INVESTIGATION OF ORGANIC DESULFURIZATION ADDITIVES AFFECTING THE CALCIUM SULFATE CRYSTALS FORMATION

Article Highlights
- The optimal experimental conditions for calcium sulfate crystals formation were found
- Mg\(^{2+}\), Al\(^{3+}\) and Fe\(^{3+}\) inhibit calcium sulfate formation, Fe\(^{3+}\) being the strongest inhibitor
- Induction time, moisture content, particle size distribution, and crystal morphology were analyzed
- The influence of organic desulfurization additives on calcium sulfate formation was studied
- Citric acid and sodium citrate can improve the removal of SO\(_2\) and quality of calcium sulfate

Abstract
In the study, the optimal experimental conditions for gypsum crystals formation were 323 K, 300 rpm stirring speed. The major impurities of Mg\(^{2+}\), Al\(^{3+}\) and Fe\(^{3+}\) were found to inhibit calcium sulfate crystals formation. Fe\(^{3+}\) caused the strongest inhibition, followed by Mg\(^{2+}\) and Al\(^{3+}\). The influence of desulfurization additives on the gypsum crystals formation was explored with the properties of moisture content, particle size distribution and crystal morphology. The organic desulfurization additives of adipic acid, citric acid, sodium citrate and benzoic acid were investigated. Citric acid and sodium citrate were found to improve the quality of gypsum. Moisture contents were reduced by more than 50%, gypsum particle sizes were respectively enlarged by 9.1 and 22.8%, induction time extended from 4.3 (blank) to 5.3 and 7.8 min, and crystal morphology trended to be thicker.

Keywords: calcium sulfate crystals, desulfurization additives, impurities, wet flue gas desulfurization.

The limestone-gypsum wet flue gas desulfurization (WFGD) process is the most widely used desulfurization technology in Chinese coal-power plants, for removing acidic compounds (SO\(_2\), HCl and HF) from flue gases [1-3]. In WFGD system, SO\(_2\) gases are absorbed by the limestone slurry, and SO\(_2\) combines with H\(_2\)O to produce HSO\(_3^-\) ions. In the slurry holding tank, HSO\(_3^-\) are oxidized to SO\(_4^{2-}\) by injected oxygen. Finally, SO\(_4^{2-}\) combine with the Ca\(^{2+}\) to produce calcium sulfate dihydrate crystals, which is an unsolvable chemical. Gypsum can be refined for commercial applications. The quality of formatted gypsum crystals is related to process conditions, including temperature, stirring speed, impurities and so on [4-6]:

\[
\text{CaCO}_3(s) + \text{SO}_2(g) + 2\text{H}_2\text{O(l)} + 0.5\text{O}_2(g) \rightarrow \text{CaSO}_4 \cdot 2\text{H}_2\text{O(s)} + \text{CO}_2(g)
\]

(1)

Mg\(^{2+}\), Al\(^{3+}\) and Fe\(^{3+}\) are three common impurity ions in wet FGD slurry. The effects of Mg\(^{2+}\) and Al\(^{3+}\) on gypsum crystallization in a CaCl\(_2\)-Na\(_2\)SO\(_4\)-H\(_2\)O system have been investigated by many authors. In the presence of Mg\(^{2+}\), the growth rate of gypsum crystal was reduced and the crystals were elongated.
while the growth rate of gypsum crystal increased in the presence of Al^{3+}.

As the emission standard of SO\(_2\) reduced to 50 mg/m\(^3\), the existing WFGD techniques were required to improve. Adding organic desulfurization additive has been proven to be the most efficient and economical means to enhance SO\(_2\) removal from power plants [3]. Organic desulfurization additives have been developed to significantly improve SO\(_2\) removal in WFGD systems in the past decade, such as formic acid, adipic acid, maleic acid, acetic acid, sodium citrate and benzoic acid [7-9]. However, there is concern that addition of desulfurization additives may undermine the quality of produced calcium sulfate crystals [10].

Purity, moisture content and particle size distribution (PSD) were usually considered as end use characteristics of gypsum. Gypsum with low quality cannot meet the standard for commercial applications and is considered as solid waste. Many organic acids have been reported to change the crystallinity and affect calcium sulfate crystal morphology (both size and shape), such as citric acid [11,12].

In this study, besides the influence of experimental conditions on the calcium sulfate crystals, the effect of four common desulfurization additives (adipic acid, citric acid, sodium citrate and benzoic acid) were also investigated.

