



Selective leaching of rare earth elements from bauxite residue (red mud), using a functionalized hydrophobic ionic liquid



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ABSTRACT

In this study the functionalized ionic liquid betainium bis(trifluoromethylsulfonyl)imide (HbetTF₂N) has been applied directly on leaching bauxite residue, for achieving selective dissolution of rare earth elements (REE) against iron. Several factors have been examined such as leaching temperature, retention time, pulp density and water addition into the ionic liquid. It was found that moderate water addition, elevated temperatures and increased retention time provide up to 70–85% REE extraction yields with respective Fe extraction yield <3%. Sc recovery showed a different leaching behavior from the rest of the REE with its extraction yield not exceeding 45%. Furthermore, no dissolution occurs for Ti and Si whereas 30% maximum extraction of Al was obtained, followed by almost total dissolution of Ca and Na content. This work shows that most REE and a fraction of Sc are associated with Calcium- and Aluminium-bearing phases in the bauxite residue, while the majority of Sc is associated probably with the remaining Fe and Ti-bearing phases. The metals dissolved into hydrophobic ionic liquid can be extracted with an acidic medium while the IL leaching agent is regenerated and after separation can be recycled to a new portion of bauxite residue. Enabling consecutive scrubbing-stripping on the ionic liquid pregnant solution an enhanced acidic Sc solution with reduced level of impurities is obtained.

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1. Introduction

Bauxite residue (BR), also known as red mud, is the major solid waste generated in the process of alumina extraction from bauxite ores. It is estimated that 1 to 2 tons of bauxite residue is generated per ton of alumina produced, leading to a global production of 100 to 150 million tons annually (Klauber et al., 2011). At present bauxite residue is disposed inland, whereas significant research effort takes place for its effective utilization. It's potential as a secondary resource for REEs production, receives escalating attention (Binnemans et al., 2015; Goodenough et al., 2016; Liu and Li, 2015; Petrakova et al., 2014), since REE are essential material for applying greener technology. REE have been labeled as highly critical metals (ERECON, 2015; EU, 2014; US, 2011), in terms of supply risk and energy-economic importance in Europe and USA. Worldwide the total REE production in 2014 estimated to be 110,000 tons, with China being the dominant producer (Gambogi, 2015). Particularly Scandium has great economic value, with principal uses on solid oxide fuel cells (SOFCs), yttrium-scandium garnets for solid state lasers and Al–Sc alloys, with applications in aerospace industry and sports equipment (Ahmad, 2003). REE extraction including Sc from BR has been studied either by direct hydrometallurgical

treatment, or by combined pyro-hydrometallurgical processes (Borra et al., 2016; Liu and Li, 2015). Studies of directly leaching BR with dilute mineral acids such as nitric, hydrochloric and sulfuric acid have been extensively conducted for dissolving selectively REE with further purification/enrichment of the pregnant solution by means of ion exchange or solvent extraction (Borra et al., 2015; Ochsenkühn-Petropoulou et al., 2002; Ochsenkühn-Petropulu et al., 1996; Smirnov and Molchanova, 1997; Wang and Cheng, 2011; Wang et al., 2013). Also sulfurous acid leaching (Fulford et al., 1991), carbonization (Yatsenko and Pyagai, 2010), bioleaching (Qu and Lian, 2013) and the use of highly acidic ionic liquids (Davris et al., 2016) have provide significant results for selective leaching of Sc or REE. Selectivity in leaching, especially against iron is crucial for producing a pregnant liquid solution (PLS) stream from which REE and Sc can be economically extracted with established solvent extraction or ion-exchange technologies. Yet individual REE concentrations in the resulting PLS are in the range of 1–10 mg/L while iron and other ions are in the range of several thousand mg/L (Borra et al., 2015; Ochsenkühn-Petropoulou et al., 2002; Wang et al., 2013).

To achieve selectivity and high metal loading upon leaching, a new treatment is proposed by leaching BR with new versatile solvents called ionic liquids (IL's). IL's are solvents consisting solely of ions. Several IL's have been studied as alternatives in metallurgical processes, providing great potential in mineral processing (Tian et al., 2010). Particularly

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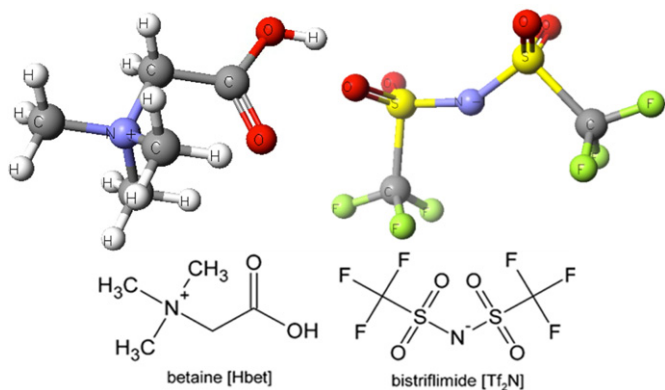


Fig. 1. HbetTf₂N molecular structure.

the use of the functionalized HbetTf₂N ionic liquid and its derivatives was found to provide selective dissolution for a range of synthetic metal oxides against Fe, Si and Al oxides (Nockemann et al., 2008b; Nockemann et al., 2006). HbetTf₂N has a switching thermomorph behavior as upon addition of water is hydrophobic at temperatures below 55 °C whereas above 55 °C forms an aqueous solution. Metals dissolved into HbetTf₂N are extracted in a subsequent stripping step with an acidic solution at ambient temperature regenerating the IL which due to hydrophobicity is separated from the aqueous solution for reuse. This leaching strategy has been studied for phosphor lamps waste powder and neodymium magnets where selective dissolution of the REE against other metals was successfully proven (Dupont and Binnemans, 2015a; Dupont and Binnemans, 2015b).

