



# Bastnaesite flotation chemistry issues associated with alkyl phosphate collectors



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## ABSTRACT

The hydrophobicity, selectivity, and adsorption state in bastnaesite flotation using alkyl phosphates were examined by contact angle and zeta potential measurements, microflotation and microcalorimetry experiments, as well as density functional theory calculations and molecular dynamics simulations. The contact angle and microflotation results show that bastnaesite flotation with alkyl phosphates (lauryl phosphate and 2-ethylhexyl phosphate) is accomplished at a remarkably lower collector concentration. Selective flotation of bastnaesite from calcite with 2-ethylhexyl phosphate increased the bastnaesite grade from 52% to 95% without sacrificing recovery when compared to lauryl phosphate. As expected, the results from density functional theory calculations, together with the microcalorimetry and molecular dynamics simulation results, suggest that the hydrophobic surface state is due to a chemisorbed monolayer of the alkyl phosphate and that the lower reactivity of 2-ethylhexyl phosphate accounts for higher selectivity when compared to results for lauryl phosphate.

## 1. Introduction

Semisoluble salt minerals, with ionic bonding and limited solubility in water, include bastnaesite ((Ce,La)FCO<sub>3</sub>), which contains mainly the cerium subgroup, and the light rare earth elements (Zhou et al., 2014). Important deposits of bastnaesite include the Mountain Pass deposit in California, USA, and the Bayan Obo deposit in Mongolia, China (Azizi et al., 2016). Gangue minerals in these rare earth deposits include calcite and quartz (Jordens et al., 2014).

Fatty acids and hydroxamates are typically reported as collectors for bastnaesite flotation (Pradip and Fuerstenau, 1985, 1991). In addition to the use of fatty acids and hydroxamic acid (Pradip and Fuerstenau, 1991; Zhang et al., 2014), significant progress in the surface chemistry of phosphate collectors has been made. Compared to normal flotation concentration of  $1 \times 10^{-4}$  M for hydroxamate, excellent flotation of bastnaesite is achieved at a low concentration of  $5 \times 10^{-6}$  M for alkyl phosphate (Liu et al., 2016). The adsorption features of lauryl phosphate on bastnaesite confirmed that lauryl phosphate has stronger hydrophobicity compared to hydroxamate at the same surface collector coverage of 8.3% (Liu et al., 2017a). Lauryl phosphate provided a stronger bastnaesite flotation response when compared to the flotation of selected calcite and quartz gangue minerals. Better selectivity for bastnaesite was achieved using lauryl phosphate when compared with

the selectivity using octyl hydroxamate as collector (Liu et al., 2017b). These results suggest that alkyl phosphate collectors may be useful for more efficient bastnaesite recovery, and thus provide improved technology for RE production from domestic resources.

Our initial evaluation indicated that the branched chain alkyl phosphate, 2-ethylhexyl phosphate, has even better selectivity compared to lauryl phosphate. The effect of the phosphate collector chemical structure on bastnaesite flotation, such as hydrophobicity, selectivity, and collector adsorption states, is the subject of this paper. The intent is to understand the effect of the alkyl phosphate chemical structure on the bastnaesite flotation response, which includes, but is not limited to, the interactions of the branched chain phosphate with bastnaesite, calcite, and quartz. The evaluation is based on contact angle and zeta potential measurements, microflotation and isothermal titration calorimetry experiments, as well as density functional theory calculations and molecular dynamics simulations. Also, a comparison and discussion regarding the use of branched chain phosphate and lauryl phosphate is included. It is expected that the results of this research will enable us to further understand the bastnaesite/calcite/quartz flotation chemistry using alkyl phosphate collectors, with consideration of chemical structure, which includes the hydrophobic surface state, selectivity in flotation, and adsorption phenomena for the design of alkyl phosphate collectors.

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## 2. Materials and methods

### 2.1. Materials

Cola®Fax PME (potassium lauryl phosphate,  $C_{12}H_{26}O_4PK$ ), 2-ethylhexyl phosphate ( $C_8H_{19}O_4P$ ) and octyl hydroxamate ( $CH_3(CH_2)_6CONHOH$ ) were provided by Colonial Chemical Incorporated Company (South Pittsburg, Tennessee, USA), Sigma Aldrich Company (Missouri, USA) and Cytec (Woodland Park, New Jersey, USA), respectively. The bastnaesite (Zagi Mountains, Pakistan), calcite and quartz (University of Utah) were used for contact angle, zeta potential, and flotation experiments. Acetone, methanol, and Di-water were used to clean the Glassware. The Di-water from a Milli-Q system (Billerica, Massachusetts, USA), having a resistivity greater than 18 M $\Omega$ , was used in all experiments. HCl and NaOH were used for pH adjustment. KCl was used as the background electrolyte for electrophoresis measurements.

### 2.2. Contact angle measurements

Captive bubble contact angles were measured by a Rame-Hart goniometer (Rame-Hart, Succasunna, NJ, USA). The average value was reported from five equilibrated captive bubble contact angles at different locations on the mineral surface. The maximum contact angle variation was found to be  $\pm 1^\circ$  (Drelich et al., 1996; Lam et al., 2001; Lam et al., 2002). Detailed procedures are available in previously published papers (Liu et al., 2017b; Shrimali et al., 2017).