MATERIALS AND METHODS

Chemicals and materials

Analytically pure adipic acid, citric acid, sodium citrate, benzoic acid, CaCl\(_2\), HCl, Na\(_2\)SO\(_4\) and Ca(OH)\(_2\) were supplied by Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). The initial pH of CaCl\(_2\) solution was adjusted by the addition of HCl and Ca(OH)\(_2\) solution; the initial pH of solution was adjusted to 5.4±0.2. The metal ions, Mg\(^{2+}\), Al\(^{3+}\) and Fe\(^{3+}\) were added as the form of MgCl\(_2\), AlCl\(_3\) and FeCl\(_3\), which were also supplied by Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China).

The pH of solution was monitored by using a Bante 901b pH meter, and solution conductivity was measured by using a Bante 901b conductivity meter. The PSD analysis was performed using an LS-POP (VI) laser particle size analyzer, and the crystal morphology structure was observed by using an SEM Quanta 250 scanning electron microscope.

The induction time was determined by the solution conductivity. In the conductivity curve, the time of peak is the induction time. At the same time, initial precipitation was observed visually and the solutions became turbid [13].

Experimental procedure

The experimental setup was a thermostatic crystallization reactor. Thermostatic water baths were used to maintain the temperature of Na\(_2\)SO\(_4\) solution storage tank and crystallization reactor at 323 K.

The first step was the addition of 250 mL 0.5 mol/L CaCl\(_2\) solution and additives or metal ions (if needed) to the crystallization reactor. The concentration of additive was 2 mmol/L, and the content of metal ions was 300 mg/L. The concentrations were set to be similar to the FGD system in coal-power plants. Then, 0.5 mol/L Na\(_2\)SO\(_4\) solution was slowly feed to the crystallization reactor by a peristaltic pump with a flow rate of 7 mL/min.

Conductivity of the reaction solution was monitored throughout the 30-min experiment. Besides, all slurry samples were taken for analyses of moisture content, PSD, and crystal morphology.

Analyses of calcium sulfate crystals properties

The quality of formatted calcium sulfate crystals was analyzed. Moisture content, particle size distribution (PSD), and crystal morphology were three targeted properties for calcium sulfate crystals.

The moisture content was analyzed with the help of a vacuum pump. A 100 mL slurry sample was compressed by suction filter at 0.1 MPa for 10 min. Then, the moisture content was obtained by measuring the reduction of water at 313 K after 24 h. The dried samples were stored in a dryer.

The PSD was analyzed by using a laser particle size analyzer and the crystal morphology was analyzed by using a scanning electron microscope. A total of 0.5 to 1.0 mg dried samples was needed for PSD analysis and crystal morphology structure analysis, respectively.

RESULTS AND DISCUSSION

The experimental conditions, such as temperature, stirring speed, impurities and so on, were investigated in this part [14,15], and the optimal experimental conditions for calcium sulfate crystals formatting were determined. The particle size distributions (PSD) of calcium sulfate crystals were determined as the quality property of calcium sulfate crystal.

Effect of temperature

The formation of calcium sulfate crystal includes two steps: nucleation and growth. The temperature during crystallization process was found to have great
influence on both crystal nucleation and growth [4,10,16]. On the one hand, increasing temperature causes lower viscosity and less strong surface tension of slurry, which will improve the ion diffusion and the nucleation rate. As a result, the initial nucleation time is reduced, while crystal growth time is increased. On the other hand, the solubility of calcium sulfate dehydrate is also decreased with increased temperature, which results in the reduction of further nucleation driving force and crystal growth rate [8]. Hence, there is an optimal temperature for calcium sulfate crystal formatting.

The PSD of calcium sulfate crystals at different temperatures are shown in Figure 1. There were three peaks in the differential distribution curves, and the grain diameters of three peaks were about 9, 20 and 75 μm. At the peak of 20 μm, the peak value of 323 K was lower than others, while at the peak of 75 μm the value was higher than others. So at 323 K, there were fewer small diameter crystals than others, and the rise of nucleation rate is greater than the decrease of growth rate.

At 323 K, the gypsum crystal particle size was the largest (\(D_{50} = 57.43 \mu m\), where \(D_{50}\) is the diameter value as the percentage of cumulative distribution reaches 50%). 323 K was chosen as the optimal experimental temperature for calcium sulfate crystal formation.

**Effect of stirring speed**

The stirring speed during calcium sulfate crystal formation process was also found to affect crystal nucleation and crystal growth.

