

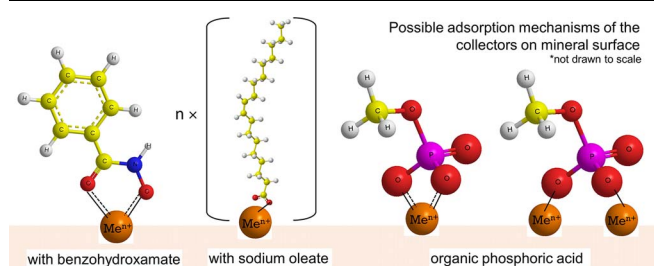
# Surface chemistry and flotation behavior of dolomite, monazite and bastnäsite in the presence of benzohydroxamate, sodium oleate and phosphoric acid ester collectors

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## GRAPHICAL ABSTRACT



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## ABSTRACT

Carboxylates, hydroxamates and organic phosphoric acids are typical collectors used for rare earth mineral flotation. Carboxylates are not selective, while hydroxamates, though selective, require high concentrations to recover a significant amount of rare earth minerals. Other collectors such as organic phosphoric acids, which showed promising rare earth minerals collecting potential, have recently been explored. However, the mechanism of organic phosphoric acid adsorption on the surface of rare earth minerals has not been very well investigated. In this study, zeta potential measurements were conducted to study the surface property of dolomite, monazite and bastnäsite in the presence of benzohydroxamate (hydroxamate), sodium oleate (carboxylate) and Flotisorb 1682 (phosphoric acid ester). These measurements, complemented with ATR-FTIR spectroscopy, evaluated the adsorption of the collectors at the surface of the minerals. The adsorption of the collectors was found to be highly influenced by the mineral cations present at the mineral/solution interface and in the solution. Possible adsorption mechanisms are proposed and discussed; some of which agree with those presented in the literature, while others provided different perspective. Although benzohydroxamate was the most selective, potential flotation processes to recover rare earth minerals using sodium oleate and Flotisorb 1682 were also suggested.

## 1. Introduction

Rare earth (RE) elements are the elements yttrium (Y) and the lanthanides [1], which could be further divided into light and heavy RE elements [2]. Due to their unique chemical properties, RE elements are

useful in high technology applications [3]. The emergence of green technologies requiring RE elements have continue to increase the demand of RE elements [4]. It has been projected that by 2025, there will be a supply shortage of some RE elements, which can only be met with constant development of new mines outside of China [5]. A number of

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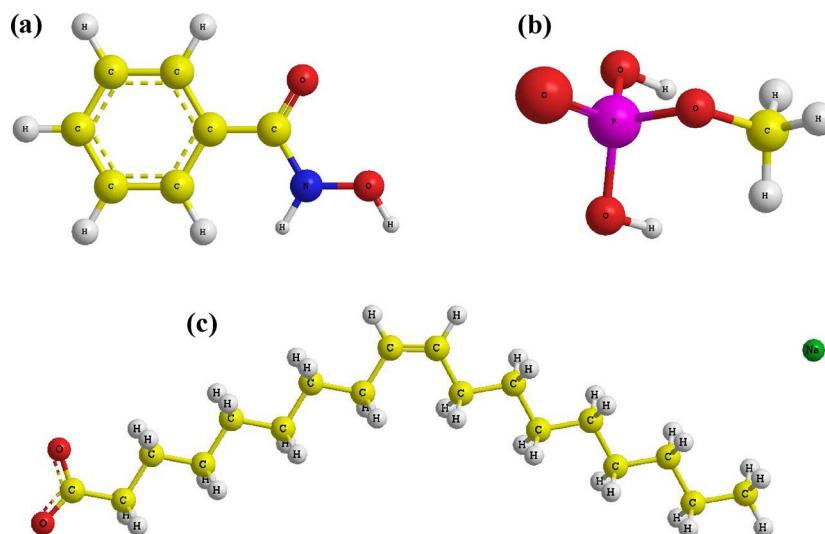


Fig. 1. Collector structure of (a) benzohydroxamate (cis); (b) organic phosphoric acid (not the actual structure of Flotisor 1682); and (c) sodium oleate.

the exploited deposits are located in Canada and among these projects, the Niobec project of Magris Resources Inc. is found to contain the largest resource of RE elements with 1058.6 million tonnes at 1.73% total RE oxide (TREO) [6]. This corresponds to 18.3 million tonnes of TREO, which is almost half of China's RE element reserve (43 million tonnes TREO) [7]. The Niobec RE deposit is adjacent to the existing niobium mine in Quebec and drill sample characterization revealed that the deposit contains bastnäsite and monazite (primary sources of light RE elements [8]), while the gangue is mostly carbonates such as dolomite. Ore characterization also indicated that the deposit has fine RE minerals' liberation size, flotation is thus an applicable method for recovering these RE minerals [9].

