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## Effect of particle size on the transformation kinetics of flue gas desulfurization gypsum to $\alpha$ -calcium sulfate hemihydrate under hydrothermal conditions

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### ABSTRACT

The effect of particle size on the transformation kinetics of flue gas desulfurization (FGD) gypsum to  $\alpha$ -calcium sulfate hemihydrate ( $\alpha$ -HH) in calcium chloride ( $\text{CaCl}_2$ ) solutions was investigated to better guide value-added FGD gypsum use. Gypsum samples from different sources were sieved into several size groups, and their transformation rates were compared. The results showed that using FGD gypsum with a smaller particle size accelerated the transformation to  $\alpha$ -HH. The size effect accelerated nucleation kinetics of  $\alpha$ -HH rather than its crystal growth rate (that is, the thermodynamic driving force for the transformation changed little with particle size variation). Analysis using a kinetics model revealed that a smaller gypsum particle size lowered the overall activation energy barrier for the transformation. This is because the smaller gypsum particles had a larger relative specific surface area and thus provided more nucleation sites and crystalline defects to promote  $\alpha$ -HH nucleation. A smaller particle size of FGD gypsum also gave a higher yield of fine  $\alpha$ -HH particles because of the increased incidence of primary and secondary nucleation coupled with attrition. This paper indicates the transformation of FGD gypsum into  $\alpha$ -HH could be effectively promoted by regulating FGD gypsum particle size.

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### Introduction

Flue gas desulfurization (FGD) gypsum is a byproduct generated in large volumes during the calcium-based wet desulfurization process in coal-burning power plants, and is mainly composed of calcium sulfate dihydrate (>90 wt%,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , DH). For the sake of environmental protection and natural gypsum mine conservation, the recycling and use of FGD gypsum are important. Transformation of FGD gypsum into  $\alpha$ -calcium sulfate hemihydrate ( $\alpha$ -HH) represents a valuable possibility (Guan et al., 2011).  $\alpha$ -HH is widely used in construction, molding, and medical rehabilitation because of its favorable physical properties and biocompatibility (Li et al., 2014; Pan et al., 2013; Singh & Middendorf, 2007; Wang et al., 2008).

The transformation of FGD gypsum to  $\alpha$ -HH proceeds via dissolution–crystallization under hydrothermal conditions (Jiang et al., 2016; Miao et al., 2015; Wang, Yang, Zhu, & Yang, 2014; Zürz, Odler, Thiemann, & Berghöfer, 1991). The solid–liquid interfaces in

the suspensions promote the nucleation of the emerging phase and thus the transformation by lowering the activation energy barrier for nucleation (Crocker & Hodnett, 2010; Kashchiev & van Rosmalen, 2003; Xu, Lan, Peng, Wen, & Ma, 2015). Taking solution-mediated carbamazepine polymorph transformation as an example, larger anhydrate parent crystals extend the transformation time to the dihydrate, indicating it is a nucleation-limited process (Liu, Wei, & Black, 2009). The transformation is markedly accelerated by grinding the anhydrate to increase lattice disorder. However, the rate-limiting step changes from dihydrate crystallization to anhydrate dissolution (Murphy, Rodríguez-Cintrón, Langevin, Kelly, & Rodríguez-Hornedo, 2002), even though fine particles usually have a relatively fast dissolution rate (Economou, Evmiridis, & Vlessidis, 1996). From this viewpoint, fine particles with a larger specific surface area would accelerate the transformation by offering more nucleation sites than particles with smaller specific surface area (Gong et al., 2008). Nucleation on the parent  $\alpha$ -HH crystal surfaces accelerates the hydration kinetics by shortening the induction time (Dumazer, Narayan, Smith, & Lemarchand, 2009). However, the transformation is delayed because of steric hindrance when the number of nuclei increases far beyond a certain point (Dumazer et al., 2009). Therefore, the effect of size-dependent surface char-

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acteristics on the transformation kinetics of FGD gypsum to  $\alpha$ -HH needs to be clarified.

The driving force created by the solubility difference between calcium sulfate phases is another important factor affecting their transformation kinetics. Temperature and electrolyte solution concentration also play vital roles in determining the driving force by affecting the solubility of products and water activity (Azimi & Papangelakis, 2011; Feldmann & Demopoulos, 2015; Fu, Guan, & Wu, 2015). According to the Ostwald–Freundlich equation (Godec, Gaberscek, & Jamnik, 2009; Mullin, 2001), smaller parent crystals would display higher solubility than larger ones, which then provides a larger driving force for transformation (Lee, Das, Sordelet, Eckert, & Hurd, 2012; Li et al., 2013). It is necessary to evaluate the effect of particle size on the driving force and transformation kinetics of FGD gypsum.

Transformation of calcium sulfate phases usually proceeds slowly during the initial period before the exponential-like transformation occurs (Farrah, Lawrance, & Wanless, 2004; Fu, Jiang, Wang, Wu, & Guan, 2013). Based on the evolution of solid and liquid components, the solution-mediated transformation from the viewpoint of parent-phase dissolution and emerging-phase nucleation and growth is classified into four major categories (Maher, Croker, Rasmuson, & Hodnett, 2012; O'Mahony, Maher, Croker, Rasmuson, & Hodnett, 2012; Qu, Louhi-Kultanen, Rantanen, & Kallas, 2006; Thirunahari, Chow, & Tan, 2011). Our previous study showed that the transformation from gypsum to  $\alpha$ -HH is a nucleation-limited process (Fu et al., 2013). Several dynamic models have been used or developed to better understand the conversion process of gypsum to  $\alpha$ -HH (Dumazer, Smith, & Lemarchand, 2010; Feldmann & Demopoulos, 2012; Lemarchand, Boudoire, Boucard, Chotard, & Smith, 2012; Skrdla, 2011; Wang, Ma, Wang, Hao, & Jiang, 2015). Of them, the dispersive kinetic model, which has only two parameters with physical meanings and fits the asymmetrical sigmoidal conversion profiles well (Skrdla, 2008; Skrdla, 2009; Skrdla, 2011; Skrdla & Robertson, 2005). Therefore, this model is used here to facilitate study of the particle size dependence of the gypsum- $\alpha$ -HH transformation kinetics.

