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Preparation of calcium sulfate whisker by atmospheric acidification method from flue gas desulfurization gypsum

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Abstract

In this paper, calcium sulfate whisker (CSW) was synthesized from flue gas desulfurization (FGD) gypsum using atmospheric acidification method. The influence of the leaching parameter (the concentration of hydrochloric acid and leaching temperature) on morphology of CSW was discussed. The optimized leaching parameter is that the concentration of HCl is 3.7 mol/L and the leaching temperature is 70 ºC. The prepared CSW have high purity and high whiteness. The width of CSW is ranged from 3 to 22 μm, and its aspect ratio is ranged from 25 to 80.

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Keywords: Flue gas desulfurization gypsum; Calcium sulfate whiskers; Atmospheric acidification method ;

1. Introduction

Calcium sulfate whisker (CSW) is widely used as filler in rubber, plastic, paint, paper industry because of its excellent physicochemical property (high thermal stability, chemical inertness, high mechanical property, and good compatibility), low-cost, and non-toxicity [1,2].

Generally, CSW is synthesized from natural gypsum, a non-renewable resource. Therefore, in recent decades, the preparation of CSW from the industrial by-product, e.g. phosphogypsum [3,4], residue of citric acid [5], waste calcium chloride [6], flue gas desulfurization (FGD) gypsum[7,8], has attracted great scientific interests because this reasonable utilization can save the natural gypsum resource and simultaneously recycle the industrial by-product and protect the environment. Among these mentioned industrial by-products, the FGD gypsum in China is in urgent need of disposal and recycling because the deposit of FGD gypsum is up to billions of tons and amount up to 50 million tons per year

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since 2009[8], which occupy a large amount of land and be hazardous to environment.

Because the FGD gypsum is mainly composed of $CaSO_4$, it is technically and economically feasible to synthesis the high value-added CSW from FGD gypsum via hydrothermal method[1,4,9] and atmospheric acidification method [8]. Compared to the hydrothermal method, the atmospheric acidification method has advantage in the mild reaction condition (atmospheric pressure and the temperature lower than 90°C). The reaction parameter of atmospheric acidification method can significantly influence the quality of the final product (purity, whiteness, morphology etc.). Therefore, in this paper, the FGD gypsum was leached by HCl solution, and the CSW was crystalized from the filtrate. The effect of concentration of HCl and the leaching temperature on the quality of CSW is detailed investigated.

2. Experimental Methods

2.1 Materials and Methods

The raw materials of FGD gypsum were derived from the Yanshan cement Co. Ltd. in Inner Mongolia province. The raw material is labeled as FGD-YL. The chemical composition of FGD-YL as determined from chemical analysis was, in percent by mass: CaO, 41.61; SO_3, 41.70; SiO_2, 4.57; Al_2O_3, 1.77; MgO, 1.85; F, 0.89; Fe_2O_3, 0.72; K_2O, 0.58; Na_2O, 0.39; TiO_2, 0.10; P_2O_5, 0.03; SrO, 0.03.

The CSW was prepared as the following procedure: 15 g of FGD gypsum was added into 300 mL HCl solution (0.5, 1.5, 2.6, 3.7, 4.8, and 5.4 mol/L). This suspension was stirred for 1 hour under 60°C. The solid part of the dispersion was separated by centrifugation. The CSW was cooling crystalized from the filtrate. The obtained CSW was labeled as CSW-C-X, where X represent the concentration of the HCl. This experiment is conducted to investigate the effect of concentration of HCl on the quality of CSW.

In order to investigate the effect of temperature on the quality of CSW, 15 g of FGD gypsum was added into 300 mL HCl solution (with the optimized concentration). This suspension was stirred for 1 hour under set temperature (50, 60, 70, 80, and 100°C). After solid-liquid separation, the CSW was cooling crystalized from the filtrate. The obtained CSW was labeled as CSW-T-X, where X represent the reaction temperature.

2.2 Characterizations

The XRD patterns were obtained with an X'Pert Pro diffractometer with a Ni filter and Cu Kα radiation ($\lambda = 0.154$ nm) generated at 40 kV and 40 mA. The scan rate was 2^o (2θ) min^{-1} with a step size of 0.01^o. TG and DSC analyses were performed with a SDT Q6000 instrument. The sample was heated from 30 to 1000°C at a heating rate of 10°C min^{-1} under a nitrogen atmosphere (60 cm^3 min^{-1}). SEM micrographs were obtained with a TM-1000 scanning electron microscope.

3. Results and Discussion

3.1 Structural and morphological characterization of the raw FGD gypsum

The major crystal phase in FGD-YL is dihydrate gypsum, indicated by the characteristic reflections at 0.756 nm, 0.427 nm, and 0.306 nm (Figure 1a), corresponding to the (020), (121), and (141) planes of dihydrate gypsum (JCPDS No. 70-983), respectively. In addition, two small reflections that correspond to *d* values of 0.334 and 0.182 nm can be assigned to quartz. The low intensity of these two reflections suggests a low content of quartz in FGD-YL. These results are in accordance with the XRF result.

Three major mass losses are clearly resolved in the TG curve of FGD-YL (Figure 1b). The first slow loss at approximately 30 to 100°C is attributed to the dehydration of the physically adsorbed water. The substantial loss (19.21%) at approximately 100 to 200°C is attributed to the dehydration of dihydrate gypsum, corresponding to the endothermic peaks at 149°C in the DSC curve. This mass loss can be used to calculate the number of crystal water in dihydrate gypsum. The calculated chemical formula is $CaSO_4 \cdot 1.80H_2O$, which is in accordance with the XRD result that the major crystal phase in FGD-YL is dihydrate gypsum. The gradual loss (2.82%) at approximately 500 to 700°C maybe attributed to the decomposition of limestone, the precursor of FGD gypsum.