Effect of sulfuric acid concentration on morphology of calcium sulfate hemihydrate crystals

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Abstract

Calcium sulfate hemihydrate whiskers were prepared in sulfuric acid-distilled water system by hydrothermal method using calcium sulfate dihydrate as raw materials. The influence mechanism of sulfuric acid concentration on morphology of calcium sulfate hemihydrate crystals was investigated. The results show that the morphology of hydrothermal products is fibrous when the suitable sulfuric acid concentration is from $5.0 \times 10^{-6}$ mol l$^{-1}$ to $5.0 \times 10^{-4}$ mol l$^{-1}$. The promoting effect of sulfuric acid on the dissolution of calcium sulfate dihydrate increases the amount of Ca$^{2+}$ in the solution, which is beneficial to the crystallization of calcium sulfate hemihydrate crystals. Meanwhile, the selective adsorption of H$^+$ produced by sulfuric acid ionization on the (310) crystal plane of calcium sulfate hemihydrate crystals can hinder the aggregation of Ca$^{2+}$ on the crystal plane, which results in preferential growth of the calcium sulfate hemihydrate crystal along the (001) crystal plane. However, when the sulfuric acid concentration is up to $5.0 \times 10^{-1}$ mol l$^{-1}$, the HSO$_4^-$ produced by the interaction of H$^+$ with SO$_4^{2-}$ can reduce the electronegativity of SO$_4^{2-}$ and inhibit SO$_4^{2-}$ adsorption on the crystal surface. So the growth of calcium sulfate hemihydrate crystals along (001) crystal plane is hindered, which leads to the decrease of the fibrous products.

1. Introduction

Calcium sulfate hemihydrate whiskers are generally fabricated under acidic conditions. Recently, natural gypsum, desulfurized gypsum and phosphogypsum were used as the raw materials to produce the calcium sulfate hemihydrate whiskers. Tan et al [1] used building gypsum as a raw material to investigate the effects of factors such as sulfuric acid concentration on the morphology of gypsum whiskers. Wang et al [2] researched the effect of pH on the morphology of gypsum whisker crystals in sulfuric acid system using phosphogypsum as the raw materials. Wang et al [3] used nickel tailings as raw materials to prepare gypsum whiskers and optimized the amount of sulfuric acid. Liu et al [4–6] discussed the effect of pH on the growth of desulfurized gypsum whiskers with desulfurized gypsum. However, there are different kinds of impurities in the industrial by-products such as desulfurized gypsum [7–9]. Otherwise, the calcium sulfate hemihydrate whiskers form a framework along the [001] direction, SO$_4^{2-}$ ions have a denser distribution on the side facets of the [110] and [100], and Ca$^{2+}$ ions have a denser distribution on the top facet of the [001], so a large number of research works have shown that impurities adversely affect the crystallization process and crystal morphology of calcium sulfate hemihydrate whiskers [10–16]. That whether the impurity ions cause changes in whisker morphology is not elucidated.

Therefore, the influence of pH value on the morphology of calcium sulfate hemihydrate crystals is not revealed. In order to avoid the influence of impurity ions on the crystallization of calcium sulfate in hemihydrates, Mao et al [17] prepared calcium sulfate hemihydrate whisker in a hydrochloric acid-water system by analyzing pure grade calcium sulfate dihydrate, and systematically studied the mechanism of the effect of pH value on the
crystallization of calcium sulfate hemihydrate whiskers. The effects of inevitable ions such as calcium ions and magnesium ions in water are not considered \[18, 19\]. Though the effect of pH on the morphology of calcium sulfate hemihydrate crystals in the sulfuric acid system was discussed, the interaction between impurity ions and pH in the crystallization process of whiskers in the hydrothermal system was not clarified, the role of H\(^+\) and SO\(_4^{2-}\) in the crystallization of calcium sulfate hemihydrate crystals was not elucidated. So the preparation and properties of calcium sulfate hemihydrate whiskers in a sulfuric acid-distilled water system using calcium sulfate dihydrate as the raw material was researched in this paper to provide a certain theoretical reference for improving the theoretical system of calcium sulfate whisker crystallization.

