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Removal and utilization of calcite existed in scheelite by preparation of calcium sulfate whiskers

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ABSTRACT

In order to eliminate the effect of calcite associated with scheelite on the scheelite flotation, hydrochloric acid was used to dissolve the calcite, and the soaking solution was used to prepare $CaSO_4$ whiskers by hydrothermal reaction with sulfuric acid at ambient pressure. First, the condition experiments of preparing $CaSO_4$ whiskers by using $CaCl_2$ and H_2SO_4 were carried out to optimize reaction parameters of the crystallization process. The optimal conditions were: at 102 °C reaction temperature, 0.5 mol/L reactant concentration and 60 min reaction time. Then based on the condition experiments and considering keeping acid concentration stable for achieving HCl recycling, Calcium sulfate whiskers with the average diameter of 1.41 μm and the average aspect ratio of 109 were prepared by the soaking solution after evaporating to half of its volume and 1.0 mol/L H_2SO_4 at 102 °C for 60 min. After ion exchange processing, the filtrate could be used as HCl in the process of HCl dissolution.

1. Introduction

Scheelite, one of the most important tungsten-bearing minerals, is often associated with other salt-type minerals such as calcite, fluorite and apatite. Flotation techniques have been used to separate them. However, flotation separation is difficult because of their similar physicochemical characteristics such as solubility, hardness, specific gravity and point of zero charge [1–3], especially the flotation separation of scheelite and calcite [4–6]. In practice, in order to achieve effective flotation separation, a large number of depressants tend to be added into the pulp or some special treatments, such as high-intensity agitating and heating, are taken in the flotation process [7–11]. However, masses of depressants used in the flotation will affect the following procedures or pollute the environment, and the special treatments mentioned above will cause high energy consumption. Furthermore, the calcite in tailings tends to be discarded and can't be effectively utilized. If the calcite is removed and utilized before scheelite flotation, it will not only be greatly beneficial to scheelite flotation but also generate additional economic benefit.

Whiskers, with high aspect ratios, have attracted much interests of researchers in recent years due to their excellent properties in optic, electric and mechanic application [12–14]. The whiskers are proposed as more effective reinforcements than traditional fibers, such as carbon fibers and glass fibers. However, the high cost of some whiskers, such as SiC whiskers, is a barrier for their widespread use. And the inexpensive calcium sulfate whiskers cause material scientists attention. Calcium sulfate whiskers, which are traditionally prepared by calcic minerals such as the natural gypsum, flue gas desulfurization gypsum and so on by means of hydrothermal reaction in an autoclave with elevated temperature under elevated pressure, can obviously enhance the mechanical properties of rubber, plastic, ceramics and paper [15–20]. Therefore, calcium sulfate whiskers have great potential to become ideal reinforcing materials. Meanwhile calcium sulfate whiskers are also used as frictional materials, insulation materials and environmental protection materials [21–23].

In this paper, we introduced a new method to eliminate the effect of calcite associated with scheelite on the scheelite flotation by using hydrochloric acid to dissolve the calcite, and the soaking solution was used to prepare calcium sulfate whiskers by the hydrothermal reaction with sulfuric acid at ambient pressure.

2. Experimental

2.1. Materials

The rough scheelite concentrate was taken from Shizhuyuan in Hunan province of China. It was analyzed by XRF and XRD, and the results were shown in Table 1 and Fig. 1. Analytically pure chemicals, e.g., calcium chloride ($CaCl_2$), sulfuric acid (H_2SO_4),

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Table 1
Chemical composition of the rough scheelite concentrate (wt.%).

WO_3	CaO	SiO_2	Al_2O_3	Fe_2O_3	Rb_2O	MnO	K_2O	MgO	O	F	S	Others
6.73	48.98	13.65	6.23	4.91	2.16	0.68	0.98	0.88	4.79	7.40	0.74	1.87

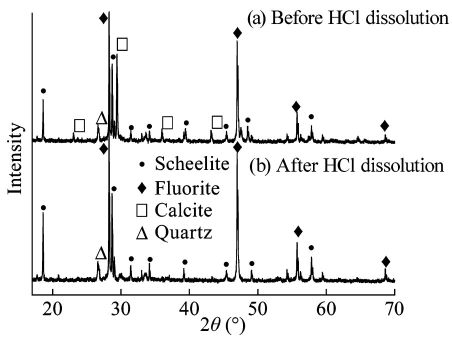


Fig. 1. XRD patterns of the rough scheelite concentrate before and after HCl dissolution.

hydrochloric acid (HCl) and anhydrous ethanol, were produced by Sinopharm Chemical Reagent Co. Ltd., Shanghai, China. Deionized water was used to prepare solutions.

