



Flotation of monazite in the presence of calcite part I: Calcium ion effects on the adsorption of hydroxamic acid



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ABSTRACT

The dissolution of minerals provides elevated concentrations of alkaline earth metal ions such as calcium (Ca^{2+}) in water which may have a significant influence on flotation performance. The effects of Ca^{2+} ions dissolved from calcite surfaces on the flotation performance of a monazite-calcite system have been investigated using micro-flotation tests followed by fundamental collector adsorption studies. The results indicate that specially adsorbed CaOH^+ via hydrogen bonding competed with hydroxamic acid for the phosphate-oxygen active sites on the monazite surface and decreased its hydrophobicity due to hydration. Electrostatically adsorbed CaOH^+ on monazite increased the adsorption density of hydroxamic acid through a chelating interaction. At higher dosages of calcium and hydroxamic acid, bulk and surface precipitation of calcium-hydroxamate occurs in the monazite-calcium-hydroxamic acid system.

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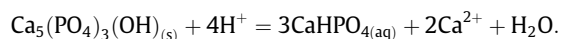
1. Introduction

Rare earth elements (REEs) are a group of 15 lanthanide elements (atomic numbers 57–71) and two transition metal elements (scandium and yttrium). There is a high demand for REEs due to their applications in catalysts, alloys, magnets, and glass polishing (Chelgani et al., 2015; Zhang et al., 2015). Monazite ($(\text{Ce, La, Y, Th})\text{PO}_4$) is a commercial rare earth mineral and usually associated with heavy minerals such as zircon, rutile, and ilmenite (Abeidu, 1972; Cheng et al., 1993; Pavez and Peres, 1994). Besides gravity, magnetic, and electrostatic separation methods, flotation has been widely used in monazite concentration due to its advantages in fine particle processing (Cheng et al., 1993). Monazite flotation has been investigated by many researchers (Abeidu, 1972; Cheng, 2000; Cheng et al., 1993; Cross and Miller, 1989; Dixit and Biswas, 1969; Pavez and Peres, 1994, 1993; Qi, 1993). Satisfactory flotation performance is achieved at pH 8–9 by using sodium oleate as a collector for monazite and sodium silicate as a depressant for zircon, rutile, and ilmenite (Cheng et al., 1993; Pavez and Peres, 1994, 1993; Qi, 1993).

However, studies on the flotation separation of monazite from carbonate minerals such as calcite and dolomite or phosphate minerals such as apatite are limited. As reported by Chan (1991), small amounts of dolomite and apatite exist in a monazite ore located in Mt Weld, Australia. Moreover, for some promising rare earth

secondary resources, such as coal fine refuse and phosphates, monazite is usually associated with carbonate and phosphate minerals (Kandil et al., 2010; Zhang et al., 2015). Minerals such as calcite, dolomite, and apatite belong to sparingly soluble minerals. Lattice ions of these minerals such as calcium ions in calcite are dissolved from the mineral surfaces into solution, which influences collector adsorption and thus flotation performance.

A number of studies have been previously conducted to evaluate calcium and multivalent cation adsorption on mineral surfaces (Ananthapadmanabhan and Somasundaran, 1985; Atesok et al., 1988; Clark and Cooke, 1968; James and Healy, 1972). Adsorption of calcium on minerals such as silica and Na-kaolinite usually increased sharply at pH values above 10 where significant amounts of calcium ions hydrolyze to CaOH^+ ions and $\text{Ca}(\text{OH})_2$ precipitates (Atesok et al., 1988; Clark and Cooke, 1968). The higher affinity of CaOH^+ compared with Ca^{2+} is mainly due to the decrease in the unfavorable solvation energy and the increase in favorable chemical energy changes (Ananthapadmanabhan and Somasundaran, 1985; James and Healy, 1972). Specific adsorption of calcium hydrolyzed species is well documented for the apatite/calcite system (Amankonah et al., 1985; Ananthapadmanabhan and Somasundaran, 1984; Mishra, 1978; Somasundaran, 1968; Somasundaran and Agar, 1972). In addition, the free Ca^{2+} ions attach to apatite surfaces in the form of $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$ via the following equation (Elgillani and Abouzeid, 1993):



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Despite similarities in the calcium adsorption mechanisms on mineral surfaces, the effects of calcium ions on flotation are more complicated and have been found to be a function of mineral characteristics, calcium ion concentration, collector type, solution pH values, etc. (Clark and Cooke, 1968; Demir et al., 2003; Liu et al., 2015; El-Salmawy et al., 1993; Santos et al., 2010; Scott and Smith, 1993). Calcium ions serve as an activator for quartz and spodumene when using anionic collectors such as sodium oleate and sodium alkylsulfonates (Clark and Cooke, 1968; El-Salmawy et al., 1993; Liu et al., 2015). However, depression of quartz and Na-feldspar occurred in the presence of calcium ions when using a cationic amine collector (Demir et al., 2003; Scott and Smith, 1993).

In the current study, the separation of monazite from calcite using froth flotation and hydroxamic acid as the collector was studied systematically using a micro-flotation apparatus. The effects of calcium ions on the adsorption of hydroxamic acid onto monazite surfaces were fundamentally investigated through electrophoresis and adsorption studies and supported by Fourier transform infrared spectroscopy (FTIR) analysis. Finally, an interaction model for the adsorption of hydroxamic acid onto monazite in the presence of calcium ions was proposed.