### 2.3. Electrophoresis measurements

The bastnaesite, calcite, and quartz samples were dry ground to  $-45\mu m$ , and 0.1% suspensions were prepared with 10 min centrifugation. A Zeta PALS instrument from Brookhaven Instruments Corporation (Holtville, New York, USA) was used, combined with the Doppler Effect and the phase shift of reflected light, to determine electrophoretic mobilities. The particle mobilities were measured as a function of pH and further converted to zeta-potentials ( $\xi$ ) by the Smoluchowski equation, as shown in Eq. (1) (Delgado et al., 2005).

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

$U$ ,  $E_\infty$ ,  $\eta$  and  $\epsilon$  are the particle mobility (m/s), the applied electric field (V/m), the viscosity of the solvent (Pa·s) and the dielectric constant (F/m), respectively. The maximum zeta potential variation was found to be  $\pm 1$  mV. More information about electrophoresis measurements can be found in the literature (Greenwood, 2004; Hunter, 1998; Liu et al., 2017b; Shrimali et al., 2016).

### 2.4. Microflotation tests

The  $100 \times 200$  mesh size class was selected for flotation. A 112 ml column cell with a porous sintered glass bottom and a magnetic stirrer were used for the microflotation experiments. One gram of mineral ( $100 \times 200$  mesh) was conditioned in the collector solution for 5 min, followed by 2 min flotation using 50 ml/min nitrogen gas flow (Shrimali et al., 2018). The average value of recovery from three microflotation tests was reported. Mixed flotation of calcite and bastnaesite was in a mass ratio of 2:1 according to the composition of Mountain Pass ore in California, USA (Pradip, 1981). Detailed information about the microflotation procedures is available in the literature (Ozkan and Yekeler, 2001; Shrimali et al., 2018).

### 2.5. Density functional theory calculations and molecular modeling

The 2-ethylhexyl phosphate and lauryl phosphate molecular

structures and charges were calculated by the Gaussian 09 program (Frisch et al., 2009) using the geometry optimisation model at the HF/6-31G(D) level. The crystal lattice parameters of bastnaesite (Donnay and Donnay, 1953), calcite (Graf, 1961) and quartz (Levien et al., 1980) were from the American Mineralogist Crystal Structure Database. The bastnaesite (100) surface (Zhang et al., 2014), calcite (104) surface (Bovet et al., 2015; Gorr, 1992) and quartz (101) surface (Skelton et al., 2011) were used for molecular dynamics simulation. The visual molecular dynamics (VMD) graphics tool (Humphrey et al., 1996) was used to build the collector on the mineral surfaces. Detailed procedures for the configuration of the collector and mineral were introduced in a previous paper (Liu et al., 2017b). The diffusion coefficient ( $D$ ) was derived using the following equation:

$$D = \frac{1}{6N_a} \lim_{t \rightarrow \infty} \sum_{i=1}^{N_a} \langle [r_i(t) - r_i(0)]^2 \rangle \quad (2)$$

where  $N_a$  is the number of diffusive atoms in the simulation cell,  $r_i(0)$  and  $r_i(t)$  are the mass center positions of the solutes at the initial time and at time  $t$ , respectively.

### 2.6. Microcalorimetry

The heat of adsorption was measured by a TAM III isothermal titration microcalorimeter (TA Instruments, USA) at 25 °C using the heat flow model. The results appear as power peaks as a function of time, and each peak represents the injection of the collector solution. The collector heat of adsorption at the mineral surface was calculated by the subtraction of the dilution heat in the blank experiment from the total heat in the standard experiment, as shown in Fig. 1. A minus 45  $\mu m$  sample of  $0.0062 \pm 0.0005$  g bastnaesite was added to the sample and reference ampoules in the standard experiment. Water (0.7 ml at pH 5.0) was added to the sample and reference ampoules in both the standard and blank experiments after 30 s of sonication. The collector solution at pH 5.0 was put into the titration syringe. A volume of 8.8  $\mu L$  ( $8.8 \times 10^{-9}$  mol), equivalent to 25% pseudo-monolayer coverage, was injected into 0.7 ml of water at pH 5 every 60 min, using the titration syringe. The heat of adsorption corresponding to 50% pseudo-monolayer coverage is reported (McFadzean et al., 2015; McFadzean and O'Connor, 2014; Taguta et al., 2017). Collector dosages were calculated according to the bastnaesite surface area and the cross-sectional area of 19.63 Å<sup>2</sup> for the phosphate headgroup (Liu et al., 2017a).

## 3. Results

Bastnaesite flotation issues, such as hydrophobicity, selectivity, and adsorption state using alkyl phosphates, are examined and discussed, based on the experimental results from contact angle and zeta potential measurements, microflotation and microcalorimetry experiments, as well as density functional theory calculations and molecular dynamics simulations.

### 3.1. Hydrophobicity

Hydrophobicity is the physical property describing the rejection or repulsion of water, and is the fundamental property which accounts for the flotation of mineral particles. In this regard, hydrophobicity of a mineral surface can be determined experimentally by contact angle measurements (sessile drop, captive bubble) (Veerasamuneni et al., 1997). The captive bubble contact angle measurements for bastnaesite, calcite, and quartz are shown in Fig. 2 as a function of pH and 2-ethylhexyl phosphate concentration. It is obvious that 2-ethylhexyl phosphate has better adsorption at an acid pH compared to an alkaline pH for both bastnaesite and calcite. Furthermore, the contact angle of bastnaesite is higher than for calcite at both 2-ethylhexyl phosphate concentrations of  $1 \times 10^{-4}$  M and  $5 \times 10^{-5}$  M, which indicates greater

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