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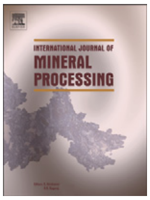

# Surface chemistry aspects of bastnaesite flotation with octyl hydroxamate

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ABSTRACT

Surface chemistry features of bastnaesite were investigated with respect to octyl hydroxamate adsorption and the wetting characteristics at different levels of hydroxamate adsorption. The wetting characteristics of bastnaesite in the absence of collector adsorption were examined using both contact angle measurements and MD simulations. As expected, it was found that bastnaesite is naturally hydrophilic. Surface chemistry studies included octyl hydroxamate adsorption by the solution depletion method. The surface state was described by sum-frequency vibrational spectroscopy (SFVS) and molecular dynamic simulations (MDS). The adsorption isotherm at low levels of hydroxamate adsorption was established and the hydrophobic surface state was described from contact angle measurements. The relationship between hydrophobicity and adsorption density was examined for the first time by MD simulations. The SFVS spectra indicate that a well-ordered monolayer was formed at a hydroxamate concentration of about $1 \times 10^{-4}$ M.

## 1. Introduction

Rare-earth elements are crucial to manufacturing many advanced products and have broad commercial and military applications. They are critical in modern electronic technologies including electronic systems and military applications such as new catalysts for automotive exhaust systems, permanent magnets for computer equipment, hydrogen storage and fueling systems for equipment in confined areas, cellphones, large wind turbines, guided missiles, TVs, fluorescent light bulbs, as well as medical diagnosis equipment and almost all military systems. When the rare-earths are alloyed with other metals, enhanced magnetic properties, strength, use at high temperature and other properties can be achieved. For example, the high-strength magnets widely used in a variety of products including electric motors and hybrid car components are made from a neodymium–iron–boron alloy.

Bastnaesite ((Ce, La) $FCO_3$), a fluorocarbonate, is one of the principle rare-earth semi-soluble salt minerals and consists mainly of the cerium subgroup or the lighter rare earths. Most bastnaesite is cerium–bastnaesite, and cerium (Ce) is the most common rare earth element in bastnaesite minerals. Concentration of bastnaesite is mainly achieved through flotation (Pradip and Fuerstenau, 1991; Yörükoğlu et al., 2003), which of course involves surface chemistry aspects of the mineral/water interface. Thus, the wetting characteristics as well as collector adsorption features are important in understanding the flotation fundamentals as well as the advancement and improvement in flotation technology for efficient recovery.

### 1.1. Wetting characteristics

No references were found on the wetting characteristics of bastnaesite surfaces. Water contact angle measurements at a bastnaesite surface (Zagi Mountain, Pakistan) were made using both the sessile drop and captive bubble methods in current research at the University of Utah. To understand the interaction of a water drop with the bastnaesite surface at the molecular level, molecular dynamics simulation (MDS) was used including the simulation of a water drop at a cerium–bastnaesite surface in the absence of collector.

### 1.2. Collector adsorption

Two major deposits of bastnaesite are the Mountain Pass deposit in the USA and the Bayan Obo deposit in China (Houot et al., 1991). The major gangue minerals for bastnaesite are barite, celestite, and calcite, all of which have similar surface properties. In industrial flotation of the Mountain Pass ore, fatty acids are used as collectors together with soda ash and lignin sulfonate as depressants. Gerdel and Smith (1989) studied the effect of lignin sulfonate on the flotation of bastnaesite from barite and found that the lignin sulfonate has a stronger depressing effect for barite than for bastnaesite. Hydroxamic and phosphonic acids as well as fatty acids have been tested as collectors for the Bayan Obo ore in China (Houot et al., 1991; Li et al., 1989). The problem with

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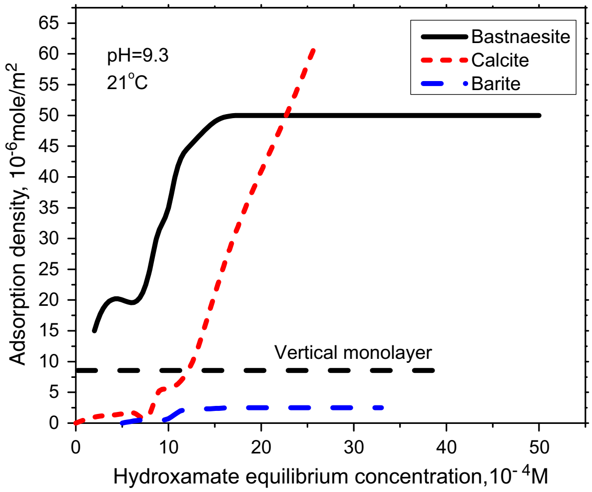

**Fig. 1.** Hydroxamate adsorption isotherms for barite, calcite and bastnaesite at 21 °C and pH 9.3 ± 0.1 (Pradip, 1981).

the use of fatty acid collectors is the low level of selectivity for such separations (Pradip and Fuerstenau, 1989). Hydroxamates, such as alkyl hydroxamate, potassium octyl hydroxamate, as well as modified hydroxamic acids (MOHA), are promising collectors, because of the functional group's specificity for rare-earth cations when compared to alkaline-earth cations. In this way the hydroxamates exhibit better selectivity than fatty acids in the flotation of bastnaesite (Pradip and Fuerstenau, 1985, 1989; Ren et al., 1997).

