Effect of Aluminum Sulfate and Succinic Acid on the Growth Law of α-Calcium Sulfate Hemihydrate under Microwave Irradiation

Yan Feng,1,2 Rongxin Guo1, and Zhiwei Lin1

1School of Civil Engineering and Architecture, Key Laboratory of Civil Engineering Disaster Prevention of Yunnan Province, Kunming University of Science and Technology, Kunming 650500, China
2Shandong Expressway Yantai Development Co. Ltd., Yantai, China

Correspondence should be addressed to Rongxin Guo; guorx@kmust.edu.cn

Received 2 November 2020; Revised 3 March 2021; Accepted 30 March 2021; Published 13 April 2021

1.Introduction

Phosphogypsum (PG) is a solid waste product that is discharged during wet phosphoric acid production processes. One ton of phosphoric acid can produce 4~6 tons of PG. Currently, the annual global production of PG is approximately 170 million tons, and the comprehensive utilization rate is approximately 5% [1]. The massive accumulation of PG has created many environmental problems, such as encroachment on land, soil pollution, and destruction of ecology, which have aroused widespread social attention. Resourceful remediation of these issues has become one of the main obstacles restricting the sustainable development of phosphorus chemical enterprises. The main component of PG is calcium sulfate dihydrate, which usually accounts for more than 85% of the total mass of the ideal raw material for the preparation of α-calcium sulfate hemihydrate. Since dihydrate gypsum forms after the hydration of α-calcium sulfate hemihydrate and is coarser and has much shorter columns, the degree of interlacement and overlap between crystals is better than that of flaky dihydrate gypsum; thus, its strength is higher. Domestic and foreign scholars have carried out extensive research on this topic. Fruitful research results have been achieved using the atmospheric salt solution method [2], the semiliquid phase method [3], recrystallization of β-calcium sulfate hemihydrate to obtain α-calcium sulfate hemihydrate [4], and the hydrothermal autoclave method.
2. Materials and Methods

2.1. Materials. In the experiment, PG was obtained from Yunnan Sanhuan Chemical Fertilizer Co., Ltd., whose chemical composition after pretreatment is shown in Table 1. Succinic acid was produced by Tianjin Kemiu Chemical Reagent Co., Ltd. Aluminum sulfate was produced by Tianjin Sailboat Chemical Reagent Technology Co., Ltd. Calcium chloride was produced by Tianjin Shentai Chemical Reagent Co., Ltd. Anhydrous ethanol and aluminum sulfate were both produced by Tianjin Zhiyuan Chemical Reagent Co., Ltd. All of these materials were of pure analytical grade. Deionized water was used when preparing the solutions.

2.2. Methods

2.2.1. Raw Material Pretreatment and Preparation of α-Calcium Sulfate Hemihydrate Powder. The test method for preparation of hemihydrate gypsum under microwave irradiation was as follows: PG was mixed with water at a ratio of 1:1, stirred, and cleaned, and the floating impurities remaining on the surface after standing were removed. The sample was cleaned four times and then dried for use. PG was pretreated by mixing it with a calcium chloride solution (mass fraction = 10%) and a crystal modifier, maintaining the solid-liquid ratio. After undergoing microwave irradiation, the solution was stirred evenly at a temperature of 100°C in an external condensing unit for 0.5 h, 1 h, 1.5 h, and 2 h. The samples were filtered and quenched using an anhydrous ethanol termination transformation process. The solid-phase product was placed in a drying oven at 55°C and dried until a constant weight was reached. The samples were reserved for SEM and XRD characterization tests.