2. Material and methods

2.1. Materials

Monazite pre-concentrate samples collected from a rare earth mine in China were purified using a shaking table and high-gradient magnet. A monazite concentrate with a purity level of nearly 98% was obtained as determined by inductively coupled plasma mass spectrometry (ICP-MS). The X-ray diffraction analysis indicated that a minor amount of cerium oxide existed in the sample.

Chunk samples of calcite collected from a limestone mine located in Kentucky, USA, were crushed and ground to minus 300 μm . X-ray diffraction analysis showed that calcite content in the sample was more than 95% and thus directly used as pure minerals.

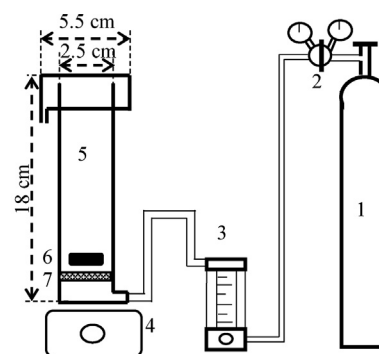
For the micro-flotation tests, the monazite concentrate and calcite material were screened to obtain material having a particle size smaller than 300 μm and larger than 150 μm . The remaining samples were ground using a corundum pestle and mortar for zeta potential, adsorption, Fourier transform infrared spectroscopy (FTIR) tests.

Octanohydroxamic acid of minimal 95% purity was purchased from TCI America. Methyl isobutyl carbinol (MIBC) of more than 99% purity was used as frother and purchased from Alfa Aesar. Other chemicals were of reagent grade and purchased from We Enable Science. Type I deionized water with a resistivity value of 18.2 $\text{M}\Omega\cdot\text{cm}$ at 25 $^{\circ}\text{C}$ was used for all the experiments.

2.2. Methods

2.2.1. Micro-flotation tests

A micro-flotation cell with a volume of 50 ml was used for the flotation tests (Fig. 1). During the tests, a suspension of the particles was achieved using a magnetic stirrer. To reduce interference of carbon dioxide, air bubbles were produced by passing pure nitrogen through a porous frit. Conditioning was conducted in a glass beaker with one gram of pure minerals in 50 ml solution. For the mixed mineral flotation tests, the ratio of monazite-to-calcite was 1:1 by weight. Solution pH values were first adjusted to predetermined values followed by the addition of metal salts and/or collectors with each conditioned for 5 min. Frother was



1-Nitrogen Tank; 2-Pressure Regulator; 3-Air Flowmeter; 4-Magnetic Stirrer; 5-Micro-flotation Cell; 6-Stirrer Bar; 7-Porous Material

Fig. 1. Schematic diagram of the micro-flotation apparatus.

added last followed by 1 min of conditioning. The solution pH values were measured and adjusted during conditioning every 2.5 min and just prior to the start of the flotation test. Given that the majority of the material floated within the first 30 s of the test, the initial pH values were considered to be more representative of the flotation conditions. The difference in the pH values measured before and after each flotation test was typically 0.2 pH units.

During the flotation tests, nitrogen flow rates were maintained at 55 ml/min while froth products were continuously removed over a period of 4 min. The concentrate and tailing samples were dried in an oven for 12 h and then cooled in a desiccator. Finally, flotation recovery values were calculated based on the sample weights. For the mixed mineral flotation tests, monazite and calcite recovery values were calculated by using the assay values obtained from acid digestion. Three repeat tests were conducted under the same condition and the experiment error measured from the recovery data indicated a standard deviation value of 1.10%.

2.2.2. Adsorption tests

Adsorption tests were conducted in a 20 ml glass beaker. Solid concentration values of 0.5% and 1% were used for monazite and calcite, respectively. Conditioning procedures were similar to that used for micro-flotation tests. After conditioning, 10 ml of the suspension was removed to a centrifuge tube and centrifuged in an IEC Clinical centrifuge at 3175 rpm. Hydroxamic acid concentration was determined using a Shimadzu 1280 UV-vis spectrophotometer based on the ferric hydroxamate method. Ferric chloride (5 mM) of 10 ml was added into 5 ml of centrifuged supernatant in a glass tube. Full wave scanning of the obtained solution showed that peak absorption occurred at 503 nm which was used for hydroxamic acid determination. For the adsorption tests at pH 11.0, pH values of the supernatant were readjusted to below 9.0 before ferric chloride addition to avoid the precipitation of ferric ions. The calcium concentration in solution was determined using induced coupled plasma (ICP) analysis. Three tests were conducted under the same condition and a standard deviation value of 0.30 $\mu\text{M}/\text{m}^2$ was obtained.

2.2.3. Zeta-potential tests

Zeta potential tests were conducted to study the effects of calcium ions on the electro-kinetic properties of monazite particles. A solids concentration of 0.05% by weight was used and conditioning procedures were similar to that used for the micro-flotation tests. Before conditioning, the solution was subjected to sonification for 1 min to thoroughly disperse the solid particles. A potassium chloride solution of 1 mM was used as a supporting electrolyte for all measurements. A standard deviation value of

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