



The effect of dissolved mineral species on bastnäsite, monazite and dolomite flotation using benzohydroxamate collector

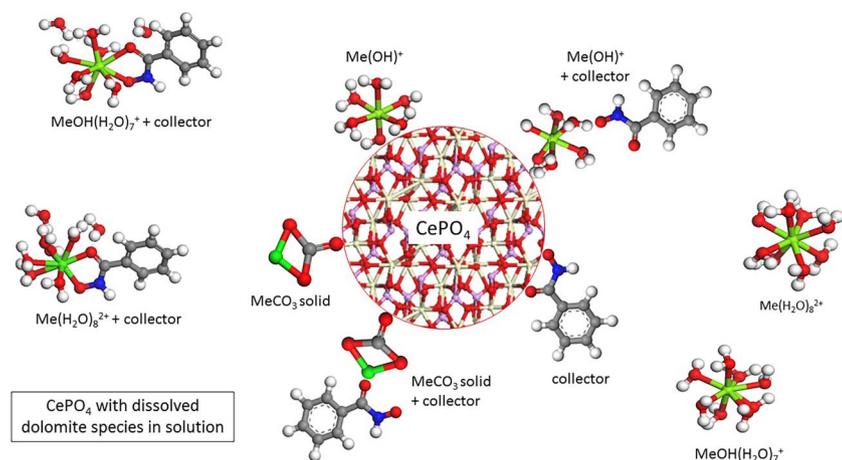


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GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:

RE minerals
Bastnäsite
Monazite
Dolomite
Flotation
DFT simulation

ABSTRACT

Flotation is the most commonly used beneficiation method for rare earth (RE) ores. Due to the dissolution characteristics of the RE minerals and the gangue minerals, they may behave similarly in a flotation system. Previous work has shown that dissolved mineral species from gangue could precipitate/adsorb at the mineral surface affecting the minerals' flotation behavior. In this work, the effect of dolomite supernatant on the surface of bastnäsite, monazite and dolomite are presented. Zeta potential measurements, complemented with flotation tests, were conducted with and without the presence of the supernatant using benzohydroxamate as the collector. XPS results confirmed the surface speciation, and DFT simulations detail the possible mineral - collector, mineral - precipitated species and precipitated species - collector interactions. The results show that carbonate precipitates and Ca^{2+} from the supernatant could adsorb onto the mineral surface through covalent bonding, both affecting the zeta potential and reducing collector adsorption. Another important finding of this study is the potential loss of the collector in the solution due to complexation with ions from the supernatant. These findings confirm that an effective rare earth mineral separation through flotation does not rely solely on the strength of collector-mineral interaction, but rather is highly dependent on the chemistry of the flotation solution. Taking advantage of, or controlling, the surface reactions should be the main target to developing a more efficient and

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cost-effective flotation process. Different measures have been proposed to reverse/reduce the detrimental effects of the dolomite supernatant to RE mineral flotation.

1. Introduction

Main sources of rare earth (RE) elements, such as bastnäsité (a RE fluorocarbonate) and monazite (a RE phosphate), are typically associated with carbonate minerals such as calcite and dolomite. These RE minerals occur naturally disseminated in the ore body [1], requiring fine liberation sizes thus making flotation to be the most common beneficiation process [2,3]. Among the RE collectors, hydroxamate-type collectors have caught the attention of the researchers due to its selectivity towards RE minerals. It is suggested that hydroxamate collectors form strong chelate with RE metals than metals from gangue minerals [4]. It is proposed that hydroxamates interact with either RE-hydroxylated species at the surface or with the RE-hydroxylated species in the solution then adsorb at the mineral surface, rendering the mineral hydrophobic [5]. However, this scenario is not straightforward because of the natural solubility of both the RE and associated carbonate minerals in solution.

These RE minerals and the associated gangue are considered salt-type minerals [6] which means that they have relatively higher solubilities than most minerals, but lower than salt minerals [7]. Since they are sparingly soluble in water, constituent ions that are dissolved may influence other mineral surfaces. Flotation studies involving single mineral flotation do not often take into account the effect of the dissolved mineral species from the gangue minerals; as such, further research involving constituent ions is encouraged [8]. RE flotation studies [9,10] concerning semi-soluble gangue minerals have noted that dissolved species could precipitate/adsorb at the surface of RE minerals affecting their flotation behavior. Although there have been several attempts to study the effect of dissolved mineral species from typical carbonate gangue minerals in mineral flotation [9,11–13], few studies concern RE minerals and most are related to calcite, but not dolomite. In addition, very few research works investigating RE flotation have considered using a solution with the dissolved carbonate mineral species (gangue supernatant) as the flotation medium. Espiritu et al. [14] studied the effect of the dolomite (gangue) supernatant on the surface property of the RE minerals such as bastnäsité and monazite. It was found that dolomite supernatant could potentially affect bastnäsité and monazite flotation due to the changes of their surface properties when exposed to the solution.