In this study the objective is to apply HbetTf₂N for achieving selective dissolution of REE against iron which is the most abundant element in BR. REE and base metals recoveries at several conditions are studied and a conceptual flowsheet of BR treatment with this innovative ionic liquid is proposed. Regeneration of the IL with an acidic medium producing an enhanced REE solution for further purification is also addressed through stripping studies as well as further processing of the leaching residue as an iron source.

2. Materials and methods

Betainium bis(trifluoromethylsulfonyl)imide was supplied by Iolitec with >97% purity. Bauxite residue samples were provided by Aluminium of Greece (AoG). Viscosity measurements conducted with a BROOKFIELD viscometer DV-1 + LV supported by a Brookfield Thermosel accessory. Mineralogical characterization was made by a Bruker D8 focus X-ray diffractometer. The particle size measurement conducted with a MALVERN Laser particle size analyzer. Infrared measurements conducted with a Perkin Elmer FTIR spectrum 100. ¹H NMR studies

Table 1
Metal oxides in BR.

Elements	Fe ₂ O ₃	Al ₂ O ₃	CaO	TiO ₂	SiO ₂	Na ₂ O	REO	LOI	Other
%wt	42.68	25.09	9.05	4.98	5.34	1.99	0.14	10.04	0.71

contacted with a Varian V300 MHz spectrometer using DMSO-*d*₆ as a solvent at 25 °C. Wet chemical analysis (fusion with a mixture of Li₂B₄O₇/KNO₃, followed by nitric acid dissolution) was applied to the solids. The metals in the solution were measured using ICP-MS and AAS. Calcium content was determined in solid sample with XRF. Atmospheric leaching experiments conducted in a mini reactor incorporated with temperature controller, mechanical stirrer and a vapor condenser. Pressure leaching conducted in a titanium autoclave reactor. After filtration the elements in the pregnant solution were stripped with HCl. Stripping treatment performed at ambient temperature applying intense stirring for 30 min at various volume ratio and then left to settle and form two separate phases, the IL and the aqueous one. The obtained acidic solution was then properly diluted for chemical analysis. Repeated stripping cycles were applied until metal content measured in the aqueous phase found to be below detection limits <50 µg/L. Total Organic Carbon, Direct TNT Method (20.0 mg/L) was used to measure carbon concentration into aqueous solutions, using a HACH DR/2500 spectrophotometer. By measuring carbon concentration into aqueous solutions IL losses were calculated.

2.1. HbetTf₂N characterization

HbetTf₂N molecular structure can be seen in Fig. 1. Ionic liquid density $\rho = 1531 \text{ kg/m}^3$, MW = 398 g/mol. FTIR (cm⁻¹) 1750 (COOH), 1477 (CH₂), 1418 (SO₂), 1346 (SO₂), 1325 (SO₂), 1176 (CF₃), 1127 (SO₂), 1051 (SO₂), 740 (CF₃). ¹H NMR (300 MHz, DMSO) δ ppm: 4.27 (s, 2H, CH₂), 3.20 (s, 9H, 3 × CH₃). Its viscosity significantly decreases as can be seen in Fig. 2 either by increasing temperature from 350 mPa.s at 50 °C to 8 mPa.s at 170 °C or by addition of water. HbetTf₂N can crystallize in ambient temperature. Although IL is hydrophobic, a small amount of water can be entrapped inside the IL contaminating it. So care should be taken in order not to allow water contamination of the IL during calculation of water addition into IL.

2.2. Bauxite residue characterization

Chemical analysis of BR sample is shown in Table 1.

The total concentration of rare earth elements (as oxides) in red mud found to be 0.14 wt%. The content of each REE is shown in Fig. 3 with its distribution among the total REE. Elements such as Tb, Ho, Tm and Lu found to be below detection limits.

Scandium oxide found to be 0.02 wt% in BR analyzed, a concentration considered to be industrially exploitable (Wang et al., 2011). BR

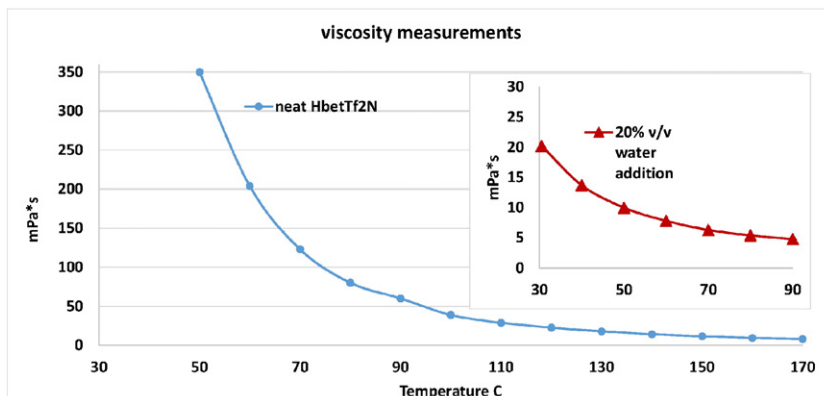


Fig. 2. viscosity measurements of the IL HbetTf₂N versus temperature °C.

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