



Liquid-liquid mineral separation *via* ionic-liquid complexation of monazite and bastnäsite—An alternate route for rare-earth mineral beneficiation



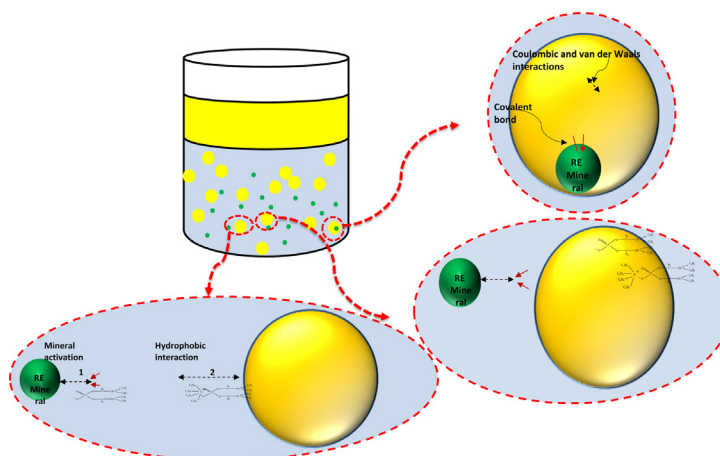
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HIGHLIGHTS

- New beneficiation method of rare earth bearing ore using phosphate/ammonium ionic liquids.
- RE selectivity vs. gangue minerals' followed sequence bastnäsite > monazite > calcite > dolomite.
- Role of ionic liquid in surface complexation and in mineral activation interpreted.
- Minerals recovery rationalized *via* zeta potential, FTIR measurements, and DFT simulations.

GRAPHICAL ABSTRACT



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ABSTRACT

The potential of liquid-liquid mineral separation mediated by ionic liquids (ILs) to beneficiate rare earth (RE) bearing minerals was investigated for the first time. Liquid-liquid separation tests were performed on actual RE-bearing ores whereas the role of ionic liquids was exposed using model monazite, bastnäsite, calcite and dolomite single minerals. The multiphase beneficiation system consisted of aqueous pulps in which IL/kerosene and IL/*n*-hexane non-polar phases were emulsified using three types of phosphonium/ammonium ionic liquids to evaluate their chelation potential. The aqueous pulp pH played a crucial role in terms of mineral recoveries with the highest RE mineral recoveries achieved at pH 4–7. Also, the newly proposed beneficiation method was found to outperform micro-flotation of the same minerals in terms of selectivity. Zeta potential measurements, Fourier transform infrared spectroscopy, and density functional theory simulations were used to interpret the mechanisms governing this new mineral separation route. The ionic liquid anionic moiety was demonstrably found to directly interact through formation of covalent bonds with the metal cation active centers, contrary to the cationic moiety which at most was involved in weaker “non-surface” Coulombic/van de Waals interactions as ion-pair

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co-ion. Hence with regard to the potential of ionic liquids in minerals beneficiation, liquid-liquid mineral separation could be envisaged as a new alternative for RE mineral separation instead of flotation.

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1. Introduction

The lanthanide series designates 15 rare-earth elements (REE) and is augmented to include yttrium and scandium due to similar chemical characteristics [1,2]. These elements are tremendously gazed at by the industry due to their importance in the fabrication of key specialty material components in a variety of cutting-edge technologies such as in magnetics, phosphors, metal alloys and industrial catalysis [3–6]. The natural occurrence of rare-earth elements, while excluding the zero-valent elemental metallic forms, comprises a diversity of mineral forms such as silicates, oxides, carbonates, phosphates and halides [1,2,7]. Among these, bastnäsite ((REE)FCO₃), monazite ((REE)PO₄) and xenotime (YPO₄) are the most important naturally-occurring rare-earth minerals (REM) [2].

In spite of the vagaries which periodically strike the market of rare earth elements, concerns about monopolistic situations and worries of supply shortages heavily weigh on the necessity to keep developing new REE mining projects. Although each project is confronted with its own unique mining and processing challenges [8], REM enrichment almost invariably relies on the same recurrent suite of mineral processing methods such as gravity, magnetic and electrostatic separations. Froth flotation, in particular, undeniably epitomizes one of the plough-horses in the mineral processing industry [1,2]. Challenges confronting the separation of rare-earth ores through flotation comprise the discrepancies inherent to REM ore composition, the highly similar surface properties of REMs as compared with some of the gangue minerals in which they are overwhelmed, and the perennial problems of poor froth flotation in terms of reagent consumption and loss in selectivity due to “non-bubble” entrainments when fine mineral particles are being dealt with [9–11]. Production of large amounts of fines through grinding is particularly critical in REM flotation. While finely ground ore is a necessity for the liberation of REM from its gangue; because of their brittleness, REMs are easily slimed during grinding [12].