2. Experiment

2.1. Materials and equipment

Calcium sulfate dihydrate (Analytical pure, Tianjin Guangfu Fine Chemical Research Institute), H\(_2\)SO\(_4\) (Analytical pure, Tianjin No. 3 Chemical Reagent Factory), distilled water (Secondary distillation) were used as the raw materials. The main instruments include Reactor (GSA-1 type, Shanghai Yancheng Instrument Co., Ltd), Digital display type mechanical stirrer (D2004W type, Shanghai No. 6 Optical Instrument Factory), Circulating Water Vacuum Pump (SHB-III type, Zhengzhou Great Wall Technology Industry & Trade Co., Ltd), Oven (101-1 type, Shanghai Experimental Instrument General Factory), Conductivity meter (MP515-01 type, Shanghai Sanxin Instrument Factory), Scanning electron microscope (SEM, SSX-550 type, Shimadzu Corporation), Synchronous Thermal Analyzer (STA449F3 type, NETZSCH), X-ray diffractometer (XRD, X’Pert PRO MPD type, Panaco), Fourier transform infrared spectrometer (FTIR, Nicolet iS10 type, Thermo Fisher Scientific).

2.2. Experimental procedures and testing methods

The process of preparation of calcium sulfate hemihydrate whiskers by hydrothermal method is shown in figure 1.

40 g of calcium sulfate dihydrate and 760 ml of secondary distilled water were configured into the slurry with a concentration of 5% by mass and an appropriate amount of sulfuric acid was added. The slurry was placed in a reaction kettle and heated to 120 °C for 30 min and then was filtered and dehydrated. Finally, the hydrothermal product was dried in an oven at 100 °C for 30 min. The slurry added with the sulfuric acid was stirred at 95 °C for 30 min at a speed of 300 r min\(^{-1}\). The calibrated ethylene diamine tetraacetic acid was used to titrate the supernatant of the slurry for measuring the Ca\(^{2+}\) concentration, and the average of the five titration results was taken as the final concentration.

Anhydrous ethanol was used to disperse the product. After spraying gold, the morphology of the hydrothermal product was observed at 2000 magnifications using an SSX-550 scanning electron microscope (SEM, acceleration voltage 200 V-30 kV). The KBr tablet method was used to make the tablets, and then the Nicolet iS10 FTIR spectrometer (Wave number accuracy is better than 0.01 cm\(^{-1}\)) was used to detect the surface
functional groups of the hydrothermal products. The appropriate amount of hydrothermal product was ground and the powder was detected using X-ray diffraction (Cu target radiation, Scan rate is 0.08° s⁻¹, Scan range is 5°–80°). STA449F3 type synchronous thermal analyzer was used for DSC-TG detection of hydrothermal products in a nitrogen atmosphere, and the heating rate was 5 °C min⁻¹. The conductivity of the calcium sulfate dihydrate solution in the sulfuric acid-water system at 95 °C was measured. Before the measurement, the conductivity meter was calibrated, and then the measuring electrode was inserted into the test solution.

3. Results and discussion

3.1. Morphology of hydrothermal products
Figure 2 shows the morphology of hydrothermal products under different sulfuric acid concentration conditions. The morphology of hydrothermal products is distinct, and the content of fibrous products changes with the increase of sulfuric acid. When the sulfuric acid concentration is 5.0 × 10⁻⁶ mol l⁻¹, there are more hydrothermal products in the form of granules and short columns, and the long diameter of the fibrous products with less content is smaller. When the sulfuric acid concentration increased to 5.0 × 10⁻⁵ mol l⁻¹, the content of fibrous hydrothermal products increased, but its length was short, and some plate-like crystals existed. When the sulfuric acid concentration is 5.0 × 10⁻⁴ mol l⁻¹, the morphology of the product is basically fibrous. When the sulfuric acid concentration is further increased to 5.0 × 10⁻³ mol l⁻¹, the content of fibrous products decreased and the number of granular and short columnar crystals increased. The sulfuric acid has a certain regulating effect on the crystal morphology of calcium sulfate hemihydrate, and the crystal morphology is better when the sulfuric acid concentration is 5.0 × 10⁻⁴ mol l⁻¹. In addition, when the sulfuric acid concentration is 5.0 × 10⁻⁶ mol l⁻¹ and 5.0 × 10⁻⁵ mol l⁻¹, there are more granular morphologies in hydrothermal products.