Some of the most common collectors for RE minerals are hydroxamates, carboxylates and organic phosphoric acids. In RE mineral flotation, carboxylates, such as fatty acids and sodium oleate, is the most widely used type of collector [10]. However, this type of collector also adsorbs to gangue minerals such as dolomite, making them float as well [11]. The use of carboxylates would thus require dolomite depressants to make flotation efficient [12]. This has led to investigations into more selective collectors, such as hydroxamates. The selectivity of this form of collector is attributed to its formation of more stable chelates with RE metal cations than with alkaline earth cations [13]. Studies on the use of hydroxamates in RE flotation have shown good recovery of bastnäsite and monazite at basic pH conditions [14–16]. However, hydroxamates require large quantities to recover significant amounts of RE minerals [14,16,17]. Another type of collector that has recently been investigated is the organic phosphoric acid. It has been used in the RE flotation at Weishan county in China and showed promising grade and recovery [18]. Recent work also suggests the potential collecting ability of Flotisor 1682 (commercial organic phosphoric acid) at certain pH conditions [16]. The adsorption of carboxylate and hydroxamate on RE minerals has already been studied and possible adsorption mechanisms have already been presented. However, the mechanism of organic phosphoric acid adsorption on the surface of RE minerals has not been investigated in detail.

In this work, the effect of these collectors on the flotation recovery of pure bastnäsite, monazite and dolomite were investigated. Zeta potential measurements and attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy provided insights on the collector adsorption at the surface of the minerals. Possible adsorption mechanisms of the collectors on the mineral surface, as well as possible flotation routes to recover RE minerals are presented.

## 2. Materials and methods

### 2.1. Material

Dolomite from Sterling Hill Mine (New Jersey, USA) was purchased from Boreal Science (Canada). Dolomite is a carbonate mineral with the formula  $\text{CaMg}(\text{CO}_3)_2$ . Monazite, a RE phosphate mineral ( $\text{REPO}_4$ ) from Eureka Farm 99 (Namibia) was purchased from Mineralogical Research Company (USA). Bastnäsite, a RE fluorocarbonate ( $\text{REFCO}_3$ ), was provided by African Rare Earths (Pty.) Ltd. (South Africa). Although the RE minerals contain several RE elements (mostly light RE elements) in their structure such as La, Ce, Nd, etc., the following discussions will consider only Ce to avoid redundancy, as these elements behave similarly.

The potassium chloride that was used as supporting electrolyte was purchased from Sigma-Aldrich (Canada); the hydrochloric acid and the potassium hydroxide that were used as pH modifiers were obtained from Fisher Scientific (Canada).

Benzohydroxamate was obtained from Sigma-Aldrich (Canada); sodium oleate was purchased from Fisher Scientific (Canada); and Flotisor 1682, a commercial organic phosphoric acid collector, was obtained from Clariant (Canada). F150, the frother that was used, was provided by Flottec (Canada). The general structure of these collectors is presented in Fig. 1. Benzohydroxamate is a chelating reagent with a bidentate group,  $\text{HO}-\text{N}-\text{C}=\text{O}$  [44], while sodium oleate has the functional group  $-\text{COO}-$  as seen in Fig. 1. Although the presented structure of the organic phosphoric acid is not the actual structure of Flotisor 1682, the structure presented follows the general organic phosphoric acid,  $\text{ROPO}_3\text{H}_2$  [19], in this case,  $\text{R} = \text{CH}_3$ .

### 2.2. Mineral characterization

The minerals were characterized using an X-ray Diffractometer using Bruker D8 Discovery X-Ray Diffractometer (Cobalt source:  $\text{Co } \alpha$ ,  $\lambda = 1.79 \text{ \AA}$ ) to identify the purity of the samples.

The elemental analysis was conducted using Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES). Samples of 0.1 g were digested at  $95^\circ\text{C}$  for 6 hours using aqua regia and was analyzed using Thermo Scientific 6000 Series Spectrometer (Thermo Fisher Scientific Inc., USA).

### 2.3. Zeta potential measurements

To obtain a particle size smaller than  $10 \mu\text{m}$  for zeta potential

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