

# Effects of Magnesium and Ferric Ions on Crystallization of Calcium Sulfate Dihydrate Under the Simulated Conditions of Wet Flue-gas Desulfurization

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**Abstract** The influences of magnesium and ferric ions in their different ratios on the rate of gypsum crystallization were studied under the conditions similar to those of wet flue-gas desulfurization(WFGD). The results show that addition of both  $Mg^{2+}$  and  $Fe^{3+}$  increased induction time and decreased the growth efficiency up to 50% compared with the baseline(without impurities) depending on the concentration and the type of impurity. The effects of  $Mg^{2+}$  and  $Fe^{3+}$  on the surface energy and the rate of nucleation were estimated by employing the classical nucleation theory. The surface energy decreased by 8% and 14% with the addition of 0.02 mol/L magnesium or ferric ions, respectively, compared to the baseline.  $Mg^{2+}$  and  $Fe^{3+}$  made the growth rate of the (020), (021) and (040) faces of gypsum crystal a much greater reduction, which leads to the formation of needle crystals compared to the baseline which favors the formation of plate or flakes. Furthermore, an edge detection program was developed to quantify the effects of impurities on the filtration rate of gypsum product. The results show that the inhibition efficiency of the presence of 0.02 mol/L  $Mg^{2+}$  and  $Fe^{3+}$  on the filtration rate of gypsum crystal ranges from 22% to 39%.

**Keywords** Calcium sulfate dihydrate; Morphology; Wet flue-gas desulfurization; Filtration rate

## 1 Introduction

The wet flue-gas desulfurization(WFGD) process is the most recognized and accepted solution to remove sulfur dioxide emissions from the coal-fired power plants. Nucleation and crystal growth of calcium sulfate dihydrate represent an important step in WFGD, because they affect the scrubber solution composition, the  $SO_2$  absorption, the absorbent utilization, the quality of byproduct and consequently the operation and economic benefits of the whole process. Air is sparged to a slurry tank where the oxidation of calcium sulfite to gypsum takes place. The separation of gypsum crystals as byproduct from the slurry in WFGD is mostly performed by belt filters in which the filtration characteristic of gypsum plays an important role. Gypsum forms small needle-like crystals having a monoclinic prismatic structure with water molecules between the calcium and sulfate ions in the unit cell<sup>[1]</sup> which increases the load of the filter and causes it to plug. Moreover, the larger the number of nuclei, the

smaller the crystals which are more difficult to filter, which would increase the operation cost. Therefore, enhancing the formation of large and uniform gypsum crystals is desired in WFGD industry.

A considerable amount of researches on the mechanism of calcium sulphate dihydrate crystal growth both in the presence and the absence of different types of chemical additives has been done. The formation conditions and the presence and the type of impurities not only influence agglomeration or dispersion behavior but predominantly alter the nucleation, morphology and size of calcium sulphate dihydrate crystals<sup>[2–6]</sup>. Trivalent transition metal cations incorporated through the faces of the crystals a cause the crystal morphology change<sup>[7]</sup>. The most used absorbent in WFGD, limestone, contains about 0.2%—2% of both ferric and magnesium ions which influence the crystallization and properties of the byproduct (gypsum). Some of additives can change the morphology<sup>[8]</sup> and retard the crystallization of gypsum

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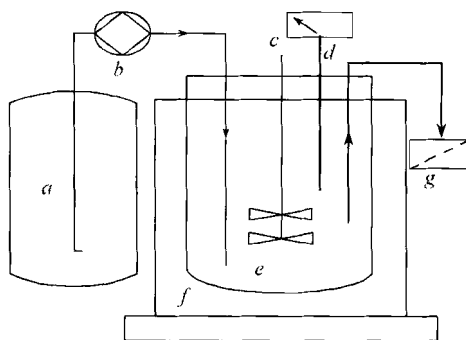
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even at their low concentrations (10—6 mmol/L)<sup>[9]</sup>. In the presence of borax and different free sulfate concentrations, crystallization kinetics of calcium sulfate dihydrate has been studied<sup>[10,11]</sup> and the growth rate of calcium sulfate was also correlated. Different orders of kinetic expressions depending on supersaturation levels have been reported<sup>[12,13]</sup>. However, all of the above studies were based on simulated conditions of phosphoric acid production which involves the lower supersaturation and higher temperature compared to the WFGD process. The present research aims at studying the effect of ionic impurities on the induction time, nucleation rate, crystal size distribution and morphology of the formed gypsum crystals in simulating the process of WFGD.

