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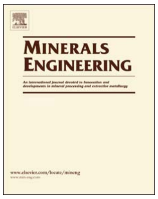

Flotation of monazite in the presence of calcite part II: Enhanced separation performance using sodium silicate and EDTA

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ABSTRACT

Selective depression of calcite in a monazite-calcite flotation system was systematically studied using micro-flotation and electrokinetic tests as well as X-ray photoelectron spectroscopy (XPS) characterization and solution chemistry calculations. Monazite was found to be depressed by both sodium silicate and sodium hexametaphosphate when calcium ions appeared in solution. It was hypothesized that co-adsorption of calcium species ($CaHCO_3^+$ and $CaCO_{3(aq)}$) and $Si(OH)_4$ as well as $SiO(OH)_3^-$ via hydrogen bonding formed a compact layer over the monazite surface, thereby reducing octanohydroxamic acid adsorption by steric hindrance. The use of citric acid or EDTA formed soluble chelates (e.g. $CaCit^-$ and $CaEdta^{2-}$) with the calcium ions which negated the flotation suppression effect. An XPS study indicated that both EDTA and citric acid chemically adsorbed on the monazite surface, while the adsorption on the calcite surface was achieved mainly through hydrogen bonding. EDTA was more effective than citric acid due to two reasons: (i) citric acid itself presented stronger depression effects and (ii) citric acid has weaker chelating properties for calcium. Using 2.5×10^{-4} M octanohydroxamic acid, 0.05 g/L sodium silicate and 6×10^{-5} M EDTA, monazite recovery of more than 90% was achieved while recovering only 20% of the calcite.

1. Introduction

Monazite is a rare earth mineral normally associated with heavy mineral sands which are a class of ore deposits and an important source of zircon, rutile and ilmenite (Cheng, 2000; Pavez and Peres, 1994). Concentration of monazite from the heavy minerals using froth flotation has been well studied (Abeidu, 1972; Cheng et al., 1993; Cheng, 2000; Dixit and Biswas, 1969; Nduwa-Mushidi and Anderson, 2017; Pavez and Peres, 1993, 1994; Qi, 1993; Zhang et al., 2016). The selective recovery of the monazite required the use of appropriate collectors (e.g., fatty acid) under mild alkaline conditions and the addition of depressants (e.g., sodium silicate) (Nduwa-Mushidi and Anderson, 2017; Pavez and Peres, 1994; Qi, 1993).

Due to an increasing demand for rare earth elements, alternative rare earth resources have been explored including materials such as coal, fly ash and red mud (Franus et al., 2015; Fulford et al., 1991; Honaker et al., 2014, 2016b, 2017; Zhang et al., 2015, 2017a, 2018b). The recovery of monazite from coal and coal byproducts using flotation was somewhat successful as reported by Honaker et al. (2014, 2017) and Zhang et al. (2015, 2017a). However, other minerals associated with the sources such as calcite, dolomite, rutile and pyrite were found to interfere with the concentration process. Espiritu and Waters (2018) also reported on the presence of dolomite in a monazite deposit as the main host mineral which results in a difficult flotation system due to its solubility published reports on the separation of monazite from minerals with higher solubility (e.g., calcite and dolomite) using a froth flotation process are few.

Research have been performed regarding the flotation separation of the other types of rare earth minerals from the more soluble minerals, e.g., calcite, dolomite, and barite (Cui and Anderson, 2017a, b; Fuerstenau et al., 1992; Pradip and Fuerstenau, 1991, 1983). Pradip and Fuerstenau (1991) did an adsorption study of octanohydroxamic acid on bastnaesite and calcite surfaces. It was found that the hydroxamate adsorption on calcite increased significantly at higher collector dosages at pH 9.3 due to surface and/or bulk precipitation of calcium hydroxamates. Cui and Anderson (2017a, b) reported that surface precipitation of $CaCO_3$ and $SrCO_3$ could occur on ancylite [$Sr(Ce,La)(CO_3)_2(OH)\cdot H_2O$] surface in basic conditions, which reduced the hydroxamate adsorption on the rare earth mineral surface.

In the current study, the separation of monazite from calcite in a combined system using froth flotation with appropriate depressants (e.g. sodium silicate) and regulators (e.g., citric acid and EDTA) was systematically studied by micro-flotation and electrokinetic tests as well as X-ray photoelectron spectroscopy (XPS) characterization and

