



Application of reactive oily bubbles to bastnaesite flotation



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ABSTRACT

Reactive oily bubble, defined as air bubbles covered with a thin layer of kerosene containing collectors, was used to float a major rare earth mineral, bastnaesite from rare earth ores. Both fatty acid and hydroxamic acid were used to generate reactive oily bubbles. The flotation of bastnaesite with reactive oily bubble was investigated by zeta potential, zeta potential distribution and induction time measurement and micro-flotation tests. The results showed a quicker attachment to bastnaesite and a stronger collecting power of reactive oily bubbles containing 100 ppm fatty acid than conventional air bubbles, resulting in an enhanced bastnaesite recovery. The flotation recovery of bastnaesite by reactive oily bubbles containing hydroxamic acid is lower than that by conventional air bubble flotation where the bastnaesite was pre-conditioned by hydroxamic acid in aqueous phase. During induction time measurement, no attachment is observed between bastnaesite particles and reactive oily bubbles containing hydroxamic acid, illustrating the importance of collector type in reactive oily bubble flotation technology. These findings suggest the superior performance of reactive oily bubble technique than conventional bastnaesite flotation method only when proper collector is used to generate the reactive oily bubbles.

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1. Introduction

Rare earth elements (shortened as RE) are a group of elements with atomic numbers ranging from 57 to 71. Yttrium with atomic number 39 is included as a rare earth element because it often occurs with other rare earth minerals in nature, and has similar chemical properties. Based on the difference in solubility of rare earth sulfates, the rare earth elements are often divided into three groups: light, medium, and heavy rare earth elements. The light rare earth elements are La, Ce, Pr and Nd. Bastnaesite, (Ce, La) CO₃ F, is considered as one of the most important sources of rare earth elements due to its richness in the light rare earth elements and its large global reserves. Bastnaesite is a kind of complex rare earth fluoride or carbonate salts. About 70% of the rare earth oxides in the world are extracted from bastnaesite (Bhushan and Kumar, 2013). Bastnaesite deposits of great industrial and economic importance are mainly located in Neimenggu (China), Mianning (China) and Mountain Pass (USA), especially the Baiyunebo deposits of China (i.e., Neimenggu deposit) accounting for 80% of the world's total REO reserves (Jordens et al., 2013).

Bastnaesite is often accompanied by calcium and barium minerals such as barite and fluorite. These accompanying minerals of much finer particle sizes are easy to form clay minerals, known as argillization in geology. For instance, the argillization of Sichuan Mianning rare earth ore can be up to 13.31–20.35%. The bastnaesite content in the rock is typically within 15%, and it is normally recovered by flotation. Although the specific gravity of Mianning bastnaesite is significantly higher than other minerals (quartz, feldspar, mica etc.), its floatability and specific gravity are quite close to the accompanying calcium and barium minerals such as barite and fluorite. Such a complex property dramatically affects the mining and separation of bastnaesite, leading to complicated process flow sheets (Houot et al., 1991).

Conventional froth flotation has been widely applied to the beneficiation of bastnaesite due to the fact that it is possible to process a wide range of fine particles. The most commonly used collectors for bastnaesite flotation are fatty acids and hydroxamic acids (Zhu et al., 2000). The commercial bastnaesite deposit in Mountain Pass, California, USA, is processed by froth flotation using a mixture of tall oil and lignin sulfonate at elevated temperature (steam conditioning) to selectively float bastnaesite from calcite and barite while using fatty acid as collector. Fuerstenau showed the superiority of alkyl hydroxamates to the fatty acids for bastnaesite flotation. Their results indicated that alkyl hydroxamates

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can achieve the desired selectivity even at room temperature (Fuerstenau, 2013). However, the application of hydroxamic acids collector in large scale has limitations due to the high price of hydroxylamine and hence high production cost. Recently, extensive researches aiming to finding new synthesis method of hydroxamic acids have been carried out to substitute the traditional costly synthesis method (Wang and Che, 1991; Yu, 2001). However, none of them has been proven to be a great success in reducing the cost of hydroxamic acid. Fatty acids, on the other hand, are the earliest and most traditional collector in bastnaesite flotation due to their widespread availability in mineral flotation. However, they show a low recovery and selectivity for bastnaesite flotation. In order to obtain high grade and recovery, an elevated process temperature and multiple flotation stages are necessary to overcome some disadvantages of this type of collectors such as limited solubility in water at ambient temperature. Fatty acid containing 17 carbons in its tail as nonpolar base provides a strong hydrophobicity, but offers a relative weak collecting power due to the single carboxyl head. Furthermore, a large amount of sodium silicate is needed as depressant to prevent collector adsorption on gangue minerals, which not only increases the cost of chemicals, but also poses potential threats to bastnaesite flotation. It is therefore critically important to find an alternative collector or an improved method for bastnaesite flotation.