To attempt evading these limitations, some researchers have explored alternative REM beneficiation methods such as using reactive oily bubbles [13] or flocculants [12] and even liquid-liquid separation [14,15]. Liquid-liquid mineral separation has been successfully applied in the beneficiation of various minerals, including fine quartz [15–19], fine REMs [15], alumina and zircon [20], casiterite [21], REE fluorescent powders [14,22], scheelite [23], galena [24], pyrite [25], wolframite [26], molybdenite and coal [27]. In spite of its proven effectiveness in mineral processing, studies on this method to beneficiate REMs are still very limited in comparison with those devolved to froth flotation. The method consists of using two immiscible liquid phases, namely, a polar phase such as an aqueous solution and a non-polar phase such as kerosene and *n*-hexane [22]. The minerals in the process are firstly pulped in the aqueous phase and activated by appropriate chelating agents, and then the non-polar organic solvent is added into the system. In this context, the minerals turning oleophilic by the chelating agents naturally migrate into the non-polar phase, whereas the hydrophilic minerals over which surface chelations are denied tend to remain in the aqueous phase [27]. The effectiveness of liquid-liquid mineral separation is highly tributary of the chelating agents being used as these should be enough selective towards the target minerals; often thus, such selection represents the weakest link in this separation method [11,15,28].

Ionic liquids (ILs), on account of the promising results achieved in chemical reaction and metal cation extractions [29–33], especially REE extraction/separation [34–38], mineral flotation [39,40] and REM leaching [41], can be regarded as potent chelating ligands in liquid-liquid mineral separation for REM beneficiation purposes. Bifunctional ionic liquid extractants, or so called Bif-ILEs, such as the phosphonium/ammonium based ones have even been demonstrated to possess advantages over conventional extractants by virtue of their cation and anion moieties being both involved in the extraction process [34]. If hitherto Bif-ILEs disclosed promising liquid-liquid extraction performances for REEs [42–48], extension of these ionic liquids to mineral beneficiation has been only marginally attempted in the open literature. For instance, our group explored the use of hydrophilic phosphonium/ammonium ionic liquids as aqueous collectors for the flotation of bastnäsite and monazite [40]. The investigation revealed that this family of ILs could even outperform traditional collectors or chelating agents from both the collecting power and selectivity point of views.

With regard to the potential of ionic liquids in minerals beneficiation, and alternatively to flotation, a liquid-liquid mineral separation process could be envisaged as a potential alternative for REM beneficiation. To the best of the authors' knowledge, such an inquiry still represents an open question in the literature thus setting down a new opportunity for research. This study is therefore offered as a first step to highlight and gain insights regarding this new variant of REM beneficiation *via* liquid-liquid mineral separation mediated by ionic-liquid complexation. To assess the approach's capability for REM enrichment, it was tested on a realistic ore provide by Niobec inc. (Saguenay, Québec). Model technical-grade single-mineral samples of monazite, bastnäsite, dolomite and calcite were also tested in order to objectify the responses from the single-factor effects stemming from the individual major REM and gangue mineral components contained in the Niobec ore. Three phosphonium/ammonium-based Bif-ILEs and two organic solvents were used in conjunction with aqueous mineral pulps whereby detailed zeta potential and Fourier Transform Infrared (FTIR) spectroscopy determinations, aided with DLVO theory and Density functional theory simulations, were performed under various conditions to expose the most remarkable physico-chemical features that characterize this new RE mineral separation method.

2. Experimental

2.1. Minerals, characterization and preparation

X-ray powder diffraction (XRPD) analyses of representative ore samples received from the rare-earth deposit of Niobec inc. (Magris Resources, Saguenay, Québec) indicate that they contain monazite and bastnäsite (Fig. 1). These REMs are mainly associated with carbonatite gangue minerals such as dolomite and calcite in agreement with other published mineralogical studies [49,50]. Technical-grade single-mineral samples were also acquired for comparative testing, namely, bastnäsite from Molycorp inc. (Mountain Pass Mine, US), and monazite (Itambé, Brazil), calcite and dolomite (from Québec) kindly provided by the Department of Geology (Laval University). Their corresponding X-ray diffractograms are shown in

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