2.2.2. Experimental Characterization and Equipment. The microwave radiation device is shown in Figure 1. The microwave frequency of the device was 2.45 GHz, the magnetron model was 1.5 kW, 2M463 K, and the rated power percentage was 70%. X-ray fluorescence spectroscopy (XRF, Axios Max, NLD) was used to analyze the elemental composition of the treated PG. An ultrasharp end-window RH target X-ray tube (4 kW) and a thermogravimetric analyzer (Mettler TGA/DSC HT 1600) were used to study the composition and phase transformation of phosphogypsum with temperature changes. The heating rate was 10.0 K/min, the heating range was 25–1000, and the heating atmosphere was nitrogen. SEM (JSM-6510 LV, Japan) and polarized light microscopy (Zeiss, Axio Imager A2M, Germany) were used to observe the crystal morphology changes with the change in parameters and to calculate the aspect ratio of the short columnar crystal. XRD (Panalytical, XPERT3POWDER, NLD) was used to analyze the image composition of the samples. The tube voltage and current of the CuKα radiation were 40 kV and 40 mA, respectively. The carbon, sulfur, oxygen, and calcium moieties on the surface of the hemihydrate gypsum crystals were analyzed by EDS (Vega 3 SBH). XPS (Thermo Fisher Scientific K-Alpha+, USA) was used to determine the binding energy of the samples. FTIR (Tensor 27, Bruker Optics, Germany) was used to analyze the group types in the hemihydrate gypsum products. The spectra ranged from 4000 to 400 cm⁻¹, each sample was scanned 10 times, and the spectral resolution was 4 cm⁻¹. The content of crystal water in the dehydrated PG products was determined by GB/T 5484-2012 "Methods for Chemical Analysis of Gypsum."

3. Results

3.1. The Growth of Calcium Sulfate Hemihydrate Crystals under Microwave Irradiation. Under microwave irradiation, PG was used as the raw material to prepare calcium sulfate hemihydrate in calcium chloride solution. When the reaction lasted for 0.5 h, 1 h, 1.5 h, and 2 h, the crystal microstructure of the solid phase was obtained; the microstructure is shown in Figure 2. When the reaction lasted for 1 h, the morphology of the solid-phase crystal changed from a sheet shape to a long columnar crystal with a length-to-diameter ratio of approximately 21. The crystal water content was 6.8% and the conversion rate reached 96%. When the reaction lasted for 2 h, the long columnar crystals in the solid phase disappeared. Under microwave irradiation, PG was prepared as a raw material in calcium chloride solution to form hemihydrate gypsum crystals, and after the initial increase, the calcium sulfate hemihydrate conversion rate...
showed a decreasing trend over time. At 1 h, the conversion rate was 96%, and as the reaction time progressed, the calcium sulfate hemihydrate crystal reverted to dihydrate calcium sulfate.

3.2. Effect of a Single Dose of Aluminum Sulfate on the Growth of Calcium Sulfate Hemihydrate Crystals

3.2.1. Laws Governing Effects of Aluminum Ion Dosage on α-Calcium Sulfate Hemihydrate. The SEM image and XRD pattern presented in Figure 3 show that when the aluminum ion content and the reaction time were 1 mM for 2 h, 3 mM for 1.5 h, and 5 mM for 1 h, the three samples all contained long columnar α-calcium sulfate hemihydrate and flakes of calcium sulfate dihydrate. The diagram in Figure 4 shows the change in crystal water content and the average length-to-diameter ratios of the columnar crystals. Figure 4 shows that, with the increase in dosage of aluminum ions from 11 to 12.3, the average length-to-diameter ratio increased from 6.38 μm to 9.7 μm. In conclusion, the addition of aluminum ions promoted an increase in the dehydration rate and the growth of hemihydrate gypsum crystals, and when the higher the number of aluminum ions was within a certain range, the promoting effect was more apparent.

3.3. Effect of 5 mM Aluminum Ions on the Crystal Morphology and Dehydration Reaction of α-Calcium Sulfate Hemihydrate. The effect of time on the growth of hemihydrate gypsum was studied by selecting the sample with a 5 mM aluminum ion content and the best reaction rate and conversion rate. Combined with the crystal morphology and product composition in Figures 5-6, it was apparent that when the aluminum sulfate crystallizer was mixed with 5 mM aluminum ions, columnar α-type hemihydrate gypsum was formed after 0.5 h, the crystal water content decreased to 6.47% after 1 h of reaction time, and the conversion rate reached 97%. After the addition of aluminum ions and as the dehydration reaction proceeded over time, the quantity of flake-shaped dihydrate gypsum crystals decreased and the quantity of columnar hemihydrate gypsum crystals increased. With increasing time, the amount of hemihydrate gypsum gradually decreased, and the amount of dihydrate gypsum increased.

