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The effect of jojoba oil on the surface properties of calcite and apatite aiming at their selective flotation

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ABSTRACT

The beneficiation of phosphate ores by froth flotation is the most efficient process used to separate apatite from calcium minerals. However, the similarity of surface properties between apatite and calcite generally leads to non-selective adsorption of reagents, rendering the selective separation of these minerals a problem, demanding a specific approach. The sedimentary phosphate deposit of Itataia, Brazil, studied in this paper, presents a complex mineralogical composition. The bulk flotation of apatite and calcite with anionic collectors in an alkaline medium followed by selective flotation of calcite at pH 5.5 using phosphoric acid or citric acid as depressant has been suggested for this ore. In the present work, contact angle measurements were performed to evaluate the behavior of jojoba oil as an alternative collector for the selective separation of apatite and calcite minerals. Jojoba oil is composed mainly of gondoic, erucic and oleic acids. The hydrophobicity studies were undertaken using a computer controlled contact angle goniometer. Additionally, the collector adsorption was evaluated through electrophoretic mobility and FTIR measurements. The results indicated that a high selectivity between calcite and apatite can be obtained by using jojoba oil as a collector at slightly acid medium, without the use of depressants. The most interesting results were achieved with a jojoba oil concentration of 200 $mg \cdot L^{-1}$ at pH 6.5, where the apatite was fully hydrophilic while calcite showed high hydrophobicity.

1. Introduction

The beneficiation of phosphate ores by froth flotation is the most efficient process used to separate apatite from gangue minerals like calcite, dolomite and quartz. It has been used in half of the world phosphate production (Sis and Chander, 2003). However, the beneficiation of phosphate ores with carbonated gangue still needs to be improved and an appropriate technology is missing in many cases.

The traditional collectors used in direct flotation of apatite from other calcium minerals have low separation efficiency mainly due to the similarity between the physicochemical properties of these minerals (Guimarães et al., 2005). Thus, in the last decades, many studies have been reported aiming at the development of new reagents for the separation of carbonate and phosphate minerals (Abouzeid et al., 2009).

An alternative process that has been applied after bulk flotation of apatite and calcite from different mineral deposits is the reverse flotation in acidic medium using fatty acids as collector and appropriate depressants, the calcite being floated and apatite depressed (Abouzeid et al., 2009; Aquino et al., 1985; Elgillani and Abouzeid, 1993; Johnston and Leja, 1978; Louzada et al., 2010; Mohammadkhani et al., 2011). This route has been proposed with successful results in laboratory and pilot plant scale by Aquino et al. (1985) for the Brazilian Itataia mineral deposit, where the direct flotation was performed in the presence of fatty acids, starch and sodium silicate at pH 10.0. In a just stage, the calcite and apatite are floated and silicate gangue depressed. Subsequently, the reverse flotation was performed at pH 5.5, adjusted with phosphoric acid, for the flotation of calcite and apatite depression.

Studies developed by Louzada et al. (2010) showed that phosphoric acid is actually also a depressant for apatite in the reverse flotation process at pH 5.5, and not only as a pH regulator. The authors presented an important alternative route for this process replacing phosphoric acid by citric acid in the acidic pH range, the results being similar to those obtained with phosphoric acid.

This work aims at investigating the potential application of jojoba oil (*Simmondsia chinensis*) as an alternative reagent in selective separation of Itataia apatite and calcite through contact angle measurements, electrophoretic mobility measurements and infrared analysis.

Jojoba is a shrub with bluish green leaves and fruits with dark brown seeds, naturally found on deserts of northwestern Mexico and southwestern United States. However, the cultivation is becoming increasingly popular in the semiarid regions of many countries, due to the composition of oil extracted from those seeds which has a wide application in lubricants, plasticizers, cosmetics and pharmaceuticals industries (Perillo and Maestri, 2005). The jojoba seeds contain about 50% oil by

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weight, which is more than twice the amount present in soybean and somewhat more than in most oilseed crops (Abu-Arabi et al., 2000).

Jojoba oil has different characteristics compared to other vegetable oils, which contain fatty acids mostly with 16 and 18 carbon atoms. It consists mainly of fatty acids and alcohols with 18, 20, 22 and 24 long-chain monounsaturated carbon atoms (Tobares et al., 2003), which combined originate linear-chain esters with two unsaturations containing 38 to 44 carbon atoms (Bouaid et al., 2007). The main fatty acid is gondoic acid (cis-11-eicosenoic), followed by erucic acid (cis-13-docosenoic) and oleic acid (cis-9-octadecenoic).

2. Experimental

2.1. Sample minerals preparation

The apatite and calcite samples from Itataia deposit used in this study were provided by the Center for Development of Nuclear Technology (CDTN), Brazil. X-ray diffraction showed that apatite is a fluorapatite and chemical analysis of both minerals presented the following results (Table 1).

For the contact angle measurements the samples were randomly selected, embedded in epoxy resin, sanded and then polished with alumina suspension of 1 μm, 0.3 μm and 0.05 μm. To remove stuck particles from the polished surface, the samples were washed with Milli-Q water, placed in an ultrasonic water bath and then dried at room temperature.