On one hand, increasing stirring speed is helpful for ion diffusion, which can reduce the possibility of high local ion concentration and obtain a uniform super-saturation of solution. On the other hand, increasing stirring speed is beneficial for the acceleration of the nucleation rate and crystal growth rate. However, dissolution is in a dynamic balance with crystallization. The increasing stirring speed is also helpful for dissolving the formed crystal nucleus. Faster stirring speed also leads to a higher possibility of breaking of formed crystals and grain refinement.

The result of stirring speed experiments is shown in Figure 2. There were also three peaks in the differential distribution curves, with grain diameters about 9, 20 and 75 μm. Obviously, the peak values of 300 rpm were lower than others at 9 and 20 μm, and the peak values of 300, 400 and 500 rpm were higher than others at 75 μm. Thus, the particle size of crystals at 300 rpm had a more concentrated distribution and the \(D_{50}\) was also bigger, so the stirring speed of 300 rpm was a good choice for the experiments.

**Effect of impurities**

\(\text{Mg}^{2+}, \text{Al}^{3+}\) and \(\text{Fe}^{3+}\) are three common impurity ions in wet FGD slurries [17-19] that undermine calcium sulfate crystallization. \(\text{Mg}^{2+}, \text{Al}^{3+}\) or \(\text{Fe}^{3+}\) affect the gypsum crystallization in a similar way, by adsorb-
ing on the crystal faces, occupying combining sites, and changing the super-saturation of solution. During the calcium sulfate crystals crystallization, Mg$^{2+}$ will retard the nucleation phase by improving the surface tension and reducing super-saturation of solution [20].

PSD of calcium sulfate crystals formed in the presence of Mg$^{2+}$, Al$^{3+}$ or Fe$^{3+}$ are shown in Figure 3. At the peaks of 9 and 20 μm, the values of Fe$^{3+}$ were higher than Mg$^{2+}$ and Al$^{3+}$. In the presence of Mg$^{2+}$, Al$^{3+}$ and Fe$^{3+}$, the peak values of 75 μm were all lower than the blank group.

The conclusion can be obtained that the Mg$^{2+}$, Al$^{3+}$ and Fe$^{3+}$ will inhibit the calcium sulfate crystal growth. At the present of 300 mg/L Mg$^{2+}$, Al$^{3+}$ and Fe$^{3+}$, the calcium sulfate crystals particle size ($D_{50}$) decreased from 57.43±0.02 to 50.38±0.02, 51.41±0.02 and 46.19±0.02 μm, respectively. The inhibiting effect of Fe$^{3+}$ on the gypsum crystallization was stronger than Mg$^{2+}$, which was also stronger than Al$^{3+}$.

**Effect of desulfurization additives**

At the experimental conditions of 323 K, 300 rpm, and no ion impurities, the effect of four common desulfurization additives (adipic acid, citric acid, sodium citrate and benzoic acid) on calcium sulfate crystals formation were studied. The induction time, moisture content, PSD and morphology of produced gypsum were all determined.

**Comparison of induction time**

Induction time is one of the most important dynamic features of crystallization processes. It is defined as the time when a constant super-saturation is created and crystals are detected [4]. The effects of each additive on the induction time of calcium sulfate crystals are shown in Figure 4. In the presence of citric acid and sodium citrate, the induction time increased from 4.3 (blank) to 5.3 and 7.8 min, respectively. Citrates can complex with Ca$^{2+}$, then decrease the initial super-saturation degree and increase the induction time. Therefore, there was enough time and space for calcium sulfate crystals to grow up in the present of citric acid and sodium citrate, and the crystal size became much larger.

![Figure 4. The induction time of calcium sulfate crystals.](image_url)

**Comparison of moisture content**

Moisture content is a macroscopic property, which is associated with particle size distribution and crystal morphology.

The moisture content of calcium sulfate dihydrate determines the cost of gypsum dehydration. In the presence of adipic acid, citric acid, sodium citrate or benzoic acid, the moisture content of produced gypsum is shown in Figure 5. The values were 38.66, 39.82, 15.5, 17.94 and 37.91%, respectively.

![Figure 5. Gypsum moisture content of calcium sulfate crystals.](image_url)

**Figure 3. PSD of calcium sulfate crystals formed with Mg$^{2+}$, Al$^{3+}$ or Fe$^{3+}$ added.**
The moisture content was relevant to the calcium sulfate dihydrate crystal shape and size. Low moisture content meant large and concentrated distributed particle size [11]. High moisture content always meant acicular and undersized crystals. The consequence of the citric acid and sodium citrate reducing the moisture content more than 50% can be observed in Figure 5.

