



Flotation chemistry features in bastnaesite flotation with potassium lauryl phosphate



Weiping Liu^{a,b}, Xuming Wang^b, Zhixing Wang^a, J.D. Miller^{b,*}

^a School of Metallurgy and Environment, Central South University, Changsha, Hunan Province 410083, China

^b Department of Metallurgical Engineering, College of Mines and Earth Sciences, University of Utah, Salt Lake City, UT 84112, USA

ARTICLE INFO

Article history:

Received 1 July 2015

Revised 24 September 2015

Accepted 12 October 2015

Available online 26 October 2015

Keywords:

Lauryl phosphate

Bastnaesite

Rare earth

Micro-flotation

ABSTRACT

Bastnaesite is a major mineral resource of importance in the production of rare earth materials. Present flotation practice uses a reagent schedule which typically includes fatty acid or hydroxamic acid as collector. In this research it was found that potassium lauryl phosphate is an appropriate collector for bastnaesite flotation. Results from contact angle and micro-flotation experiments for bastnaesite are reported using potassium lauryl phosphate as collector. Better bastnaesite flotation is achieved at a low level of lauryl phosphate addition when compared to the use of octyl hydroxamate as collector. Initial evaluation suggests that potassium lauryl phosphate should be a promising collector for bastnaesite flotation.

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1. Introduction

The rare earth fluorocarbonate mineral, bastnaesite (Ce,La)FCO₃, is a semi-soluble salt mineral, which minerals are characterized by their ionic bonding and are distinguished from soluble salt minerals by their limited solubility in water. The mineral bastnaesite consists mainly of the cerium subgroup or the lighter rare earths elements (Bulatovic, 2010). Two major deposits of bastnaesite are the Mountain Pass deposit in California, USA, and the Bayan Obo deposit in Mongolia, China (Jordens et al., 2013; Houot et al., 1991).

Industrial flotation of the Mountain Pass ore is practiced with fatty acids as collectors, with soda ash and lignin sulfonate as depressants and with elevated pulp temperatures in order to achieve acceptable selectivity (Pradip, 1981). Phosphoric esters, as well as fatty acids, have been tested as collectors for the Bayan Obo ore (Houot et al., 1991).

The problem with the use of fatty acid collectors is the low level of selectivity in bastnaesite flotation (Fuerstenau and Pradip, 1988). Alkyl hydroxamate, potassium octyl hydroxamate, as well as modified octyl hydroxamic acid (MOHA), are promising collectors, because of the functional group's specificity for rare-earth cations when compared to the hydroxamate's stability with alkaline-earth cations (Fuerstenau and Pradip, 1988; Nagaraj, 1988). In this way, the hydroxamates exhibit a better selectivity

than fatty acids in the flotation of bastnaesite at concentrations $>1 \times 10^{-4}$ M (Fuerstenau and Pradip, 1988; Pradip and Fuerstenau, 1985; Ren et al., 1997). The surface chemistry features of the octyl hydroxamate/bastnaesite system have been researched recently at lower concentrations $\leq 1 \times 10^{-4}$ M (Zhang et al., 2014). However, the application of the hydroxamate collector is limited by its cost. Such selective collectors are generally more expensive to produce than traditional fatty acid collectors; the fatty acid is \$0.70–1.00/lb compared with \$4.00–6.00/lb for hydroxamic acid.

Consequently research efforts are appropriate to identify economic and selective collectors for the flotation of rare earth minerals, especially bastnaesite. In addition to fatty acid and hydroxamic acid, phosphorous-containing anionic collectors for bastnaesite include phosphonate collectors (Zhang and Jian, 1981; Zhang et al., 1982) and phosphate collectors (Chehreh Chelgani et al., 2013; Jordens et al., 2014; Srinivas et al., 2004; Zhou and Luo, 1989, 1990). Some researchers have reported that alkyl phosphates have better performance as collectors for bastnaesite than alkyl phosphonates (Zhou and Luo, 1989, 1990).

However, the fundamental surface chemistry associated with alkyl phosphate adsorption at the bastnaesite surface is still unknown. Therefore, a preliminary evaluation of the surface chemistry features of potassium lauryl phosphate flotation of bastnaesite has been conducted. The results for micro-flotation of bastnaesite with potassium lauryl phosphate and octyl hydroxamic acid are compared. The discussion includes wetting characteristics, surface tension results, micro-flotation results and the results from electrophoretic measurements.

* Corresponding author.

E-mail address: Jan.Miller@utah.edu (J.D. Miller).

2. Materials and methods

2.1. Materials

Cola[®]Fax PME from Colonial Chemical Incorporated Company was purchased as a 30 wt.% solution of potassium lauryl phosphate (C₁₂H₂₆O₄PK), and the price was \$0.98/lb. Research grade octyl hydroxamic acid (CH₃(CH₂)₆CONHOH) of high purity was provided by Cytec and used for micro-flotation experiments.

The bastnaesite sample was from the Zagi Mountains in Pakistan. For contact angle measurements, the bastnaesite surface was polished and cleaned by rinsing with acetone, methanol and copious amounts of de-ionized (DI) water, followed by blow drying with high-purity nitrogen. The samples were then treated with plasma and again dried with high-purity nitrogen gas. Then the contact angle measurements were made. For micro-flotation experiments the bastnaesite was ground with a mortar and pestle. The ground sample was washed, dried and sized. After sizing, the 100 × 200 mesh size class was taken for flotation.