The surface complexation model of carbonate minerals have been presented in detail by Van Cappellen et al. [15]. It is suggested that upon in contact of carbonate in water, two primary hydration sites will occur: (1) hydroxylated cation sites ($> \text{MeOH}^+$) and (2) protonated anion sites ($> \text{CO}_3\text{H}^-$), where $>$ represents mineral lattice and Me the mineral cation. For monazite, two surface sites are also present: (1) phosphate sites ($> \text{P}(\text{OH})_2$) and (2) hydrated RE sites ($> \text{RE}(\text{OH})_2$) [16]. These surface sites provides interaction sites for other metal cations and anions in the solution [15,17].

Some of the calcium and magnesium from dolomite could dissolve out in the solution; they could occur in different species which could interact with the mineral surface leading to surface precipitation and/or adsorption [15,18]. To be able to study the effect of the dissolved dolomite species on bastnäsité, monazite and dolomite; zeta potential, hydrophobicity and interactions at molecular scale were investigated in the presence of benzohydroxamate, a common RE mineral collector. These were conducted using electrophoretic measurements, microflotation tests and quantum mechanical simulations based on density functional theory (DFT). For information on zeta potentials in flotation, flotation and DFT simulations, readers are referred to Fuerstenau and Pradip [19], Wills and Finch [20] and Rai [21], respectively.

2. Experimental methodology

2.1. Material

Bastnäsité was obtained from African Rare Earths (Pty.) Ltd. (South Africa). Monazite (Eureka Farm 99, Namibia) was acquired from Mineralogical Research Company (USA). Dolomite (Sterling Hill Mine, New Jersey) was purchased from Ward's Science (USA).

Sodium chloride (supporting electrolyte); hydrochloric acid and potassium hydroxide that were used as pH modifiers were obtained from Fisher Scientific (Canada). Benzohydroxamic acid was obtained from Sigma-Aldrich (Canada), F150 (a common frother) was obtained from Flottec (Canada).

The dolomite supernatant was prepared by placing 75 g of dolomite with particle size - 106 + 38 μm in 1500 mL deionised water. The suspension was mixed for 8 h at elevated temperature of 60 °C. The suspension was allowed to cool before passing through a filter with a grade of 413 (particle retention of 5 μm) to recover the supernatant.

2.2. Zeta potential measurements

Mineral samples were pulverized in a Planetary Monomill, Pulverisette 6 (Fritsch, Germany). The D_{50} obtained was 2.3 μm for dolomite, monazite and bastnäsité. A solution of 1×10^{-3} M NaCl was used as the indifferent background electrolyte and the dolomite supernatant was used as a medium. Prior to addition of the mineral samples, the solutions of NaCl, supernatant and collector were pH adjusted using hydrochloric acid and potassium hydroxide. For the measurements with supernatant then collector, the minerals were first conditioned with the supernatant for a certain amount of time (0, 30, 60, 120 and 240 s) prior to addition of the collector. For every measurement, the 100-ppm mineral suspension was kept mixed to ensure that the particles were suspended. Zeta potential measurements were then taken using a NanoBrook 90Plus Zeta Particle Size Analyzer (Brookhaven Instruments, USA).

2.3. Microflotation

Microflotation tests were conducted using a modified Hallimond tube (Fig. 1). The flotation cell volume is approximately 170 mL, made of glass, and comprised of three parts - the lower part has a silicate frit at the bottom; the extensor part connects the lower part and the upper part, and the upper part is where the floated fractions can be collected.

One (1) gram of mineral sample, with a particle size range - 106 + 38 μm , was placed in a beaker with 30 mL deionised water (adjusted to desired pH) and a magnetic stirring bar ensured that the mineral particles remained in suspension. The pH of the suspension was adjusted prior to addition of the collector, and was maintained during the 5-min conditioning. For the tests with dolomite supernatant, the minerals were first exposed to the supernatant for 2 min (adjusted to desired pH), before the collector was added. The suspension was then transferred to the cell and was next added with 140 mL of pH adjusted water. Air was introduced through the cell at a flowrate of 40 mL/min. Flotation was conducted for 1 min. The floated and non-floated fractions were collected, filtered, dried and weighed in order to calculate the recovery.

2.4. X-ray photoelectron spectroscopy (XPS)

The surfaces of dolomite, monazite and bastnäsité, in the presence

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