3.3.1. Mechanism of the Effect of a Single Doping Ratio of 5 mM Aluminum Ions on the Growth of α-Calcium Sulfate Hemihydrate Crystals. The EDS energy spectra shown in Figures 7-8 show that, in addition to oxygen, sulfur, calcium, and silicon on the α-calcium sulfate hemihydrate crystals, aluminum also has a relatively uniform distribution on the crystal surface; XPS analysis revealed that the aluminum 2p peak in the calcium sulfate hemihydrate crystal was located at a binding energy of 74.75 eV, which suggested the presence of aluminum ions in the sample [11]. It was found that s2p can be fitted to two peaks, and the two peaks are located at binding energies of 169.4 eV [14] and 170.45 eV. The binding energy of the first peak at 169.4 eV is attributed to calcium and sulfate ions, and the binding energy of the second peak at 170.45 eV is attributed to sulfur and sulfate ions. The second peak shifted by 0.52 eV within a reasonable error range [11], which preliminarily shows that sulfate ions can change the growth rate of crystals by adsorbing α-calcium sulfate hemihydrate crystals. Figure 9 shows that the XRD pattern of the three main peaks of hemihydrate gypsum shifted to the left after a reaction time of 1 h with an aluminum ion content of 5 mM. The calculated unit cell parameters were \( a = 12.0124 \), \( b = 7.3778 \), \( c = 8.5478 \), \( \alpha = 90.0^\circ \), \( \beta = 97.23^\circ \), and \( \gamma = 90.0^\circ \), and the particle size was 79.92 nm. These data were compared with the data in the standard calcium sulfate hemihydrate crystal PDF card. The data in the standard calcium sulfate hemihydrate crystal PDF card are \( a = 12.028 \), \( b = 6.932 \), \( c = 12.691 \), \( \alpha = 90.0^\circ \), \( \beta = 90.138^\circ \), and \( \gamma = 90.0^\circ \). In comparison, it was determined...
that the $\beta$ angle of $\alpha$-hemihydrate gypsum changed, and the c-axis length became shorter as the b-axis side length increased. The doping of aluminum ions led to a change in cell parameters of the hemihydrate gypsum. The change in hemihydrate gypsum unit cell parameters reflects the change in the crystal growth environment [16, 17]. Due to the nonthermal effect of microwaves [18, 19], aluminum and sulfate ions are more easily combined than they are during normal heating; therefore, aluminum ions are doped during the growth process. The mechanism of aluminum ion crystal transformation under microwave irradiation involves the combination of aluminum ions and sulfate radicals changing

Figure 2: Polarizing microscope photo and changes in crystal water content (c) without a modifier at a heating temperature of 100°C for 2h: (a) 0.5 h; (b) 1 h; (c) 1.5 h; (d) 2 h.
the crystal morphology of calcium sulfate hemihydrate, which is different from the crystal transformation mechanism under conventional heating [15].

3.4. Effect of Succinic Acid on the Growth of Calcium Sulfate Hemihydrate Crystals under Microwave Irradiation

3.4.1. Effect of Succinic Acid Content on α-Calcium Sulfate Hemihydrate. Under microwave irradiation, PG was used as the raw material and mixed with a succinic acid conversion agent (dosing amounts of 0.01%, 0.02%, and 0.03%), and hemihydrate gypsum crystals were prepared in calcium chloride solution. The samples were analyzed when the reaction proceeded to 1.5 h, and the results are shown in the following figures: Figure 10 shows the microscopic morphology of the solid-phase crystal obtained in 1.5 h was basically short hexagonal prism crystals (see Figures 10(a) and 10(b)), and the measured water content of the crystals was 7.23% and 6.89%, respectively. The conversion rates of calcium sulfate dihydrate crystals to calcium sulfate hemihydrate were 94% and 96%, respectively. When the content of succinic acid was 0.03%, the plate-like crystals in the solid phase obtained over 1.5 h increased (see Figure 10(c)), the measured water content of crystallization was 9.44%, and the conversion rate of calcium sulfate dihydrate crystals to calcium sulfate hemihydrate decreased to 81%, indicating that some of the calcium sulfate hemihydrate crystals were converted back to calcium sulfate dihydrate. The effect of different succinic acid contents on the crystal size of calcium sulfate hemihydrate is shown in Figure 11(c). It can be seen from the figure that, with increasing succinic acid content, the aspect ratio of the prepared calcium sulfate hemihydrate crystals decreased from 2.3 to 1.3, but the average size of the crystals first increased and then decreased. The above-mentioned experiments prove that when the crystal
Figure 4: Changes in crystal water content at a heating temperature of 100°C when aluminum ion dosage was 1 mM, 3 mM, and 5 mM for 2 h (a). The average aspect ratio and average diameter of calcium sulfate hemihydrate crystal (b) at a heating temperature of 100°C when aluminum ion dosage and heating time were 1 mM for 2 h; 3 mM for 1.5 h; and 5 mM for 1 h.

