Effects of AlCl₃ on the Crystal Morphology of Calcium Sulfate Whisker Prepared from FGD Gypsum

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Abstract. Utilizing the purified flue gas desulfurization (FGD) gypsum as raw material and AlCl₃ as crystal modifier to prepare calcium sulfate whiskers (CSWs) by hydrothermal method, the effects of the AlCl₃ concentration and the pH of reaction slurry on the crystal morphology of CSWs were discussed. The results show that the AlCl₃ concentration and the pH of reaction slurry had a significant effect on the crystal morphology of CSWs. CSWs grown in the AlCl₃-H₂O slurry had diameters ranging from 2 to 6 μm and aspect ratio above 80 μm, and their phase structure was calcium sulfate hemihydrate (HH).

1. Introduction
With the environmental protection, much attention has been given to the preparation of CSWs from flue gas desulfurization (FGD) [1-3]. However, compared with the CSWs prepared from chemical agents or high quality gypsum, the quality of CSWs prepared from FGD gypsum need still be improved. Because of the sparing solubility of FGD gypsum, it has no effect to control its crystallization by changing the temperature and super saturation of the reaction solution. According to reported studies, the crystal morphology of CSWs could be controlled by a proper crystal modifier, which maybe leaded to improve the quality of CSWs [4, 5]. Some metal ions, such as Na⁺, K⁺, Mg²⁺, Cu²⁺, etc. have a significant effect on the crystal morphology and size of CSWs [2, 6-9].

However, the effects of each metal ion on the crystal morphology and size of CSWs were completely different. Therefore, using AlCl₃ as crystal modifier, the influences of AlCl₃ concentrations and pH of reaction slurry on the crystal morphology were investigated to improve their quality in this paper.

2. Experimental
2.1. Sample Preparation
The FGD gypsum used in this study was supplied by a power plant in Henan Province, China. Aluminum chloride (AlCl₃, >99 % purity), Sodium hydroxide (NaOH, >99 % purity) and sulfuric acid (H₂SO₄, density=1.84 g/cm³) were provided by Luoyang Chemical Reagent Co. Ltd., China.

Based on our previous studies [2, 6, 8], the purified FGD gypsum was ball-milled and then shifted into an autoclave. Sulfuric acid was used to adjust pH, meanwhile, a scheduled amount of AlCl₃ crystal modifier was added into the slurry. The mixed slurry was heated at 120~140 °C for 90 min.
Finally, the hydrothermal products were rapidly filtered, washed and dried to constant weight at 80~200 °C.

2.2. Characterizations
The preliminary observations of samples were detected by a digital biological microscope (BA200, made by MOTIC China Group CO., LTD.). The morphology of samples was observed using a scanning electron microscope (SEM, QUANTA 450, made by FEI). The phase analysis of samples was determined using an X-ray diffractometer with nickel-filtered Cu Kα radiation, λ=0.154 178 nm, 2θ=5°~80° (XRD, X’Pert PRO MPD, made by PANalytical B.V.).

3. Results and Discussion
Figure 1 shows the effect of AlCl 3 concentrations on the crystal morphology of CSWs prepared from the purified FGD gypsum by hydrothermal method.

![Figure 1. Microscopy images of the samples prepared at different AlCl 3 dosage (×100): (a) 0 %, (b) 2.0 %, (c) 4.0 %, (d) 6.0%.](image)

Almost no CSWs could be obtained in the reaction slurry without the additive of AlCl 3, and a large of short columnar and gradual products could be easily observed from Figure 1(a). With the increment of AlCl 3 concentration, short columnar and gradual products were gradually reduced. At an AlCl 3 concentration of 2.0 %, the crystallization of products obviously changed from the short columnar and granular morphology to the needle morphology, but the crystal distributions in terms of diameter and length were not uniform. As the AlCl 3 dosage was 4.0 %, the obtained hydrothermal products were relatively best and mainly presented needle morphology, and its mean aspect ratio was about 80. However, with further increases of AlCl 3 concentration, the mean aspect ratio was reduced instead. This indicates that the AlCl 3 concentration has a significant effect on the crystal morphology of CSWs.

Due to the sparing solubility of gypsum, pH value has a significant effect on the solubility of the FGD gypsum, which would further affect the crystal morphology of hydrothermal products. Therefore, it was necessary to study the effects of pH on the crystal morphology of hydrothermal products. Figure 2 shows the influence of pH on the morphology of hydrothermal products.

As adding 10⁻³ M sulfuric acid or sodium hydroxide into the reaction slurry, the whiskers with a small diameter could be obtained, but their aspect ratio was relatively low. In both reaction systems,
many short columnar and gradual products could still be easily found. Moreover, some fascicular crystals could be observed when added sodium hydroxide into the reaction slurry. Neither sulfuric acid nor sodium hydroxide was added into the reaction slurry, the obtained calcium sulfate whiskers had bigger lengths and smaller diameters, and the distribution of length and diameter was more uniform. Therefore, pH also had a significant effect on the crystal morphology of the hydrothermal products when using FGD gypsum as raw material.

![Microscopy images](image)

**Figure 2.** Microscopy images of the samples prepared at different pH and with AlCl₃ as crystal modifier (×100): (a) H₂SO₄, 10⁻⁵ M, (b) H₂SO₄, 0 M, (c) NaOH, 10⁻⁵ M.

Due to in the AlCl₃-H₂O system, the obtained calcium sulfate whiskers have a relatively uniform crystal morphology. Therefore, it is necessary to detect its microstructure. Figure 3 is the XRD pattern of whisker sample prepared in the AlCl₃-H₂O system conditions. It demonstrates that the phase of products is hemihydrate sulfate calcium and no second phase can be detected. The previous investigations had also reported that metal ions could markedly effect the crystal morphology of CSWs, but no effects on their phase, which could be testified by Figure 3 [2, 6-9].

![XRD pattern](image)

**Figure 3.** XRD pattern of the sample prepared in the AlCl₃-H₂O system.
Figure 4. SEM images of the sample prepared in the AlCl₃-H₂O system.

Figure 4 is the SEM images of CSWs prepared in the AlCl₃-H₂O system conditions. Only a few of gradual products can be observed besides CSWs when 4.0 % AlCl₃ is added into the reaction slurry from Figure 4. Simultaneously, a small amount of precipitates on the surface of CSWs could also be detected, which may be caused by the precipitation of the impurities of FGD gypsum [2].

Combining the microscopy images in Figure 1, 2 and 4, it can be found that CSWs of a diameter about 2–6 um and aspect ratio above 80 can be obtained when 4.0 % AlCl₃ is added into the reaction slurry, which indicates that the CSWs prepared from FGD gypsum can be effectively improved when using AlCl₃ as crystal modifier.

4. Conclusions
Utilizing the purified FGD gypsum as raw material and AlCl₃ as crystal modifier, CSWs could be prepared. The AlCl₃ concentration and the pH of reaction slurry had a significant effect on the crystal morphology of CSWs. In the AlCl₃-H₂O slurry, CSWs with relatively uniform crystal morphology could be obtained. The obtained CSWs had diameters ranging from 2 to 6 um and the aspect ratio above 80 μm, and their phase structure was calcium sulfate hemihydrate (HH).

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