3.2. Analysis of the dissolution process of calcium sulfate dihydrate
The preparation process of calcium sulfate hemihydrate whisker consists of two steps of ‘dissolution-recrystallization’ continuous reaction. The dissolution process of calcium sulfate dihydrate has a greater effect on the crystallization of calcium sulfate hemihydrate whiskers [20]. The Ca²⁺ concentration and conductivity of the solution was measured to clarify the role of sulfuric acid in the dissolution of calcium sulfate dihydrate. It can
be seen from figure 3 that the $\text{Ca}^{2+}$ concentration in the solution increases with the increase of the sulfuric acid concentration. The values of sulfuric acid concentration increase from 12.80 mmol $\text{l}^{-1}$ to 14.64 mmol $\text{l}^{-1}$, so the solubilizing effect of sulfuric acid increases with the increase of sulfuric acid concentration. The conductivity of the calcium sulfate dihydrates supernatant solution and sulfuric acid solution increases with the increase of sulfuric acid concentration, which can be seen in figure 4. However, the increment in the conductivity of $\text{Ca}^{2+}$ and $\text{SO}_4^{2-}$ generated by the ionization of calcium sulfate dihydrate reduces with the increase of sulfuric acid concentration. Since the calcium sulfate dihydrate solution mainly contains $\text{Ca}^{2+}$, $\text{SO}_4^{2-}$, $\text{H}^+$ and $\text{OH}^-$, when the strong electrolyte concentration is low, the conductivity of the solution is proportional to the ion concentration. According to the results in figures 3 and 4, when the sulfuric acid concentration increases, $\text{H}^+$ in sulfuric acid reacts with $\text{SO}_4^{2-}$ to form $\text{HSO}_4^-$, which reduces the total amount of ions in the solution and the conductivity increment decreases with the increase of the sulfuric acid concentration.

Figure 3. Effect of sulfuric acid concentration on $\text{Ca}^{2+}$ concentration in solution.

Figure 4. Variation of solution conductivity with sulfuric acid concentration.

TG-DSC curves of hydrothermal products under different concentrations of sulfuric acid are shown in figure 5. The crystallization water in the hydrothermal product is removed at about 100 °C. The weight loss of hydrothermal products with sulfuric acid concentrations of $5.0 \times 10^{-3}$ mol $\text{l}^{-1}$, $5.0 \times 10^{-4}$ mol $\text{l}^{-1}$, $5.0 \times 10^{-5}$ mol $\text{l}^{-1}$ and $5.0 \times 10^{-6}$ mol $\text{l}^{-1}$ were 7.08%, 7.66%, 7.01% and 15.44% under 140 °C, respectively. When the sulfuric acid concentration is $5.0 \times 10^{-3}$ mol $\text{l}^{-1}$ and $5.0 \times 10^{-4}$ mol $\text{l}^{-1}$, the weight loss of the hydrothermal product is slightly larger than the theoretical content of crystal water of calcium sulfate.
hemihydrate, which is 6.21%. It may be due to the presence of adsorbed water on the surface of the hydrothermal product. When the sulfuric acid concentration is $5.0 \times 10^{-6}$ mol l$^{-1}$, the weight loss rate of hydrothermal products is much greater than the theoretical content of crystal water of calcium sulfate hemihydrate. The DSC curve has an obvious endothermic peak near 130°C and the mass loss is closer to the content of crystal water in calcium sulphate dihydrate. And the intensity of the endothermic peak is the largest when the sulfuric acid concentration is $5.0 \times 10^{-6}$ mol l$^{-1}$. It can be seen that the hydrothermal product is a mixture of calcium sulfate dihydrate and calcium sulfate hemihydrate, and the content of calcium sulfate dihydrate is higher.