Figure 5: SEM photo (200x) at reaction times of (a) 0.5 h; (b) 1 h; (c) 1.5 h; and (d) 2 h when the aluminum ion concentration was 5 mM.
conversion agent contains only small levels of dopant, with increasing succinic acid content, the control effect on the microscopic morphology of the calcium sulfate hemihydrate crystals is continuously strengthened, and the aspect ratio of the crystals is continuously reduced.

3.4.2. Effect of Time on the Crystal Morphology and Dehydration Reaction of α-Calcium Sulfate Hemihydrate under a Single Doping Ratio of 0.02% Succinic Acid. Figures 12–13 show that when the reaction of 0.02% succinic acid is carried out for 1.5h, the plate-shaped calcium sulfate dihydrate crystals have basically been transformed into short hexagonal prism-shaped α-type hemihydrates with an aspect ratio of approximately 1.5. Hydrated gypsum crystals have a conversion rate of approximately 96%; as the reaction progresses to 2h, the main component in the product becomes calcium sulfate dihydrate flakes. Compared with the non-transforming agent, the addition of 0.02% succinic acid has better control over the crystal morphology of calcium sulfate hemihydrate, and the aspect ratio of calcium sulfate hemihydrate crystals is reduced from 21 to 1.5, but it is extended. At the same time, the incorporation of the crystal conversion agent did not affect the conversion rate law of calcium sulfate
dihydrate to calcium sulfate hemihydrate, the conversion rate first increased, and then decreased with time, and it had no effect on the maximum conversion rate. This was the result of microwaves being strong electromagnetic waves, and the generated microwave plasma usually contains high energy atoms, molecules, and ions that are not involved in thermodynamic methods, thereby reducing the activation energy of the reaction and accelerating the reaction.

3.4.3. Mechanism of the Effect of a Single Doping Ratio of 0.02% Succinic Acid on the Growth of α-Calcium Sulfate Hemihydrate Crystals. The α-type calcium sulfate hemihydrate crystal grows faster on the (111) crystal plane than other crystal planes without the intervention of the crystal conversion agent; therefore, it will grow into needle-like crystals. This crystal morphology forms because there are Ca\(^{2+}\) and SO\(_4^{2-}\) ions in the direction of the crystal c-axis. For the two free end valence bonds of the ions [20], the growth of crystal faces is faster than that of other crystal faces. The reason why organic acids control the change in crystal shape under other heating methods is that the complexation of carboxyl groups and calcium ions forms a cyclic complex, which slows the growth rate of these crystal faces and changes the crystal shape [5]. As shown in Figure 14 and Table 2, the end surface perpendicular to the c-axis of α-calcium sulfate hemihydrate has approximately the same strength, weight, and atomic content as the carbon parallel to
Figure 10: Crystal morphology of the solid phase obtained by succinic acid (doped with (a) 0.01%; (b) 0.02%; (c) 0.03%) for 1.5 h.

Figure 11: Continued.
Figure 11: Solid-phase crystallization water content (a), solid-phase XRD pattern (b), and crystal size (c) of succinic acid (doped with 0.01%, 0.02%, and 0.03%) for 1.5 h.