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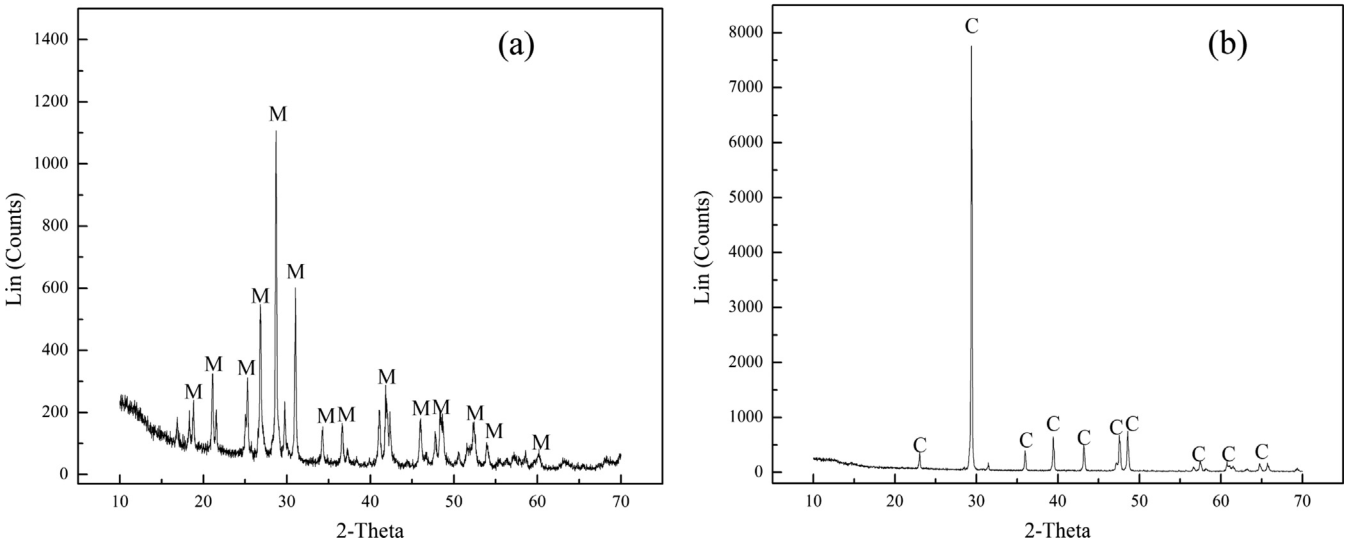

Fig. 1. XRD patterns of (a) pure monazite (M) and (b) calcite (C) minerals.

solution chemistry calculations. An in-depth understanding was obtained for the important role calcium ions play in the monazite-calcite flotation system in terms of selective depression. An efficient reagent scheme was formulated based on the test results and evaluated for its performance in achieving an efficient monazite-calcite separation.

2. Materials and methods

2.1. Materials

Monazite pre-concentrate was obtained from a rare earth mine in China and calcite samples were collected from a limestone mine in Kentucky, USA. The monazite pre-concentrate was upgraded using a shaking table and a permanent neodymium magnet bar. The permanent magnet primarily removed hematite from the pre-concentrate. As a result of the upgrading, monazite and calcite concentrates with a purity level of nearly 95% were obtained for the study as determined by inductively coupled plasma mass spectrometer (ICP-MS) and X-ray diffraction (XRD) analysis (Fig. 1). The material used for micro-flotation tests was from a narrow particle size fraction of 300 × 150 μm which was attained by screening the monazite material. Crushing and screening was needed for the calcite sample. For the zeta potential and adsorption studies, representative portions of the two materials were ground using a corundum pestle and mortar to achieve a particle size below 5 μm.

Octanohydroxamic acid of minimal 95% purity was purchased from TCI America for use as the collector. Methyl isobutyl carbinol (MIBC) of more than 99% purity was used as the frother and purchased from Alfa Aesar. Technical grade sodium silicate and ACS grade sodium hexametaphosphate were purchased from Fisher Scientific for use as calcite depressants. Citric acid and ethylenediaminetetraacetic acid (EDTA) of ACS grade were used as regulators and purchased from VWR. Trace metal grade hydrochloric acid and ACS grade sodium hydroxide that purchased from Fisher Scientific were used to regulate slurry pH values. All other chemicals used in the study such as the calcium chloride and potassium chloride were of ACS grade and purchased from Fisher Scientific.

2.2. Methods

2.2.1. Micro-flotation tests

A micro-flotation cell with a volume of 50 mL was used in the study. Air bubbles were generated by sparging nitrogen through a porous material fixed at the bottom of the cell. Pure minerals of 1 g were first mixed with 50 mL of deionized water in a glass beaker and conditioned using a magnetic stirrer. Next, the solution pH value was adjusted via the addition of sodium hydroxide or hydrochloric acid solutions. Subject to the purposes of tests, calcium ions, regulators, depressants and collector were added sequentially with 5 min of conditioning after each addition. Finally, frother was added and the solution was conditioned for another 30 s. The solution pH values were adjusted every 2.5 min during the conditioning process and the values measured directly before the flotation tests were recorded.

After conditioning, the solution was transferred into the cell and flotation was conducted continuously for a period of 3 min using nitrogen at a flow rate of 55 mL/min. The flotation concentrates and tailings were dried in a desiccator and the dry weights were measured and recorded for recovery calculations. For the combined mineral flotation tests, monazite was mixed with calcite at a mass ratio of 1:1 and recovery values were calculated 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. Electrokinetic tests

Zeta potential measurements were conducted to study the effects of calcium, regulators and depressants on electrokinetic properties of monazite and calcite. Particles of monazite and calcite finer than 5 μm were used in the study. Approximately 0.04 g solids were dispersed in 40 mL of 1×10^{-3} M potassium chloride solution by 30 s of sonification. Conditioning procedures were similar to that used for the micro-flotation tests. After conditioning, the suspension was settled for 5 min and the supernatant was collected for measurement. Electro-kinetic tests were conducted using a ZetaPlus zeta potential analyzer manufactured by Brookhaven Instrument Corporation. Three repeated tests were conducted under the same condition and the experimental error measurement indicated a standard deviation value of 2.23%.

2.2.3. X-ray photoelectron spectroscopy (XPS) characterization

XPS characterization was performed to study the surface chemistry changes of the minerals after interacting with the different reagents. Monazite and calcite particles finer than 5 μm were used in the study. The conditioning procedures were similar to that used for the micro-flotation and electrokinetic tests. The samples were dried at room temperature in an oven. The characterization was conducted using a PHI VersaProbe III XPS equipment. Spectra were acquired using a monochromatic Al K-alpha X-ray source (1486.6 eV) at 100 W over 1400 × 100 μm area at 45° angle. The samples were prepared in the