3.3. Surface functional group and phase analysis of hydrothermal products

Figure 6 shows that the infrared spectrum analysis of the hydrothermal products was performed in order to clarify the influence of sulfuric acid concentration on the surface functional groups of hydrothermal products. In figure 6(c), the absorption peaks at 3611.25, 3552.20, 1620.44 cm$^{-1}$, are the hydroxyl absorption peaks of crystal water inside the crystal, and the hydroxyl stretching vibration peaks [21] at 3406.22 cm$^{-1}$ corresponding to the hydroxylation of calcium ion on the surface of the hydrothermal product, 1152.70, 1006.89, 658.29, 600.61 cm$^{-1}$ characteristic absorption peaks corresponding to $\text{SO}_4^{2-}$ group. Among them, the antisymmetric vibrational absorption peak of two groups degenerates [22] at 1152.70 cm$^{-1}$. In figure 6(a), the hydroxyl peak at 3611.25 cm$^{-1}$ of the hydrothermal product basically disappeared, the hydroxyl peak intensity and peak shape at
3552.20 cm\(^{-1}\) changed, and at 1620.44 cm\(^{-1}\) the peak shape becomes narrower. It is indicated that the chemical environment of the crystal water in the hydrothermal product has changed, which may be caused by the high content of calcium sulfate dihydrate in the hydrothermal product. In figure 6(b), the absorption peak at 1152.70 cm\(^{-1}\) shifts to 1168.66 cm\(^{-1}\) because the degree of hydroxylation of the ions on the surface of the hydrothermal product is small, which makes SO\(_4^{2-}\) group characteristic peaks to be weaker. In figure 6(d), the anti-symmetric stretching vibrational absorption peaks of SO\(_4^{2-}\) group is split, and two new characteristic absorptions appear at 1172.74 cm\(^{-1}\) and 1095.93 cm\(^{-1}\). The change of the sulfuric acid concentration causes the change of the characteristic absorption peaks of hydroxyl and SO\(_4^{2-}\) groups on the surface of hydrothermal products, which affects the growth environment and surface functional group composition of hydrothermal products.

XRD analysis was performed on the hydrothermal products in order to reveal the effect of different concentrations of sulfuric acid on the degree of crystallization and phase composition of hydrothermal products in figure 7. The characteristic diffraction peaks of \(\alpha\)-calcium sulfate hemihydrate crystals are the diffraction peaks at 2\(\theta\) = 14.82°, 25.74°, and 29.82°, which correspond to the (100), (001) and (200) planes. And the characteristic diffraction peak of calcium sulfate dihydrate crystal are the diffraction peaks at 2\(\theta\) = 11.78°, 20.86°, 23.54°, and 29.26°, which correspond to the (020), (221), (131) and (241) planes. When the sulfuric acid concentration is higher than 5.0 \(\times\) 10^{-5} mol l\(^{-1}\), there is only the phase of calcium sulfate hemihydrate in the samples. However, there are obvious heterophases when the sulfuric acid concentration is equal to 5.0 \(\times\) 10^{-4} mol l\(^{-1}\). The hydrothermal product is composed of calcium sulfate hemihydrate and calcium sulfate dihydrate. In addition, when the concentration is 5.0 \(\times\) 10^{-4} mol l\(^{-1}\), the intensity of the diffraction peak is high and the peak shape is sharp. The concentration of sulfuric acid also has a certain effect on the crystallinity of calcium sulfate hemihydrate, and that the crystallinity of calcium sulfate hemihydrate is best in those produced under the condition of 5.0 \(\times\) 10^{-6}–5.0 \(\times\) 10^{-4} mol l\(^{-1}\) sulfuric acid concentration.

The crystal growth of calcium sulfate hemihydrate has a preferred orientation with the increase of sulfuric acid concentration. The strong diffraction peak intensity of (100) and (001) planes shows that the calcium sulfate hemihydrate crystal grows along the normal direction of (100) and (001) planes, which is more conducive to the formation of calcium sulfate hemihydrate whisker [23]. Figure 8 shows the crystallinity of the strongest diffraction peak of calcium sulfate hemihydrate. The crystallinity of calcium sulfate hemihydrate crystal increases with the increase of sulfuric acid concentration. When the concentration of sulfuric acid is 5.0 \(\times\) 10^{-4} mol l\(^{-1}\), the crystallinity of the strongest diffraction peak is 0.3607, which shows that the crystallinity of calcium sulfate hemihydrate crystal is the best. When the concentration of sulfuric acid increased under certain conditions of temperature and reaction time, the morphology of calcium sulfate hemihydrate crystal changes greatly in figure 2. The appearance of the crystal changes from short column and granular to fibrous shape, the length of calcium sulfate hemihydrate crystal increases along the C-axis, and the degree of crystallization gradually tends to be complete.

