed in the chemical reaction process, which was verified by Raman spectroscopy.

Analysis of the formation factors of thaumasite. The structural formula of thaumasite is $Ca_3[Si(OH)_6]CO_3SO_4 \cdot 12H_2O$; in its structure, cylinders of $Ca_3[Si(OH)_6 \cdot 12H_2O]^{4+}$ were closely arranged parallel to the *c*-axis of the crystal, and CO_3^{2-} and SO_4^{2-} were staggered to fill the gaps between the cylinders. The chemical reaction of its formation was as follows:

$$Ca_3\left[Si(OH)_6 \cdot 12H_2O\right]^{4+} + CO_3^{2-} + SO_4^{2-} \rightarrow Ca_3\left[Si(OH)_6 \cdot 12H_2O\right]CO_3SO_4 \tag{9}$$

The chemical reaction rate-determining step in Eq. (4) was the formation of $Ca_3[Si(OH)_6 \cdot 12H_2O]^{4+}$. Therefore, the formation of thaumasite depended on $Ca_3[Si(OH)_6 \cdot 12H_2O]^{4+}$ formation.

In the chemical reaction rate-determining step of the formation of $Ca_3[Si(OH)_6 \cdot 12H_2O]^{4+}$, calcium ions in the structure were usually coordinated with oxygen atoms in H_2O, and the studies proved that their preferred coordination number was 6 to 8. Therefore, Ca^{2+} ions were initially present in the form of $Ca[H_2O]_6^{2+}$ in water. In the chemical reaction process, when there was a strong alkaline environment, $Ca(H_2O)_6^{2+}$ was converted into $Ca(H_2O)_7^{2+}$ and $Ca(H_2O)_8^{2+}$ in the following forms [27]:

$$Ca\left(H_2O\right)_6^{2+} + H_2O\hat{U}Ca\left(H_2O\right)_7^{2+},\ Ca\left(H_2O\right)_7^{2+} + H_2O\hat{U}Ca\left(H_2O\right)_8^{2+} \tag{10}$$

During the formation of thaumasite, the silica tetrahedron gradually changed from $Si(OH)_4^{4-}$ to $Si(OH)_6^{2-}$. The central element Si in the $Si(OH)_6^{2-}$ anion was sp^3d^2 hybridized, and six hybrid orbitals were inserted into the six vertices of the octahedron. These hybrid orbitals overlapped with the 2*p* orbitals of coordinated oxygen atoms to form six covalent bonds [28].

When the pH of the solution was increased from 9 to 10.7, the neutral silicate monomer was converted to $Si(OH)_5^-$, whereas when the pH was higher than 10.7, silicate salts reacted with OH^- ions. As the surface OH group was ionized to the anion position of SiO^-, the particles were also negatively charged [29].

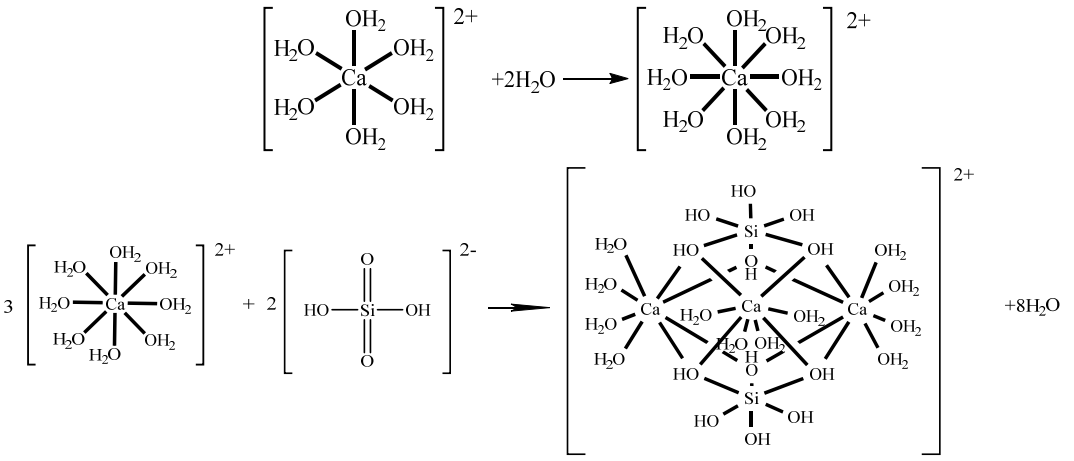
$$Si(OH)_4 + OH^- = (HO)_3SiO^- + H_2O,\ (HO)_3SiO^- + OH^- = (HO)_2SiO_2^{2-} + H_2O \tag{11}$$

The Si-O bond was not a pure ionic bond but also had some covalent properties [30].

Another raw material silicate participated in the chemical reaction, in which Si could form a $[SiO_4]^{4-}$ tetrahedron structure. When calcium ions were present in the solution, the following chemical reactions occurred with Si-O bonds [31]:

$$2 \equiv Si\text{-}O^- + Ca^{2+} \rightarrow (\equiv Si\text{-}O)_2\,Ca \tag{12}$$

Therefore, according to the above analysis, the $Ca_3[Si(OH)_6 \cdot 12H_2O]^{4+}$ formation process can be expressed as follows. To facilitate observation of the spatial structure of thaumasite, in the $Ca_3[Si(OH)_6 \cdot 12H_2O]^{4+}$ formation structure, $Si(OH)_6^{2-}$ was added, which changed the valence state of the structure



(13)

According to a report in the literature, if SO_4^{2-} anions are added to the solution alone, they cannot promote the formation of thaumasite [20]. In this experiment, to form thaumasite, $Si(OH)_4^{4-}$ was gradually transformed into a $Si(OH)_6^{2-}$ coordination anion, and this material first needed to form a silicate monomer. In an alkaline environment, $(HO)_3SiO^-$ and $(HO)_2SiO_2^{2-}$ were the main components [29, 32]. According to the literature [33], NH_3 can increase the coordination of silicate. The $(NH_4)_2SiO_3$ that was formed by these

two ions was extremely unstable and finally underwent a double hydrolysis reaction to form SiO_4^{4-} anions. This step could promote the rapid formation of thaumasite. The addition of excess SO_4^{2-} as $(NH_4)_2SO_4$ to the solution could promote the reaction of thaumasite.

Conclusions. As a common corrosion product of cement-based materials, thaumasite is often present in structural engineering materials. In a solution of Ca^{2+}, SiO_3^{2-}, CO_3^{2-}, SO_4^{2-}, and OH^- ions, the presence of NH_4^+ ions can affect the formation of thaumasite. Laser Raman spectroscopy was an effective method for detecting thaumasite. In the presence of ammonium ions, the spectral band of thaumasite was detected in the reaction product, and SO_4^{2-} anions in the solution accelerated the reaction. Neither Cl^- anions nor an alkaline environment effectively enhanced this trend. Based on the laser Raman spectroscopy data, the rate of direct thaumasite formation in solution at a low temperature was still higher than that at ambient temperature. However, the promotional effect of ammonium sulfate on the formation of thaumasite was stronger than that at a low temperature. The presence of ammonium ions could reduce the Gibbs free energy and increase the rate of the chemical reaction. Through the double hydrolysis reaction, the addition of ammonium ions promoted the coordination of silicate in the solution and increased the formation rate of thaumasite.

Acknowledgments. This work was supported by Hubei Superior and Distinctive Discipline Group of "Mechatronics and Automobiles" (XKQ2021027) and National Natural Science Foundation of China (No. 52074112).

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