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Full Length Article

Study of reverse flotation of calcite from scheelite in acidic media

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ABSTRACT

A new coated-reactive reverse flotation method based on the generation of CO_2 bubbles at a calcite surface in acidic solution was used to separate calcite from scheelite. The dissolution kinetics of coated and uncoated calcite were studied in sulfuric acid. The CO_2 bubbles generated on the uncoated calcite particle surface are enough to float the particle. However, most of these bubbles left the surface quickly, preventing calcite from floating. Here, a mixture of polyvinyl alcohol polymer and sodium dodecyl sulfonate was used to coat the mineral particles and form a stable membrane, resulting in the formation of a stable foam layer on the calcite surface. After the calcite is coated, the generated bubbles could be successfully captured on the calcite surface, and calcite particles could float to the air-water interface and remain there for more than one hour. Flotation tests indicated that a high-quality tungsten concentrate with a grade of more than 75% and a recovery of more than 99% could be achieved when the particle size was between 0.3 and 1.5 mm. The present results provide theoretical support for the development of a highly efficient flotation separation for carbonate minerals.

1. Introduction

Calcite is one of the most common gangue minerals in mineral processing [1]. The efficient separation of calcite from valuable minerals has long been a focus and challenge in the field of mineral processing, and especially in the processing of calcium-containing minerals such as scheelite, fluorite, and apatite [2–4]. Scheelite ($CaWO_4$) is an important tungsten-containing mineral [5]. The most common commercially used flotation technique for the separation of scheelite from calcite involves depressing the calcite with sodium silicate, followed by floating with conventional fatty acid collectors [6–8]. However, the separation of scheelite from calcite is difficult to achieve because scheelite and calcite not only have the same cation in their crystals but also have similar physical and chemical properties, such as hydrophobicity, hardness, solubility, and specific gravity values [9–11]. Achieving efficient separation requires the addition of depressants and collectors, which have high selectivity, to increase the hydrophobic difference between the mineral surfaces [12–15]. In addition, more stringent reagent systems and accurate equipment operating parameters are required. However, these approaches have encountered difficulties [16].

It is well known that calcite reacts with acid to generate carbon dioxide bubbles. However, the generation of CO_2 bubbles on carbonate mineral surfaces has not received much attention in flotation processes. In fact, these bubbles can be conducive to the minerals' separation [17]. This phenomenon was first observed in the reverse separation of apatite from dolomite and calcite. Deng et al. [18] investigated the flotation separation of apatite from dolomite in acidic media. The authors found that shorter sulfuric acid conditioning times led to better separation results. The main example of the use of carbon dioxide bubbles produced by carbonate minerals in flotation separation was reported by El-Midany et al. [19,20], who called their method "Reactive Flotation." They used a coating agent (polyvinyl alcohol, 3%) to coat the coarse particles of dolomite and apatite, allowing the particles to be successfully separated in a sulfuric acid solution. The experimental results indicated that the MgO in the phosphate concentrate could be reduced to less than 1%.

Despite the improved separation of dolomite from apatite using the "Reactive Flotation" method, the underpinning mechanism has rarely been studied and remains unclear. In this study, the effects of a coating pre-treatment on calcite flotation from scheelite were investigated using a coating technique to pre-treat the minerals. The ability of calcite to produce bubbles, its dissolution kinetics data, and the changes in the calcite surface before and after the acid treatment were investigated. A high-speed camera, micro-flotation and scanning electron microscopy (SEM) were used to

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define the mechanisms. The prospect of applying this coating pretreatment technology in calcite reverse flotation was discussed.

2. Materials and methods

2.1. Materials and reagents

The scheelite and calcite samples used in the experiments were prepared from handpicked crystals obtained from Malipo deposits in Yunnan, China. They were washed with distilled water and dried, before being crushed, sieved, and classified to obtain the desired particle size fractions. Mineralogical and chemical analyses and X-ray diffraction (XRD) (D/Max 2200, Rigaku, Japan) spectra indicated that the purity of the particles of each mineral exceeded 96% with only minor impurities present in the sample. The results of the XRD analyses are shown in Fig. 1.

Sulfuric acid (98% by mass), polyvinyl alcohol (PVA, average M_w 120,000 and >85% degrees of hydrolysis) and sodium dodecyl sulfonate (SDS, analytical grade) were purchased from Sinopharm Chemical Reagent Co. Ltd., Shanghai, China. Tap water was used throughout the experiments, and all the experiments were conducted at 26 °C ± 1 °C.

2.2. Experimental platform and methods

2.2.1. High-speed camera experiment system

The dynamic process recording system used to capture the calcite and acid reaction consisted of a high-speed camera (MacroVis Eosens-300, Germany), a monocular microscope, a cold light source (XD-300-250W, China), and a computer. This system is shown in Fig. 2.

