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The effect of dissolved calcite species on the flotation of bastnaesite using sodium oleate

Zhoujie Wang[a], Houqin Wu[a], Yanbo Xu[a], Kaiqian Shu[a], Shuai Fang[a], Longhua Xu[a,b,*]

[a] Key Laboratory of Solid Waste Treatment and Resource Recycle Ministry of Education, Southwest University of Science and Technology, Mianyang, Sichuan, PR China
[b] State Key Laboratory for Environment-friendly Energy Materials, Southwest University of Science and Technology, Mianyang, Sichuan, PR China

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ABSTRACT

The flotation behavior of bastnaesite, a major mineral source of rare earth elements, is strongly affected by the dissolved species of gangue minerals that change the solution chemistry and mineral surface properties. In this work, the effect of dissolved calcite species on the flotation of bastnaesite was investigated by conducting micro-flotation experiments, zeta potential measurements, Fourier-transform infrared (FT-IR), and X-ray photoelectron spectroscopy (XPS) analysis. Micro-flotation experiments confirmed that calcium and carbonate ions in calcite supernatant significantly reduced the flotation of bastnaesite in strongly alkaline condition. Zeta potential measurements showed that the IEP of higher bastnaesite was obtained after the addition of calcite supernatant species. Species distribution diagram demonstrated that the adsorption of sodium oleate on the surface species of bastnaesite was inhibited by the generation of calcium-containing hydroxy complexes and precipitates. FT-IR analysis suggested that the decrease the sodium oleate concentration in solution and the generation of calcium oleate precipitate on the mineral surface are possible reasons for the reduced recovery. XPS analysis further revealed that the metal carbonates and hydroxy complexes of calcium adsorbed on the bastnaesite surface in the presence of calcite supernatant, which concealed the surface active sites, caused the decrease in bastnaesite flotation recovery.

1. Introduction

The term rare earth element (REE) refers to 17 metal elements of lanthanides, scandium, and yttrium (Gupta and Krishnamurthy, 1992). Because of their special electron configuration, REEs have their unique magnetic, fluorescent, and chemical properties that make them indispensable in many fields, including metallurgy; military, petrochemical, and medical industries; and in applications such as fine ceramics, energetic materials, and luminescent materials (Cao et al., 2018). There are approximately 250 REE-containing minerals in the earth's crust, but only a dozen of them have been exploited (Jordens et al., 2013). Furthermore, among these minerals, only bastnaesite, monazite, and the weathered crust elution-deposited rare earth ores are valuable in industrial production. The Sichuan Panxi Mianning rare earth ore is of the single bastnaesite type. Bastnaesite ((REE)FCO_3, $S_{Ba} = 10^{-5.33}$ mol/L) is a semi-soluble salt mineral (Zhang et al., 2013) that is mainly composed of the cerium subgroup and the lighter REEs (Bulatovic, 2010). While it is the main ore source of light REEs, it is often associated with other semi-soluble minerals such as calcite ($CaCO_3$, $S_{Ca} = 10^{-4.18}$ mol/L) and fluorite (CaF_2, $S_{Fl} = 10^{-4.07}$ mol/L). During the separation process, calcium ions from the surface of these gangue minerals dissolve, and may affect collector adsorption on minerals surface, and hence, the flotation performance (Zhang et al., 2017; Cao et al., 2019; Espiritu et al., 2019; Wang et al., 2019). Although the effects of these inevitable ions on the flotation of apatite (dos Santos et al., 2010), chalcopyrite (Deng et al., 2013) and smithsonite (Zhao et al., 2018) have been well studied, the case for bastnaesite has not been well investigated yet.