Figure 7. XRD patterns of hydrothermal products under different concentrations of sulfuric acid (a) 5.0 \(\times\) 10^{-6} mol l\(^{-1}\); (b) 5.0 \(\times\) 10^{-5} mol l\(^{-1}\); (c) 5.0 \(\times\) 10^{-4} mol l\(^{-1}\); (d) 5.0 \(\times\) 10^{-3} mol l\(^{-1}\).
When the sulfuric acid concentration is less than $5.0 \times 10^{-4}$ mol $\text{l}^{-1}$, the ionized $\text{H}^+$ and $\text{SO}_4^{2-}$ are selectively adsorbed on the surface of calcium sulfate hemihydrate crystals. $\text{SO}_4^{2-}$ as a growth element crystallizes on the (100) and (200) planes of calcium sulfate hemihydrate crystals, which is conducive to the radial growth of calcium sulfate hemihydrate crystals [23]. Figure 8 shows the grain size of the strongest diffraction peak of calcium sulfate hemihydrate product calculated by Scherrer formula. The grain size of the crystal plane of calcium sulfate hemihydrate product (200) increases with the increase of sulfuric acid concentration. The grain size is from 7.98 nm to 47.26 nm when the sulfuric acid concentration is from $5.0 \times 10^{-6}$ mol $\text{l}^{-1}$ to $5.0 \times 10^{-3}$ mol $\text{l}^{-1}$. The distribution of calcium sulfate hemihydrate crystal is more uniform with the increase of sulfuric acid concentration, which also promotes the growth of calcium sulfate hemihydrate crystals.

However, $\text{H}^+$ selectively adsorbs on the crystal plane of the crystal (310) and bonds with the oxygen atoms on the surface, which reduces the electronegativity of the crystal plane $\text{SO}_4^{2-}$ and the specific surface free energy of the crystal plane, which hinders the adsorption of the growth units on the crystal plane [24]. The combined effect of $\text{SO}_4^{2-}$ and $\text{H}^+$ finally causes the morphology of the crystal to change from a short columnar shape to a fibrous shape in figure 2. In addition, sulfuric acid can promote the dissolution of calcium sulfate dihydrate and increase the supersaturation of calcium sulfate hemihydrate, which is beneficial to the crystallization of calcium sulfate hemihydrate crystals to some extent. However, when the sulfuric acid concentration is $5.0 \times 10^{-3}$ mol $\text{l}^{-1}$, $\text{HSO}_4^{-}$ generated by $\text{H}^+$ and $\text{SO}_4^{2-}$ reduces the electronegativity of $\text{SO}_4^{2-}$ and weakens the electrostatic effect between $\text{SO}_4^{2-}$ and $\text{Ca}^{2+}$. The growth of calcium crystals along the (001) plane has a certain inhibitory effect [25]. Moreover, because the growth of calcium sulfate hemihydrate crystals is a complex and slow process, the aggregation rate of the calcium sulfate hemihydrate is accelerated in super-saturated solution, which results in not enough time for the lattice arrangement and is not in favour of crystal growth [20]. So when the sulfuric acid concentration is $5.0 \times 10^{-3}$ mol $\text{l}^{-1}$, the crystallisation of the calcium sulfate hemihydrate hydrothermal product is poor (shown in figure 2(d)). It can be seen that the appropriate sulfuric acid concentration is beneficial to the crystallization of calcium sulfate hemihydrate, and the crystal quality of fibrous hydrothermal products is the best when the sulfuric acid concentration is $5.0 \times 10^{-4}$ mol $\text{l}^{-1}$.

**4. Conclusions**

(1) The sulfuric acid concentration in the sulfuric acid-distilled water system has a certain regulation effect on the morphology and phase composition of calcium sulfate hemihydrate hydrothermal products. The appropriate sulfuric acid concentration is beneficial to the crystallization of calcium sulfate hemihydrate whiskers. When the sulfuric acid concentration is $5.0 \times 10^{-4}$ mol $\text{l}^{-1}$, the crystal morphology of calcium sulfate hemihydrate hydrothermal products is mostly fibrous.

(2) When the sulfuric acid concentration is less than $5.0 \times 10^{-4}$ mol $\text{l}^{-1}$, the solubilization effect of sulfuric acid on calcium sulfate dihydrate increase the number of $\text{Ca}^{2+}$ in the solution. So the nucleation and growth of calcium sulfate hemihydrate is promoted. $\text{H}^+$, which can selectively adsorb on (310), leads to the preferential growth of calcium sulfate hemihydrate crystals along the (001) crystallographic plane.
Therefore, the crystal morphology of the product changes from short column to fiber with the increase of the sulfuric acid concentration.

(3) The excessive supersaturation of calcium sulfate hemihydrate affects adversely the crystal growth when the sulfuric acid concentration is \(5.0 \times 10^{-3}\) mol l\(^{-1}\). The growth of the crystal plane eventually leads to the crystal morphology of the hydrothermal product being mainly granular and short columnar.

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