It has been shown in a previous study that the reactive oily bubble improves not only the collecting power but also the selectivity in sulphide mineral flotation with a reduced dosage of collector (Liu et al., 2002a). Addition of collector in oil increases the collector distribution, decreases the total collector consumption, and minimizes unnecessary interactions among the collector, frother, and other flotation chemical species in the pulp. To reduce the use of collector and to increase the collecting power of collector in bastnaesite processing, the use of reactive oily bubble flotation technique was studied. Both fatty acid and hydroxamic acid were used to generate reactive oily bubble in this study. The zeta potential distribution and the induction time of reactive oily bubble-bastnaesite particle attachment were measured to investigate the improved flotation mechanism. Micro-flotation tests were conducted to further confirm the advantage of this reactive oily bubble flotation technology.

2. Materials and methods

2.1. Materials

Kerosene (Fisher Scientific) was used as the model oil, while reagent grade HCl and NaOH (Fisher Scientific) were used as pH modifiers. Ultra-high purity KCl (>99.999%, Fisher Scientific) was used as supporting electrolytes to prepare KCl solutions. The bastnaesite concentrate used in this study was from Baotou deposit, China. To remove the potential collector and other impurities on the surface of bastnaesite concentrate, the bastnaesite sample was washed with HCl solutions of pH 3, and rinsed with reagent grade ethanol (Fisher Scientific) followed by de-ionized water. The sample was then vacuum-dried for 6 h at 60 °C. The sample prepared as such was dry ground and sieved to different particle size ranges for different measurements. The obtained bastnaesite sample was analyzed by XRD, SEM and XRF.

2.2. Sample characterization

Room-temperature scanning electron microscope (SEM) experiments were performed at Alberta Center for Surface and Engineering Science (ACES). The bastnaesite samples were examined using

a scanning electron microscope (SEM) Vega-3 (Tescan) with an EDX detector (Oxford Instruments).

The X-ray diffraction measurement was performed using a RIG-AKU Rotating anode XRD system (Rigaku RU-200B). The power of X-ray tube was set at 40 kV and 110 mA. Scan speed for the continuous mode was 2° per minute. An EDAX ORBIS XRF spectrometer was operated up to 1000 mA to determine chemical composition of mineral samples.

2.3. Zeta potential and zeta potential distribution measurement

Zeta potential distributions were measured using a Zetaphometer III (SEPHY/CAD) equipped with a laser-illumination, a digital-video-viewing system and a rectangular electrophoresis cell containing a pair of hydrogenated palladium electrodes. The details on the experimental procedures can be found elsewhere (Liu et al., 2002b). A 10 mM KCl solution was used as the supporting electrolyte for the zeta potential distribution measurements. An average value of the zeta potential distribution was calculated and considered as the overall zeta potential of the suspended solids. The zeta potential distribution measurements for each condition were repeated at least nine times and the average values as well as the standard deviations as error bars were reported.

Kerosene in water emulsions and bastnaesite suspensions were prepared for zeta potential distribution measurement. A water-in-kerosene emulsion was prepared by placing 5 drops of kerosene in 80 mL of 10 mM KCl solutions under sonication by a 550 Sonic dismembrator (Fisher) for 15 min. The emulsion was then left for 20 min to keep the temperature and emulsion droplet size in equilibrium. The average size of oil droplets remaining in the emulsion was determined to be 515.3 ± 42.9 nm, suitable for zeta potential distribution measurement. The bastnaesite particles were dry ground in a mortar and then mixed with 10 mM KCl solution to prepare a stock suspension. The upper layer of the stock suspension with sub-micron size bastnaesite particles ($D = 543.1 \pm 85.7$ nm) was used for the zeta potential distribution measurement. Before zeta potential distribution measurement, both of the kerosene-in-water emulsion and the bastnaesite suspension were diluted to 0.01–0.1 wt% by 10 mM KCl testing solution to obtain the dispersion with right concentration of dispersed phases suitable for zeta potential distribution measurement. The temperature was maintained at 22.0 ± 0.5 °C.

2.4. Induction time measurement

Induction time of bubble-particle attachment was used to evaluate the efficiency of particle-bubble attachment and hence flotation performance. As a critical parameter, a shorter induction time corresponds to a higher flotation recovery (Yoon and Yordan, 1991; Gu et al., 2003). The induction time measurement was conducted by an in-house built induction timer equipped with a macro lens connected to a CCD camera. Before the experiment, the glass cell and a piece of silica wafer (1 cm × 1 cm) were cleaned using sulfuric acid to remove any contaminants. The clean wafer was then placed onto the inside bottom of the glass cell. The stock bastnaesite suspension with particles between 150 and 212 μm in diameter was transferred into the glass cell using a plastic pipette. The coarse bastnaesite settled down quickly and formed a mineral particle bed on the silica wafer. Extra caution was taken to make sure an even thickness of mineral bed on the wafer. In a typical induction time measurement, an air bubble or reactive oily bubble is generated at the one end of a glass capillary tube immersed in testing liquid. The other end of the glass capillary is fixed on the diaphragm of a speaker. Applying a given voltage through a computer controlled amplifier drives the capillary glass tube by extension of the speaker diaphragm and hence the bubble towards

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