2.2. Experimental procedure

2.2.1. HCl dissolution

Rough scheelite concentrate from the scheelite flotation plant was dried and ground. 5% HCl was added gradually into the powder with stirring until the powder didn't produce bubbles. After filtration, the soaking solution was used to prepare calcium sulfate whiskers.

2.2.2. Preparation of calcium sulfate whiskers

A given amount of calcium chloride (AR) or the soaking solution was firstly added into a three-necked flask equipped with a reflux condenser on top of it. The solution was stirred with a magnetic stirrer at a constant rate of 200 rpm and heated at the required temperature in an oil bath, and then the same preheated amount of H_2SO_4 (AR) was added by a peristaltic pump at a constant flow rate. Samples were taken out after different reaction time. The filtration for samples was carried out under vacuum, and the filter cake was washed with the boiling deionized water. To prevent the crystal phase transition during the processing, the remained water and organic solvents in samples must be removed further by washing with anhydrous ethanol and dried at 80 °C for 2 h.

2.3. Characterization

The structures of the samples were determined by X-ray diffraction (XRD D8 Advanced, Bruker, Germany) using Cu Kα radiation (λ = 1.54178 Å), with a scanning rate of 5° per minute and a scanning 2θ range of 5° to 90°. The soaking solution, the filtrates after filtration of calcium sulfate whiskers and after ion exchange processing were analyzed by the inductively coupled plasma-atomic emission spectrometry (ICP-AES, PS-6, Baird, USA). Hydrogen ion and chloride ion were determined by acid-base titration and silver content method (GB6549.2-86), respectively. The morphology of calcium sulfate whiskers was observed by the optical microscope (DFC 480, Leica Microsystems Ltd. Germany) and the scanning electron microscope (SEM, Quanta 200, FEI, USA). Before SEM, whiskers after drying was diluted with anhydrous ethanol, coated on the glass substrate and then sprayed with gold. The length and diameter of calcium sulfate whiskers were measured by microscope observation and the number of crystals measured was in the range of 50–100 for each group.

3. Results and discussion

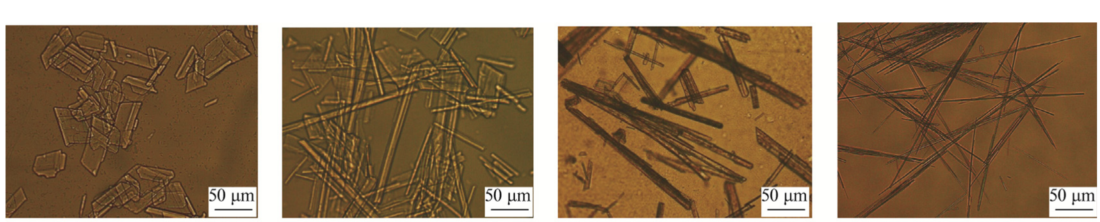
3.1. Preparation of calcium sulfate whiskers by using calcium chloride (AR)

In the process, we explored the influence of reaction temperature, reactant concentration and reaction time on the preparation of calcium sulfate whiskers and found the optimum preparation conditions.

3.1.1. Influence of reaction temperature

Reaction temperature had a significant influence on the crystallization process of calcium sulfate whiskers owing to the change of calcium sulfate solubility and the viscosity and density of the solution in HCl-H_2O system [24,25]. Under certain reactant concentrations, different reaction temperature could give rise to different crystalline phases. In contact with water, $CaSO_4{\cdot}2H_2O$ was found to be a stable phase under standard conditions [26]. In the hydrothermal treatment, $CaSO_4{\cdot}2H_2O$ was converted to $CaSO_4{\cdot}0.5H_2O$ at 99 °C or so. Although at this temperature anhydrite was the thermodynamically stable phase, its nucleation was kinetically retarded, which made $CaSO_4{\cdot}0.5H_2O$ with metastable phase easily formed [27]. With the increase of temperature, $CaSO_4{\cdot}0.5H_2O$ continued to transform into anhydrite [28].

In this study, experiments at 88 °C, 93 °C, 98 °C and 102 °C (the boiling point of the system at ambient pressure) were performed to explore the influence of reaction temperature on the crystallization process of calcium sulfate whiskers. Under the stirring rate of 200 rpm, equal volumes (100 mL) of calcium chloride (AR) and sulfuric acid (AR) with equal concentration (0.5 mol/L) were mixed to react for 60 min. As shown in Fig. 2, the crystals obtained at 88 °C



(a) 88 ℃ (b) 93 ℃ (c) 98 ℃ (d) 102 ℃

Fig. 2. Microscope photos of calcium sulfate whiskers at different reaction temperature.

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