2.2.2. Recording the reaction process

The reaction was carried out in a self-made transparent plexiglass trough, with a microscale placed at the bottom of the tank. The reaction process was recorded using a high-speed camera. The volume of the reaction solution was 100 mL, and the sulfuric acid concentration was 1% by mass. After the camera parameters were set up, coated or uncoated calcite particles of the desired size were added into the reaction tank, and the reaction process was observed on the computer display. Finally, the required video clips were selected and converted to images.

2.2.3. Collection of bubbles

A sample (10 g) of high crystallinity calcite particles with particle size between 5 and 10 mm were selected and placed into 500 mL of sulfuric acid solution with the desired concentration for 5 min. All the desorbed bubbles were collected through the drainage method and the volume of the bubbles was measured. The total area of these calcite particles was determined using a microscope. Subsequently, the volume of CO_2 generated per unit area of calcite was calculated. The above experiments were repeated twice.

2.2.4. Scanning electron microscopy

The surface morphology of calcite before and after the treatment with sulfuric acid (concentration of 0.5% or 1.5%) was measured using SEM (JSM 5600LV, Japan) equipped with a Noran Vantage 4105X energy dispersive X-ray spectroscopy (EDS) detector. Calcite particles (3–5 mm) with smooth surfaces were selected and added to sulfuric acid for 10 min, after which the particles were collected, air-dried, and used for SEM analyses.

2.2.5. Coating method

The coating agent consisted of a mixture of SDS and PVA in a ratio of 1:10. Before mixing, PVA flakes were gradually dissolved in de-ionized water at 90 °C with continuous mixing by a magnetic stirrer for 30 min, followed by the addition of a solution of SDS with the desired concentration to the PVA solution. The mixture was agitated for 10 min.

A solution containing a certain concentration of the coating agent was prepared, and mineral particles were added to this solution for a conditioning time of 10 min. After conditioning, the particles were removed out and fed into a plexiglass trough equipped

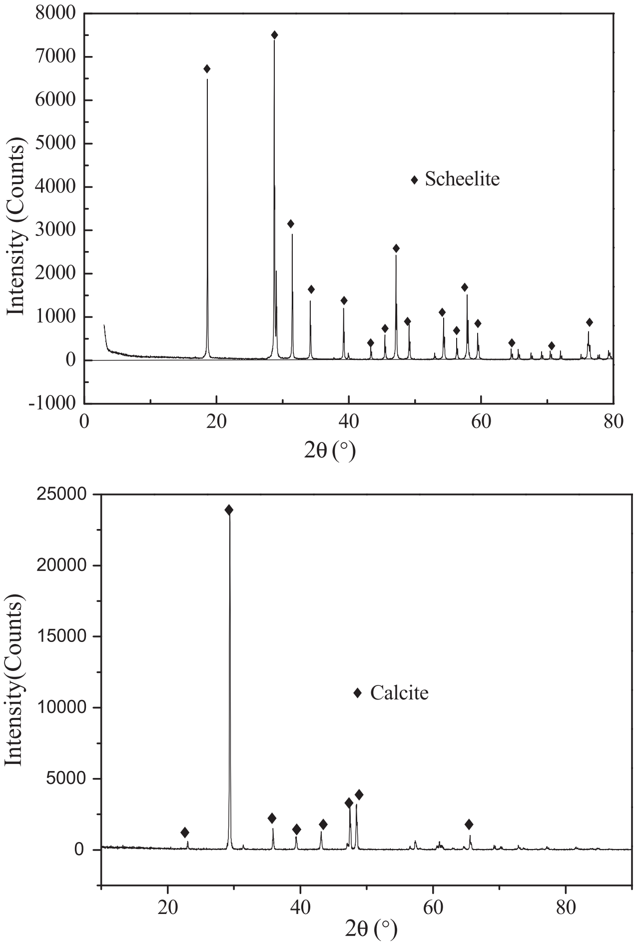

Fig. 1. XRD patterns of scheelite and calcite.

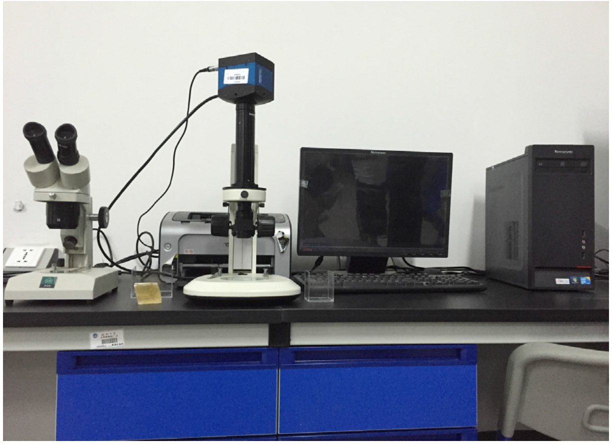

Fig. 2. High-speed camera experimental set-up.