



Preparation of α -calcium sulfate hemihydrate from FGD gypsum in K, Mg-containing concentrated CaCl_2 solution under mild conditions

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ABSTRACT

To prepare α -calcium sulfate hemihydrate (α -HH) from flue gas desulfurization (FGD) byproduct under atmospheric pressure, the dehydration of FGD gypsum in a concentrated Ca and Mg chlorides solution medium at 95 °C was investigated, and the effects of K^+ ions were focused on. The crystal water content variation, material phases, and morphological characteristics of the dehydration products were examined and compared. The solubilities of α -HH in the mixed salt solutions with different K^+ ion concentrations were also determined. It was found that with low concentration of K^+ ions in the mixed salt solution (i.e. 0.001–0.035 M), the dehydration rate was enhanced, while with higher K^+ ion concentration (i.e. 0.087–0.263 M), this process was retarded. α -HH was the dehydration product when K^+ ion concentration was at appropriate level, while anhydrite (AH) occurred when K^+ ion concentration was above 0.173 M. K^+ ions were assumed to behave as a capping agent to control the morphology of the α -HH, resulting in crystals of lower aspect ratio. FGD gypsum can be successfully transformed into α -HH in concentrated Ca and Mg chloride solution under mild conditions, and K^+ ions play an important role in the process.

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1. Introduction

Wet flue gas desulfurization (FGD) processes using calcium-based absorbent are dominating the flue gas scrubbing market around the world due to their high sulfur dioxide removal efficiency, reliability, and relatively low cost. Large quantities of FGD gypsum are produced by these systems as byproduct, which has raised many environmental concerns. Heavy metal elements such as Cd, Cr, Cu, Ni, Pb, Zn, Hg, and As are usually present in FGD gypsum, and chemicals such as fluoride, chloride, and sulfate are often leached out when FGD gypsum is directly piled on or disposed of in landfills [1,2]. Efforts have been made to utilize FGD gypsum from the technical and economic point of view. The utilizations of FGD gypsum in construction industry to produce wallboards and concrete blocks or in cement industry as an additive have been commonly adopted [3]. At the same time, explorations for new technologies of FGD gypsum utilization or disposal are undergoing [4–6].

The main composition of FGD gypsum is calcium sulfate dihydrate (DH) that is apt to dehydrate into calcium sulfate hemihydrate (HH) at elevated temperature. HH has two forms: the β form is usually used in the construction industry; while the α form, due to its better workability and higher strength, has been applied in molding, special binder systems, and dental materials, as well as

the construction industry. Commercial processes (e.g. the SICOWA-ProMineral autoclaving process from Germany and the Omega process in the USA) produce α -HH at elevated temperature and pressure, and hence are energy-intensive [7]. Therefore, autoclave-free α -HH preparation processes and processes utilizing synthetic dihydrate gypsum (e.g. FGD gypsum) as raw material are more attractive [8].

Dehydration takes place when DH is kept under autoclaving condition or even under atmospheric pressure when mixed with certain electrolytes solution medium (e.g. phosphoric acid, sulfuric acid, calcium chloride, and sodium chloride [9–12]). The dehydration product can be HH or anhydrite (AH), depending on the operating parameters. Although the detailed information is still not very clear, the dehydration of DH was assumed to proceed preferentially through a dissolution–recrystallization mechanism under these conditions [13,14]. Since the components within a crystallization system (i.e. main compositions, impurities, or crystal modifiers intentionally added in) often have profound effects on the nucleation, the crystal growth, and the properties of the products, it is very important to explore the behaviors of the components involved for the purpose of the process and product quality control. In the case of calcium sulfate phases (DH, HH, and AH), the transition direction between the calcium sulfate phases and the transformation rate may change with different background electrolyte concentration [15]. At the same time, certain chemicals such as Na^+ , K^+ , Cr^{3+} , Mg^{2+} , Al^{3+} , and citrate ions may incorporate into CaSO_4 crystals [16–18] or adsorb on certain crystal faces [19–21], which may result in different crystal size and morphology.

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Zürz et al. [8] successfully prepared α -HH with FGD gypsum in several boiling inorganic salt solutions and tried to use some organic additives to improve the quality of the binder obtained. Also, it has been stated in several patents [22,23] that FGD byproduct could be transformed into α -HH in mixed salt solutions under relatively mild condition. However, to our best of knowledge, little has been addressed on the exact effects of certain solution compositions on the dehydration or transformation process from FGD DH to α -HH in electrolyte solutions. Here we try to demonstrate that α -HH can be prepared with FGD gypsum as raw material in a mixed salt solution under atmospheric pressure, and that the process can be controlled by adjusting the concentration of certain composition in the aqueous system to obtain desired products.

In most wet FGD systems, calcium is the major chemical composition of the absorbent, and magnesium element is often brought in with calcium-based absorbent. So, a Ca–Mg–Cl solution was used as the dehydration medium to transform FGD DH into α -HH under atmospheric pressure in this study. Since K^+ ions may exert significant influence on the crystallization process of calcium sulfate phases, its effects on the transformation or dehydration of FGD DH into α -HH were systematically investigated. Simultaneous thermogravimetry and differential scanning calorimetry (TG–DSC) and X-ray diffraction (XRD) were employed to investigate the dehydration processes of FGD DH in the mixed salt solutions with and without KCl. The morphologies of the dehydration products were examined and possible mechanism of the effects of K^+ ions was discussed.