For electrophoretic mobility and FTIR measurements, the calcite and apatite samples were ground in a porcelain mortar and then screened to obtain the desired size fraction (−37 μm). The samples for electrophoretic mobility studies were placed in beakers with Milli-Q water for desliming. Then the suspension was agitated for a few minutes and allowed to settle for a predetermined time, calculated according to the settling rate of 10 μm size particle in accordance with Stokes law.

2.2. Reagents

The reagent solutions used in the present work were prepared with purified and deionized water from a Milli-Q apparatus, presenting electric resistivity of 18.2 MΩ·cm and pH 5.9. The pH of the solutions was monitored by an Orion digital pH meter, 710A model. The jojoba oil, supplied by Ferquima, is mainly composed of gondoic acid (69.4%), erucic acid (14.3%) and oleic acid (12.4%). The jojoba oil was saponified in a reflux system and continuous stirring for 2 h at 85 °C. The ethanol and sodium hydroxide used were obtained from Vetec and were all of analytical grade.

2.3. Contact angle measurements

The contact angle measurements were carried out using a Dataphysics Goniometer, OCA 15 Plus model, with a CCD video camera, and an electronic syringe unit. The system was controlled by the software SCA 20. In this study, the captive bubble technique was used, following a procedure similar to that performed by Drelich et al. (1996), where the mineral crystal was placed in a rectangular glass chamber containing the solution and the bubble was placed under the sample. The contact angle results presented in this study always refer to the advancing contact angle.

Table 1
Chemical analysis (wt.%) of apatite and calcite from Itataia deposit.[a, b]

Mineral	CaO	P_2O_5	SiO_2	MgO	Al_2O_3	Fe_2O_3	LOI[a]	Others[b]
Apatite	58.4	29.9	4.4	0.08	1.7	2.5	1.7	1.48
Calcite	55.0	0.03	0.27	0.07	0.10	0.13	43.7	0.75

[a] Loss on Ignition at 1000 °C.
[b] Others: SO_3, K_2O, MnO, SrO, Nb_2O_5, Cl, Na_2O.

To remove any contaminants adsorbed on the mineral surfaces, a cleaning procedure including polishing with a 0.05 μm alumina suspension followed by thorough rinsing with Milli-Q water, and then cleaning in an ultrasonic bath was performed before each experiment.

2.4. Electrophoretic mobility measurements

The zeta potential measurements were undertaken on Rank Brothers Mark II equipment with flat cell, containing a rotating prism system, platinum electrodes and video camera. They were carried out as a function of pH, which was adjusted using diluted HCl and NaOH solutions. However, the use of the phosphoric acid as a pH regulator could be considered for an industrial flotation system. Potassium nitrate (KNO_3) 10^{-3} mol·L^{-1} was used as an indifferent electrolyte. The measurements of the electrophoretic mobility of apatite and calcite minerals were carried out before and after interaction with the collector solution and performed with each mineral separately. For an applied flotation system, the effect of the ions released by calcite on the apatite's zeta potential and vice-versa should be considered (Ofori Amankonah and Somasundaran, 1985; Ofori Amankonah et al., 1985).

The zeta potential values were calculated from the measured electrophoretic mobility using the Smoluchowski equation.

2.5. ATR-FTIR spectroscopy

The infrared spectra were obtained on Perkin Elmer spectrometer, model Spectrum 100, equipped with an Attenuated Total Reflectance (ATR) accessory. The instrument was purged with dry nitrogen for 2 h to remove water vapor and carbon dioxide from the chamber. The spectra were taken at 4 cm^{-1} resolution and represented on the basis of an average of 200 scans.

The experimental procedure used for the detection of adsorbed jojoba oil on the apatite surface was similar to that employed by Rao et al. (1990). Initially 0.5 g of apatite powder was added to 40 mL of 200 mg·L^{-1} jojoba oil solution at different pH values. After 20 h in an orbital shaking the suspension was filtered through a 0.22 μm Millipore filter. The solids were air dried overnight at room temperature. Samples of untreated powder were used as reference.

3. Results and discussion

3.1. Effect of jojoba oil on the hydrophobicity of apatite and calcite

The results of contact angle measurements of apatite and calcite as a function of pH in the presence of 100 mg·L^{-1} of jojoba oil are presented in Fig. 1. The apatite presents zero contact angle in the acid pH range, whereas the calcite presents high contact angle, around 70°, for pH values lower than 5.5. For higher pH values, there was a significant increase of the apatite contact angle, reaching around 60°. Calcite, however, shows a decrease in the contact angle, tending to stabilize around 40°.

The results obtained at a jojoba oil concentration of 300 mg·L^{-1} are presented in Fig. 2. By comparing them with the results shown in Fig. 1, an increase in the hydrophobicity of both apatite and calcite can be observed in a narrow pH range, between 6.0 and 7.0. The contact angle values reached by calcite were a little higher than 70°, and apatite showed a much higher hydrophobicity above pH 6.0, reaching stable contact angles values around 55° at higher pH values.

Based on these results, contact angle measurements were carried out at pH 6.5, varying the jojoba oil concentration (Fig. 3). It can be observed that apatite remains completely hydrophilic ($\theta = 0°$) at a jojoba oil concentration between 50 mg·L^{-1} and 200 mg·L^{-1}. Above this concentration there is an increase in the apatite contact angle, tending to stabilize around 30°.

In the case of calcite, the corresponding increase of the contact angle value, which started at 100 mg·L^{-1}, was from 40° to 72°, followed by