Comparison of calcium sulfate crystal PSD

Particle size is the major property of calcium sulfate crystals, and $D_{50}$ is the diameter value as the percentage of cumulative distribution reaches 50%. Obviously, in Figure 6a, in the presence of citric acid and sodium citrate, the particle sizes of calcium sulfate dihydrate crystals were bigger than others. In the group of differential distribution curves, there was only one peak for citric acid and sodium citrate experimental groups, the peaks of 9 and 25 μm were gone. Furthermore, the peak value of sodium citrate rose from 75 to 90 μm. The complexation between citrate and $\text{Ca}^{2+}$ decreases the initial super-saturation degree and correspondingly increases the growth time and space [21]. As a result, the crystal size became much larger in the presence of sodium citrate. In Figure 6b, the cumulative distribution curves of citric acid and sodium citrate were on the right of the blank group.

Comparison of calcium sulfate crystal morphology

Calcium sulfate dihydrate crystals formed without any additive, showed needle-like shapes, with flat cross sections and smooth surface (Figure 7). In the presence of adipic acid or benzoic acid, there were no obvious effects on crystal morphology. However, the effects of citric acid and sodium citrate on crystals morphology were significant (Figure 8). Citric acid was found preferably to adsorb on c-axis that had the fastest growth rate [21]. In Figure 8a, calcium sulfate crystals transformed to irregular and thick flaky, with flat cross section, and non-smooth surfaces. Obviously, there was a trace of flaky growth on the formed crystals surface, which made the crystals thicker and greater. In Figure 8b, with the help of sodium citrate, the citrate concentration was higher than the citric acid, leading to a higher growth rate.

![SEM image of calcium sulfate crystals without any additive.](image)

Citric acid and sodium citrate had significant impacts on calcium sulfate dihydrate crystals morphology, which led to a non-flat crystal surface. And citric acid and sodium citrate changed the gypsum crystals morphology from needle-like shape to thick slab-like and columnar shape.

CONCLUSIONS

The investigation of experimental conditions, including temperature, stirring speed, and impurities,
showed that the optimal experimental temperature was 323 K, optimal stirring speed was 300 rpm, and Mg$^{2+}$, Al$^{3+}$, and Fe$^{3+}$ were the major impurities that should be considered. Those impurities inhibited the gypsum crystals formation, and Fe$^{3+}$ ions caused the strongest inhibition, followed by Mg$^{2+}$ and Al$^{3+}$.

The moisture content, particle size distribution and crystal morphology were the investigated properties of calcium sulfate crystals. Four common organic desulfurization additives - adipic acid, citric acid, sodium citrate and benzoic acid - were selected to research the influence of desulfurization additives on the calcium sulfate dihydrate crystals formation. Citric acid and sodium citrate were found to improve the quality of gypsum. Moisture contents were reduced by more than 50%, calcium sulfate particle sizes were respectively enlarged by about 9.1 and 22.8%, induction time extended from 4.3 (blank) to 5.3 and 7.8 min, and crystal morphology trended to be thicker, especially in the presence of sodium citrate.

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REFERENCES

UTICAJ ORGANSKIH ADITIVA ZA DESULFURIZACIJU NA FORMIRANJE KRISTALA KALCIJUM-SULFATA

Rezultati dobijeni u ovom radu pokazuju da su optimalni uslovi za formiranje kristala gipsa temperatura od 323 K i brzina mešanja 300 min⁻¹. Jioni Mg²⁺, Al³⁺ i Fe³⁺, koji su glavne nečistoće, inhibiraju formiranje kristala kalcijum sulfata. Fe³⁺ jon pokazuje najjače inhibitorno dejstvo. Uticaj aditiva desulfurizacije na formiranje kristala gipsa je praćen preko sadržaja vlage, distribucije veličine čestice i morfologije kristala. Pri tome je praćen uticaj organskih aditiva poput adipinske kiseline, limunske kiseline, natrijum citrata i benzoeve kiseline. Istraživanje pokazuje da limunska kiselina i natrijum citrat poboljšavaju kvalitet gipsa, sadržaj vlage je redukovan više od 50%, dok je veličina čestica gipsa uvećana 9,1 i 22,8%, redom, vreme indukcije je povećano sa 4,3 (slepa proba) na 5,3 i 7,8 min, dok morfologija pokazuje tendenciju povećanja kristala.

Ključne reči: kristali kalcijum sulfata, aditivi desulfurizacije, nečistoće, vlažna desulfurizacija dimnog gasa.