2. Materials and methods

2.1. Materials

The mixed salt solutions prepared with reagent grade chlorides and deionized water were used as the dehydration medium. The compositions of the medium are 3.0 M $CaCl_2$ and 1.0 M $MgCl_2$, with KCl concentration varying from 0 to 0.263 M.

The FGD gypsum obtained from a local coal power plant with a volume mean particle size of 40.5 μm was used as the raw material for the dehydration experiments. For composition determination, the FGD gypsum was treated according to the Methods for Chemical Analysis of Gypsum (China standard GB/T 5484-2000). In brief, 0.2–0.5 g dry solid samples were digested with strong alkali or acid and filtrated to transform the elements into certain volume of liquids, then the liquids were used for further elements determination. Ca, Mg, K, Fe, Al, Na, Cr, and Ni were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES, Leeman Prodigy, USA). As, Hg, Cd, Pb, and Zn were determined by atomic fluorescent spectrometry (AFS-3100, Beijing Kechuang Haiguang Instrument Co. Ltd., PR China). SiO_2 content was determined by firstly transforming it into K_2SiF_6 that hydrolyzes into equal molar of HF under neutral condition, and then titrating the HF with NaOH solution. S was determined by direct analysis of dry samples on an Infrared carbon–sulfur analyzer (IRCSA, HCS878C2, Sichuan Jingke Instrument Co. Ltd., PR China). Crystal water content was determined by simultaneous thermogravimetry and differential scanning calorimetry (TG–DSC, STA 409PC, NET-ZSCH, Germany). Traces of heavy metals (0.44 mg/kg Hg and 7.10 mg/kg Cr) were found in the FGD gypsum. Main compositions of the FGD gypsum are given in Table 1.

2.2. Methods

The dehydration experiments were performed in a 1.7 l double-walled glass reactor equipped with a glass condenser on top of it. Typically, the slurry in the reactor was stirred with a Teflon impeller at a constant rate of 200 rpm. The temperature was monitored by a thermometer inserted into the reactor and kept constant at 95 °C (± 0.3 °C) by the circulating oil flowing through the jacket.

The procedure was as follows: 1 l of the mixed salt solution was added into the reactor and preheated to the fixed temperature. Then, 324 g of FGD gypsum previously dried under atmospheric condition was added into the reactor to form the reaction slurry. During the reaction or crystallization, 15 ml of slurry was withdrawn at certain time intervals and filtrated by vacuum filtration. The solid samples were immediately washed with boiling deionized water for four times, rinsed with acetone for one time, and dried at 60 °C in an oven for 2 h. The solid was examined under a metallographic microscope (XJP-6A, Chongqing Optical & Electrical Instrument Co. Ltd.) to investigate the crystal morphology and to determine whether the DH had totally transformed into α -HH. When the transformation had completed, the supernatant solution was withdrawn and immediately filtered by a syringe filters with 0.22 μm cellulose membrane. 2.5 ml of the clear filtrate was taken by a glass pipet and diluted with deionized water in a 100 ml volumetric flask. Then, 20 ml of the diluted filtrate was taken and further diluted in a 50 ml volumetric flask. The contents of K and S were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES, IRIS Intrepid II XSP, Thermo Electron). The solubility of α -HH, expressed as $CaSO_4$ mmol/l, was calculated from the S analysis.

The powder samples were examined by X-ray diffraction (XRD, D/Max-2550pc, Rigaku Inc.) with $Cu K\alpha$ radiation at a scanning rate of 8°/min in the 2θ range from 5° to 70°.

To perform TG–DSC analysis for calcium sulfate phases identification and crystal water content determination, 20 mg dry sample was sealed in an Al_2O_3 crucible with a lid and scanned at a rate of 10 °C/min under N_2 gas atmosphere.

3. Results and discussion

3.1. Dehydration of FGD DH in Ca–Mg chloride salt solution

The chemical composition analysis result shows that the main composition of FGD gypsum is calcium sulfate dihydrate (DH) (Table 1), as can be confirmed by the XRD pattern and DSC curve of the 5 min sample (Fig. 1 and Fig. 2). When mixed with the heated Ca–Mg salt solution, DH was inclined to dehydrate. This dehydration process from DH to HH can be identified by the variation of the XRD patterns of the solid samples withdrawn. As illustrated in Fig. 1, HH formed after about 2 h of dehydration. Since XRD method alone can not distinguish the two forms of HH crystal (i.e. α -HH and β -HH) [24], thermal analysis was carried out to record TG–DSC curves of the samples. As illustrated in Fig. 2, the endothermic peaks at 153 °C and 174.5 °C on the DSC curve of the 5 min sample denotes a two-step losing of firstly the 1.5 and then the remained 0.5 water molecule in the dihydrate crystal when heated. It was evident that the area of the first peak gradually shrank with time. An exothermic peak immediately following the second endothermic peak occurred on the DSC curve of the 3 h sample, which indi-

Table 1
The chemical composition of the FGD gypsum (wt%).

CaO	SO_3	SiO_2	CO_2	MgO	K_2O	Fe_2O_3	Al_2O_3	Na_2O	Crystal water	Total
31.76	43.87	2.00	0.04	0.03	0.03	0.14	0.25	0.01	19.88	98.01

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