Dissolved ions from mineral surfaces undergo many reactions including adsorption, complexation, hydrolysis, and surface or bulk precipitation, which can strongly affect the interaction between the minerals and other reagents (Fuerstenau et al., 1992; Nunes et al., 2011; Zhu et al., 2011; Houqin et al., 2018). Moreover, since the best conditions of flotation can be predicted by the solution chemistry calculations, the fundamental study of solution chemistry is especially important for the flotation of salt-type minerals (Yuehua et al., 2003). The effects of metal ions on flotation are complicated, and depend on the metal ion concentrations, solution pH value, collector type, and mineral characteristics etc. (dos Santos et al., 2010; Tian et al., 2017a; Fang et al., 2018). It is known literature from calcium ion in flotation pulp

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[*] Corresponding author.
E-mail addresses: xulonghua@swust.edu.cn, neuxulonghua@163.com (L. Xu).

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activates the flotation of spodumene and quartz when sodium oleate (NaOL) is used as a collector (El-Salmawy et al., 1993; Wang et al., 2007; Liu et al., 2015), while it acts as a depressant for Na-feldspar and quartz when a cationic amine is used as a collector (Scott and Smith, 1993; Demir et al., 2003). Besides these, the dissolved calcium and magnesium ions of associated gangue could be adsorbed on the surface of RE minerals, affecting their flotation behaviors when hydroxamic acid is used as a collector. (Espiritu et al., 2018a; Cao et al., 2019). Under alkaline conditions the flotation of celestite is inhibited due to the specific adsorption of carbonate and bicarbonate on the celestite surface (López-Valdivieso et al., 2000). Moreover, the precipitation of carbonate formed with metal cations in the solution can also inhibit the flotation of RE minerals, but the effect is not remarkable (Espiritu et al., 2018a).

In the case of bastnaesite, the inhibitory effects of calcium or carbonate species on flotation have been well documented (Scott and Smith, 1993; Zhang et al., 2017; Kupka and Rudolph, 2018). However, the exact mechanism of suppression is still being investigated (Shi et al., 2014; Xu et al., 2017a), and the relevant details remain largely unidentified. Therefore, this study was aimed to understand how the underlying inhibition mechanism of dissolved of calcite species (mainly calcium ions and carbonate) inhibit the flotation of bastnaesite.

2. Materials and methods

2.1. Materials and reagents

Bastnaesite samples were supplied from Maoniuping Rare Earth Mine in MianNing County, Sichuan, China. After gravity separation and magnetic separation, the most impurities and gangue minerals can be removed. Mineral particles with the size of $-75 + 38\,\mu m$ were obtained for the micro-flotation experiments and X-ray photoelectron spectroscopy (XPS) analysis. The separated bastnaesite was ground to approximately 2 μm using an agate mortar for the zeta potential measurements, Fourier-transform infrared (FT-IR) spectroscopy analysis. X-ray diffraction (XRD) patterns (Fig. 1) and X-ray fluorescence spectra (XRF, Table 1) were used to obtain the chemical compositions and content of the mineral (Xu et al., 2013). The purified mineral sample of calcite was obtained from Tongliang District, Chongqing, China. The results of XRD and XRF indicated that the prepared bastnaesite and calcite samples were of high purity.

The calcite supernatant was prepared by placing 50 g of calcite with a particle size of $-75\,\mu m$ in 1000 mL deionized (DI) water (Ulupure Instrument Equipment Co., Ltd. Xian, China). The suspension was mixed for 1 h using a magnetic stirrer, and allowed to precipitate for half an hour, and then filtered through a filter paper to recover the supernatant. The amounts of calcium and carbonate ions in the supernatant analyzed using inductively coupled plasma optical emission spectrometry (ICP-OES, OPTIMA8300) were determined as to be 4.5 and 44.8 ppm, respectively.

Information about the reagents used in this study is presented in Table 2. Sodium oleate (NaOL, $CH_3(CH_2)_7CH = CH(CH_2)_7COONa$) was used as a collector for the flotation of bastnaesite. Hydrochloric acid (HCl) and sodium hydroxide (NaOH) were used for pH adjustment. Sodium chloride (NaCl) of analytical grade was used as a background electrolyte solution for the zeta potential measurements. All other reagents were of analytical grade, and DI water with a resistivity value of 18.25 MΩ cm at 25 °C was used in all tests.