In this paper, FGD gypsum and analytical reagent (AR)-grade gypsum samples were screened into several size groups, and the kinetics of their transformation to  $\alpha$ -HH in calcium chloride ( $\text{CaCl}_2$ ) solutions at 95 °C was investigated by tracking the evolution of the solid components with the aid of the dispersive kinetic model. The role of particle size was probed from the viewpoint of nucleation and growth through experiments and the change of activation energy through the dispersive kinetic model.

## Materials and methods

### Materials

AR-grade anhydrous  $\text{CaCl}_2$  (purity  $\geq 96.0\%$ ) was purchased from Sinopharm Chemical Reagent Co., Ltd., China. AR-grade DH (purity  $\geq 99.0\%$ ) was purchased from Shanghai Silian Industrial Co., Ltd., China. FGD gypsum samples denoted as BS FGD gypsum and JX FGD gypsum were obtained from two local power plants (Banshan and Jiaying power plants, Zhejiang, China, respectively). The DH contents of BS and JX FGD gypsum were determined to be 95.92 and 95.97 wt%, respectively, according to the Methods for Chemical Analysis of Gypsum (China National Standard, GB/T 5484-2012).

### Size classification

The gypsum raw materials were dried at 45 °C in an oven to remove excess surface free water and facilitate the subsequent size sieving. The particle size distributions (PSDs) of FGD and AR

gypsum samples were first determined prior to size classification. Based on the PSDs, the JX FGD gypsum was separated into three groups using square-mesh sieves; namely, JX-G1 (300–380 mesh), JX-G2 (400–425 mesh), and JX-G3 (below 450 mesh). The AR gypsum was screened into four groups: AR-G1 (180–200 mesh), AR-G2 (280–300 mesh), AR-G3 (380–425 mesh), and AR-G4 (below 425 mesh).

### Phase transformation

The transformation of FGD and AR gypsum samples into  $\alpha$ -HH was performed under hydrothermal conditions. Stock solution (1 L) prepared by dissolving anhydrous  $\text{CaCl}_2$  in deionized water (3.00 m or 3.50 m) was transferred into a double-walled glass reactor and heated to 95.0 °C by flowing oil in the jacket. The temperature was monitored with a thermometer and controlled within  $\pm 0.2$  °C. The solution was stirred with a Teflon impeller at 250 rpm, and the vapor was recycled with a condenser on top of the reactor. Gypsum (100 g) was added to the solution and its conversion was tracked by sampling at certain time intervals. Aliquots of the hot suspension were withdrawn and quickly vacuum filtered. The solid was washed four times with hot water, rinsed with acetone once, and then dried at 45 °C in an oven. The phase evolution was investigated by several solid characterization techniques.

### Solubility determination and solid characterization

To evaluate the effect of particle size on the driving force for transformation, the solubilities of gypsum samples of different sizes were determined by measuring the  $\text{SO}_4^{2-}$  concentration using the dissolution-equilibrium method. An excess amount of gypsum was dissolved in the  $\text{CaCl}_2$  solution at elevated temperature, and then the resulting suspension was sampled at specific time intervals. The samples were filtered through a 0.22- $\mu\text{m}$  membrane. The concentration of  $\text{SO}_4^{2-}$  in the liquid then was tested by the turbidity method using a spectrophotometer (ET99731, Tintometer GmbH, Germany) (Yang, Wu, Guan, Fu, & Ye, 2009).

The solid component was characterized by thermogravimetry–differential scanning calorimetry (TG-DSC, STA-409PC, Netzsch, Germany). The solid (about 8 mg) was sealed in a lidded  $\text{Al}_2\text{O}_3$  crucible and scanned at a rate of 10 °C/min under  $\text{N}_2$  gas atmosphere. The crystal water content was obtained from the TG curve, based on which the mole fractions of DH and  $\alpha$ -HH were calculated. The PSDs were determined by a laser particle size analyzer (Mastersizer 2000, Malvern, UK), and specific surface areas were obtained. Before testing, the solids were dispersed in anhydrous ethanol facilitated by ultrasonication. Crystal morphologies were investigated using a metallurgical microscope (XJP-6A, Chongqing Optical & Electrical Instrument Co. Ltd., China) and scanning electron microscopy (SEM; S-4800, Hitachi, Japan).

## Results and discussion

### Transformation kinetics of FGD gypsum to $\alpha$ -HH

The evolution of the overall crystal water content and DSC curve of the solid samples during the transformation of FGD gypsum (including JX and BS gypsum samples) to  $\alpha$ -HH are presented in Fig. 1. Fig. 1(a) shows that the crystal water content of the JX sample is almost constant during the first 8.0 h, decreases slightly at 9.0–11.0 h, and then falls rapidly to 6.19% (close to the theoretical crystal water content of  $\alpha$ -HH of 6.21%) at 14.0 h. In the DSC curve (Fig. 1(b)), the sample obtained at 10.0 h presents two characteristic endothermic peaks of DH at 157.1 (corresponding to the loss of 1.5  $\text{H}_2\text{O}$ ) and 180.8 °C (corresponding to the loss of the remaining 0.5  $\text{H}_2\text{O}$ ), indicating this sample remains in the DH phase and

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