## 2 Experimental

### 2.1 Experimental Apparatus

The experimental apparatus consisted of a stirred batch cylindrical crystallization reactor, made of PVC, with a working volume of 2 L. The peristaltic pump was a variable speed digital pump capable of pumping 2.5—10 mL/min depending on the desired value of residence time. The stirring is carried by a two-blade stirrer with 450 r/min to keep the slurry in suspension without damage the crystal. Under those conditions the crystallization process was simulated in the typical slurry sump of WFGD.



**Fig.1** Experimental apparatus for measuring effects of ions on crystallization of calcium sulfate dihydrate

a. Feed tank; b. peristaltic pump; c. stirrer; d. conductivity analyzer; e. reactor; f. water bath; g. sample point.

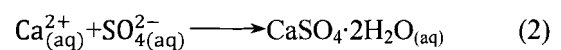
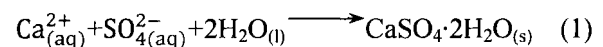
### 2.2 Materials and Methods

Two 1 L of solutions of calcium chloride and sodium sulfate were prepared from the reagents of reagent grade and the deionized water was heated to the ideal temperature before starting the experiment. The calculated amounts of impurities, such as MgCl<sub>2</sub>

and FeCl<sub>3</sub>, were also dissolved in the solution of calcium chloride which was added to the reactor before the addition of Na<sub>2</sub>SO<sub>4</sub>. As soon as the reactor system had reached a state of a constant temperature, the addition of Na<sub>2</sub>SO<sub>4</sub> was performed by starting the peristaltic pump connecting to reactor by tube. Slurry samples from the crystallization reactor were also taken Periodically from the outlet and immediately filtered (0.22 μL, Millipore) to separate the solution. The filtrate was measured for calcium concentration by EDTA titration and the solid crystal was characterized by XRD (Rigaku-D/Max-2550pc), SEM (Hitachi SEM-S-570), and determined for particle size distribution by a Malvern Mastersizer (2000).

### 2.3 Calculation of the Supersaturation Level

The supersaturation level of calcium sulfate dihydrates can be determined by considering the following liquid-solid equilibrium in the reactor:



$$S = \frac{\alpha_{\text{Ca}^{2+}} + \alpha_{\text{SO}_4^{2-}} - \alpha_{\text{w}}^2}{K_{\text{sp}}} = \frac{m_{\text{Ca}^{2+}} + m_{\text{SO}_4^{2-}} - \gamma_{\pm}^2 \alpha_{\text{w}}^2}{K_{\text{sp}}} \quad (3)$$

where  $K_{\text{sp}}$  is solubility product of gypsum and  $S$  is the saturation ratio. The solubility of gypsum can be calculated *via* the sum of the quantity of the free calcium ions and the associated calcium sulphate species. Therefore, the total solubility is

$$[\text{Ca}]_{\text{total}} = m_{\text{Ca}^{2+}} + m_{\text{CaSO}_4} = \frac{K_{\text{sp}}}{\alpha_{\text{w}}^2 (m_{\text{SO}_4^{2-}}) \gamma^2} + K_{\text{a}} (m_{\text{Ca}^{2+}}) (m_{\text{SO}_4^{2-}}) \gamma^2 \quad (4)$$

where  $\gamma$  is the mean activity coefficient of calcium-sulphate,  $K_{\text{a}}$  is the equilibrium constant and  $\alpha_{\text{w}}$  is activity of water. A variety of methods have been used for calculating calcium sulphate solubility in pure and mixed metal sulphate solutions. Because of the high ion strength in WFGD, an extended Debye Huckel equation which can accurately model gypsum solubility up to 2 mol/L is adopted to calculate the activity coefficients<sup>[14]</sup>:

$$\lg \gamma = \frac{-A |Z_{\text{Ca}} Z_{\text{SO}_4}|}{1 + \sqrt{I}} + B_{\text{CaSO}_4} I + \frac{(0.06 + 0.6 B_{\text{CaSO}_4}) |Z_{\text{Ca}} Z_{\text{SO}_4}| I}{\left(1 + \frac{1.5}{|Z_{\text{Ca}} Z_{\text{SO}_4}| I}\right)^2} \quad (5)$$

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