Figure 12: SEM images of solid-phase crystals obtained under different reaction times in the presence of 0.02% succinic acid: (a) 0.5 h; (b) 1 h; (c) 1.5 h; and (d) 2 h.
the c-axis side, which indicates that there is no selective succinic acid doping or adsorption.

Figure 15 shows that the two absorption peaks at 3165.29 and 3560.01 cm\(^{-1}\) are the two absorption peaks of crystal water in α-calcium sulfate hemihydrate, while the absorption peaks at 598.25 cm\(^{-1}\) and 1152.22 cm\(^{-1}\) are caused by the flexural vibration and asymmetric stretching of sulfate radicals [21]. However, the FTIR does not include the free carboxyl COO\(^-\) absorption peak in the range of 1750–1770 cm\(^{-1}\), the liquid or solid carboxyl absorption peak in the range of 1670–1725 cm\(^{-1}\), or the carboxylate absorption peak in the 1550–1650 cm\(^{-1}\) range. This test

**Figure 13:** Solid-phase crystallization water content and XRD patterns obtained under different reaction times in the presence of 0.02% succinic acid.

**Figure 14:** SEM photo of succinic acid at 0.02% and 1.5 h at 100°C.

<table>
<thead>
<tr>
<th>Crystal face</th>
<th>Strength%</th>
<th>Weight%</th>
<th>Atom%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.167</td>
<td>6.88</td>
<td>12.56</td>
</tr>
<tr>
<td>2</td>
<td>0.250</td>
<td>7.00</td>
<td>11.87</td>
</tr>
</tbody>
</table>

**Table 2:** EDS of two points in SEM photo (%).
shows that the succinic acid crystal conversion agent inhibits the growth rate of hemihydrate gypsum crystals on the c-axis crystal surface under microwave irradiation and controls the morphology of hemihydrate gypsum crystals, but it is not adsorbed onto the hemihydrate gypsum crystals. Succinic acid remained on top or was mixed into the hemihydrate gypsum crystals and was eliminated from the hemihydrate gypsum system with the filtrate or absolute ethanol in the filtration stage.

4. Conclusions

The \( \alpha \)-type calcium sulfate hemihydrate was prepared by the salt solution method under microwave irradiation, and the effect of two crystal conversion agents, succinic acid, and aluminum sulfate, on the growth of hemihydrate gypsum crystals was studied. The following conclusions were drawn from the analysis, and the results of this paper are summarized as follows:

(1) In the microwave irradiation method in which salt solutions were used, pretreated PG was used as the raw material, the average aspect ratio of the hemihydrate gypsum crystals without the crystal conversion agent was 2.1 after reaction for 1 h, and the conversion rate reached 96%; single-doped succinic acid was converted to the crystalline form at 0.02%, the length-to-diameter ratio of hemihydrate gypsum crystals was approximately 1.5 after 1.5 h, and the conversion rate reached 96%. When the aluminum sulfate conversion agent was doped at only 5 mM, it reacted for 1 h. The aspect ratio of gypsum crystals was approximately 12.3, and the conversion rate reached 97%.

(2) Under microwave irradiation, when PG was used as a raw material and calcium chloride solution was not mixed with a crystal conversion agent, mixed with aluminum sulfate alone, or mixed with succinic acid alone, the conversion law of calcium sulfate dihydrate crystals to calcium sulfate hemihydrate was uniform. Therefore, the conversion rate first increased and then decreased with time. Under microwave irradiation with salt solutions, the time required for the dehydration reaction of calcium sulfate dihydrate was significantly shortened; an appropriate amount of aluminum sulfate conversion agent continued to accelerate the dehydration reaction process, and an appropriate amount of succinic acid conversion agent affected the crystal form of hemihydrate gypsum. The appearance was well controlled.

(3) Under microwave irradiation, succinic acid did not enter or adsorb onto the hemihydrate gypsum crystals during the reaction but appeared in the crystal growth stage, and one-half of it was eliminated from the reaction with the filtrate after the crystal transformation was completed. The crystalline system incorporated aluminum ions into hemihydrate gypsum crystals when they grew.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

This research was funded by the National Natural Science Foundation of China (11562010) and Kunming University of Science and Technology Analysis and Testing Fund (2020M20172110016).

References