2.2. Micro-flotation experiments

Micro-flotation experiments were carried out using a flotation equipment of XFG type (Fig. 1, Changchun, China) with an impeller speed of 1700 rpm (Shu et al., 2019b). Firstly, 2 g of mineral sample with a particle size range of $-75 + 38\,\mu m$ was placed inside a 40-mL flotation cell containing a desired amount of DI water. Secondly, in the absence of depressant, NaOH or HCl solutions were used to adjust the suspension pH to desired level during stirring for 7 min. In the presence of depressant, the suspension pH was adjusted using HCl or NaOH during stirring for 5 min, followed by addition of the depressant ($CaCl_2$ or Na_2CO_3), and the suspension was conditioned for 2 min. Then, the collector was added, and the suspension was stirred for 3 min. Finally, after scraping (5 min), the products were filtered, dried, and weighted, and the flotation recovery was determined (see Fig. 2).

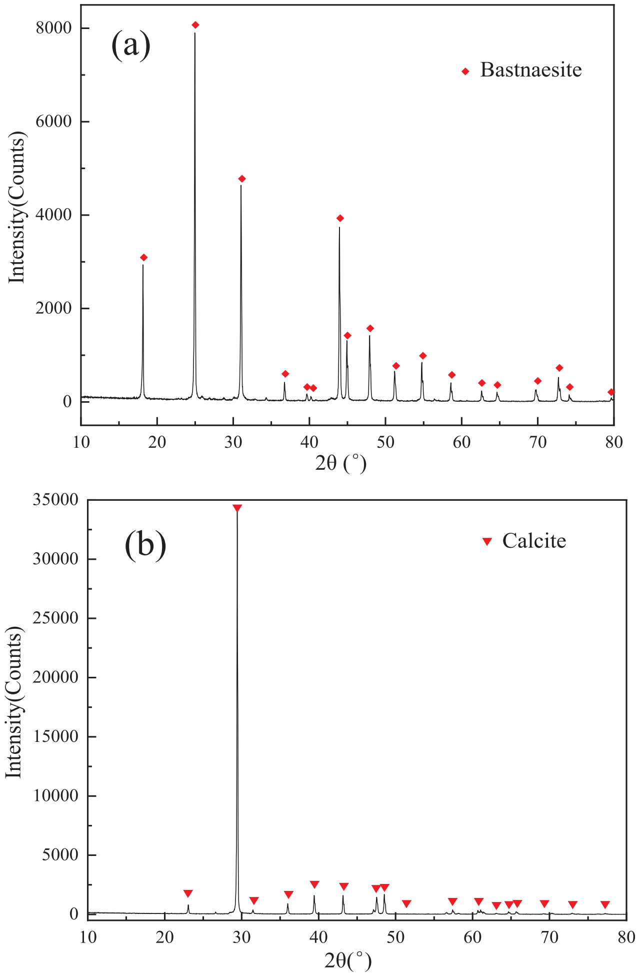

Fig. 1. XRD patterns of (a) the purified bastnaesite sample and (b) the purified calcite sample.

Table 1
Chemical composition of the bastnaesite and calcite samples (mass fraction, %).

Bastnaesite	CeO_2	La_2O_3	Nd_2O_3	Pr_2O_3
	44.74	37.15	11.00	3.28
Calcite	CaO	SiO_2	MgO	Fe_2O_3
	98.32	0.90	0.35	0.11

2.3. Zeta potential measurements

The zeta potential measurements of bastnaesite was carried out using a Malvern Zetasizer Nano ZS90 instrument (Malvern Instrument Co., UK) equipped with a rectangular electrophoresis cell at 25 °C. For each measurement, 30 mg of approximately 2 μm purified bastnaesite powder was added into 1×10^{-3} mol/L NaCl solution (made with DI water or supernatant) to form a suspension containing 0.01 wt%. At a given pH and reagent concentration, the suspension was conditioned in a beaker using a magnetic stirrer for 15 min with a speed of 600 rpm.