All other glassware was cleaned by rinsing with acetone, methanol and copious amounts of DI water and dried by high-purity nitrogen gas. De-ionized water was obtained from a Milli-Q system (Billerica, MA). The resistivity of the water was above 18 MΩ in all experiments.

2.2. Turbidity and pK_a measurements

In order to assure that no precipitation occurred within the potassium lauryl phosphate solution, the turbidity of aqueous solutions of potassium lauryl phosphate was measured as a function of concentration using a DR/850 Portable Colorimeter (Hach Company). The instrument was adjusted to measure turbidity by using the “program 95” of the instrument. The meter was zeroed with 10 ml of de-ionized water (blank) and the turbidity of collector solutions read directly from the instrument. The turbidity of de-ionized water is 0 FAU (Formazin Attenuation Unit). If the turbidity of collector solution is 0 FAU (Formazin Attenuation Unit), the collector solution should be transparent. If precipitation occurs, then the turbidity value will increase. More applications and details of turbidity measurement can be found in the literature (Goncharuk et al., 2009; Onweluzo and Akuagbazie, 2010).

The pK_a was measured by the potentiometric titration method using a pH electrode to monitor the course of titration. The pK_a value was calculated from the change in shape of the titration curve compared with that of a blank titration without lauryl phosphate present. For an excellent introduction to the method for determination of pK_a, interested readers should consult Babić et al. (2007) and Reijenga et al. (2013).

2.3. Contact angle measurements

Contact angles were measured with a Rame-Hart goniometer (Rame-Hart, Succasunna, NJ) using the captive bubble technique. The measurement of an intermediate contact angle was accomplished by the release of an air bubble from the needle tip after formation with a syringe, the bubble was then captured beneath the bastnaesite surface, followed by film rupture and bubble attachment. The equilibrium contact angle was measured for all cases of attachment. For each specific measurement, at least five bubbles were generated and measured at different locations on the surface. The reported values are average values from these measurements. The maximum experimental variation in contact angle was found to be ±1° (Drelich et al., 1996b; Lam et al., 2001, 2002). Readers interested in learning more about the contact angle measurement

technique and the nature of hydrophobic and hydrophilic surfaces should consult Drelich et al. (1996a, 2011).

2.4. Electrophoresis measurements

Zeta potential is the electric potential in the interfacial double layer at the slipping plane and can be affected by pH and solution composition (Schwer and Kenndler, 1991). It is widely used for quantification of the magnitude of the electrical charge. In the present study, bastnaesite samples from the Zagi Mountains, Pakistan were dry ground to −45 μm. Before measurement, bastnaesite suspensions of 0.1% were prepared and centrifuged for 10 min. Zeta potentials of bastnaesite (Zagi Mountain, Pakistan) were measured using a ZetaPALS instrument, Brockhaven Instruments Corporation, measurements from which are based on the doppler effect combined with a phase shift of the reflected light. Bastnaesite particle mobilities were measured at different pH values and then converted to zeta-potentials (ξ) using Smoluchowski's model as follows:

$$U = \frac{\varepsilon \xi}{4\pi\eta} E_{\infty} \quad (1)$$

where U is the particle mobility, E_{∞} is the applied electric field ε and η are the dielectric constant and viscosity of the solvent. Readers interested in learning more about the zeta potential measurement technique should consult reviews by Greenwood (2003) and Hunter (1998).

2.5. Micro-flotation tests

The micro-flotation tests for bastnaesite with lauryl phosphate (Cola[®]Fax PME) and hydroxamic acid as collectors were performed using a 112 ml column cell with a porous sintered glass bottom for gas dispersion and a magnetic stirrer. In each test, the bastnaesite sample (100 × 200 mesh) of 1 g was added to the collector solution and then conditioned for 5 min by magnetic stirring. After that the sample, together with solution, was transferred to the flotation cell. The flotation tests were conducted for 2 min using nitrogen at a flow rate of 50 ml/min. Each micro-flotation test was repeated three times, and the mean value of recovery was reported. Further information about the micro-flotation cell design and procedure can be found in the literature (Ozkan and Yekeler, 2001; Partridge and Smith, 1971).

3. Results

3.1. Turbidity measurements

The turbidity of potassium lauryl phosphate solution as a function of concentration is shown in Fig. 1. It is evident that the collector is soluble at concentrations of less than 1 × 10^{−4} M. Flotation experiments were conducted below this concentration.

3.2. Distribution of species in solution

The acid dissociation constant (pK_a) is a quantitative measure of the strength of an acid in solution. Each acid has a different pK_a, knowledge of which is essential for understanding solution behavior. Further understanding of the acid dissociation constant (pK_a) with respect to solution pH, and its method of determination, can be found in the literature (Reijenga et al., 2013).

Potassium lauryl phosphate (C₁₂H₂₆O₄PK) is a salt comprised of one potassium ion and hydrogen ion, and the acid mono alkyl phosphate (denoted as ROPO₃[−], where R corresponds to C₁₂H₂₅). When C₁₂H₂₆O₄PK is dissolved in pure water, there are two equa-

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