The stability constants for the complexes formed between hydroxamic acids and metal cations depend on the metal cation position in the periodic table (Fuerstenau and Pradip, 1984). The complexes formed with alkaline earth metal cations, such as $Ca^{2+}$, $Ba^{2+}$, etc., have the weakest strength. While complexes formed with rare-earth elements are much stronger. Thus, hydroxamate collectors have a better selectivity for bastnaesite flotation from gangue minerals, such as calcite and barite (Pradip and Fuerstenau, 1983). It might be expected that hydroxamate adsorption by bastnaesite would involve a surface chelating reaction (chemisorption). It has been suggested that the cations ($La^{3+}$, $Ce^{3+}$) from the mineral surface form hydroxyl complexes in solution, reabsorb at the surface, then interact with the hydroxamate and form stable surface complexes with rare-earth minerals (Pradip and Fuerstenau, 1983). If the monolayer adsorption of hydroxamate collectors at bastnaesite surfaces is an endothermic chemisorption reaction, such as observed for oleate adsorption by fluorite (Lu et al., 1998) then the observation that an increase in temperature tends to increase the selectivity of bastnaesite flotation (Pradip and Fuerstenau, 1985) could be expected. The floatability of rare-earth minerals with hydroxamate collectors is pH dependent and maximum floatability of bastnaesite can be obtained at about pH 9 (Fuerstenau and Pradip, 1984).

Pradip (1981) measured the equilibrium adsorption density of hydroxamate at bastnaesite, barite and calcite surfaces as a function of the equilibrium concentration of hydroxamate (Fig. 1). Assuming the hydroxamate group to have a cross sectional area of 20.5 Å$^2$, the monolayer adsorption density would be $8.1 \times 10^{-6}$ mol/m$^2$. However, when the concentration of hydroxamate is as low as $5 \times 10^{-4}$ M, the adsorption density at the bastnaesite surface already exceeds one monolayer in coverage. The results have been reported for hydroxamate concentration where surface precipitation is expected and suggest that the initial adsorption would involve chemisorption. Besides, the limiting factor for hydroxamate adsorption below monolayer coverage needs to be considered and defined. Then the monolayer adsorption concentration can be determined.

In order to have a better understanding of the fundamental aspects of adsorption at low concentrations of hydroxamate, adsorption density as well as the hydrophobic surface state have been studied. The adsorption density of hydroxamate at low concentrations has been measured and the corresponding hydrophobic surface state is considered utilizing both contact angle measurements as well as MD simulations. The adsorption isotherm at low concentrations of hydroxamate as well as the possible adsorption mechanism is considered and discussed in combination with reported data from the literature. The hydrophobic surface state of bastnaesite at different levels of hydroxamate adsorption below monolayer coverage is studied using contact angle measurements as well as MD simulations and the relationship with adsorption density is established. The behavior of interfacial water molecules at the bastnaesite surface with hydroxamate adsorbed is examined by MD simulations. Conditions for what appears to be the formation of a well-ordered monolayer are defined based on SFVS spectra. It is intended that these results will provide fundamental understanding and further insights with respect to bastnaesite flotation chemistry including, the hydrophobic surface state, the nature of the hydroxamate adsorption reaction, collector dosage for selective flotation, etc.

With results from MDS the surface state can be examined in more detail, to describe not only collector organization, but also hydration phenomena and eventually, the level of hydrophobicity as defined by contact angle measurements.

## 2. Materials and methods

### 2.1. Sample preparation

For adsorption isotherm measurements, bastnaesite samples from Zagi Mountain, Pakistan, were dry ground to −45 μm. Prepared samples were confirmed to be bastnaesite by X-ray diffraction. The surface area of the ground samples was evaluated by the Brunauer–Emmett–Teller (BET) adsorption method utilizing nitrogen gas with a Micromeritics ASAP 2020 analyzer. The surface area was found to be 0.7622 m$^2$/g.

Research grade octyl hydroxamic acid ($CH_3(CH_2)_6CONHOH$) of high purity from Cytec was used to investigate the adsorption density at low concentrations of hydroxamate, the hydrophobic surface state of bastnaesite (contact angle measurements), and to characterize the

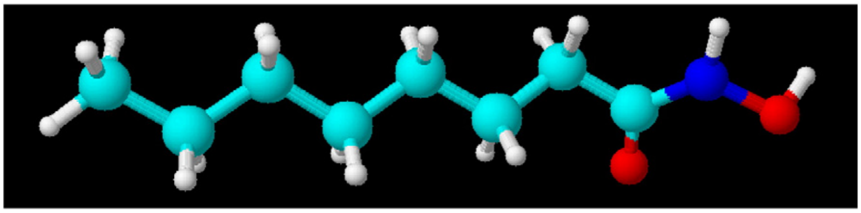

**Fig. 2.** Structure of octyl hydroxamic acid (red: oxygen; blue: nitrogen; light blue: carbon; white: hydrogen).