THE USE OF IONIC LIQUIDS FOR RARE EARTH ELEMENT EXTRACTION FROM BAUXITE RESIDUE

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Abstract

In this paper the results of leaching bauxite residue with two ionic liquids are addressed for selectively extracting rare earth elements against iron. Two groups of interest were studied. The first associates with imidazolium ionic liquids incorporating the hydrogen sulfate anion and the latter with functionalised ionic liquid betainium bistriflimide. During leaching tests various conditions were applied such as temperature pulp density and water content. The imidazolium family showed good selectivity of rare earth elements at temperature range 130-150 °C achieving recoveries up to 40 % for selected rare earths like scandium while iron dissolution remain low between 2-5 %. Yet as temperature exceeds 150 °C large amount of iron dissolves in the ionic liquid inhibiting selectivity. Also from the leaching experiments with betainium bistriflimide the rare earth element recovery range between 20-50 % with negligible dissolution of iron at temperatures 60-90 °C, yet almost total dissolution of calcium and sodium occurs.

Introduction

Bauxite residue is the main metallurgical by-product produced from alumina refineries worldwide. Despite a vast amount of scientific effort for its effective utilisation\(^1\)\(^2\) it still remains a polymetallic matrix that hasn’t been effectively exploited for its valuable metals found within. This study is focused on utilising new versatile solvents called ionic liquids (IL’s) for selectively dissolve valuable metals such as rare earth elements (REE) from the bauxite residue leaving iron, the metal with the highest concentration undissolved. From the literature of metal processing using ionic liquids\(^3\) two types are of interest: The imidazolium IL’s with high acidity incorporating the HSO\(_4\)\(^-\) anion like the 1-ethyl-3methyl-imidazolium hydrogen sulfate (EmimHSO\(_4\)) and the functionalised betainium bistrifluoromethylsulfonylimide (HbetTf2N). Both IL’s are capable on dissolving rare earth oxides and also providing a selectivity against iron oxide thus giving great potential for processing Bauxite residue by selectively leaching REE.
Experimental

Ionic liquid 1-ethyl-3methyl-imidazolium hydrogen sulfate (EmimHSO₄), obtained from Sigma Aldrich with 95 % purity. Betainium bistriflimide (HbetTf2N) with > 97 % purity obtained from iolitec by custom synthesis. Bauxite residue was provided by Aluminium of Greece (AoG). Viscosity measurements contacted with a BROOKFIELD viscometer DV-I+LV supported by a Brookfield Thermosel accessory. Solid characterisation was made by a Bruker D8 focus X-ray diffractometer. The grain size measurement contacted with a MALVERN Laser particle size analyzer. Infrared measurements conducted with a Varian V300MHz spectrometer using DMSO-d₆ as a solvent at 25 °C. Chemical analysis obtained by the fusion method with a mixture of Li₂B₆O₇/KNO₃, followed by nitric acid dissolution. The metals in the solution were measured by ICP-MS and AAS. Calcium was determined with XRF. Leaching experiments conducted in a mini reactor incorporated with a Teflon sensor for temperature controlling, mechanical stirrer and a vapor condenser.

Materials characterisation:

EmimHSO₄: Density ρ=1367 kg/m³, MW=208.24 g/mol. FTIR (cm⁻¹): 3151 (imidazole ring), 3106 (imidazole ring), 1636 (O-H), 1572 (C=C), 1454 (CH₃), 1431 (SO₂), 1389 (CH₃), 1211 (SO₂), 1160 (SO₂), 1089 (HSO₄⁻), 1023 (C-N-C), 960 (O-S-O). ¹H NMR spectrum: (DMSO) δ (ppm) 1.41 s [3H, N-CH₂-CH₃], 3.84 s [3H, N-CH₃], 7.69 d [2H, N-CH-CH-N], 9.13 s [1H, N-C(H)-N]. HbetTf2N: Density ρ=1531Kg/M³, MW=398g/mol. FTIR (cm⁻¹) 1747 (COOH), 1477 (CH₂), 1418 (SO₂), 1346 (SO₂), 1325 (SO₂), 1178 (CF₃), 1129 (SO₂), 1050 (SO₂), 741 (CF₃). ¹H-NMR (300 MHz, DMSO) δ ppm: 4.27 (s, 2H, CH₂), 3.20 (s, 9H, 3 × CH₃). Bauxite residue characterisation has been described elsewhere indicating exploitable amount of Sc oxide.⁴

Results and Discussion

The case of EmimHSO₄:

Ionic liquid EmimHSO₄ was found to dissolve easily 100 g/l of selected rare earth oxides (REO) under elevated temperatures, from a range of 90 to 210 °C and for short times.⁴ Additionally, synthetic iron oxide (Fe₂O₃) dissolution was found to be highly affected by temperature, providing a temperature depended selectivity between REO and Fe₂O₃ along with retention time. Figure 1 provides dissolution comparisons of synthetic oxides of Nd₂O₃ and Fe₂O₃ at elevated temperatures. Nd oxide dissolves rapidly (< 10 minutes) whereas Fe oxide was studied for retention time of 24h. Also it
was found that dissolution of Nd into EmimHSO₄ greatly increases its viscosity due to metal complex formation.

![Comparison of dissolving synthetic Nd₂O₃ and Fe₂O₃ after 24h](image1)

![Viscosity (cP) of EmimHSO₄ + REO 100g/L solution at different temperatures](image2)

**Figure 1:** Dissolution of 100 g/l Nd and Fe oxides versus temperature (left), viscosity comparisons between EmimHSO₄ and EmimHSO₄-Nd solution (right)

Preliminary experiments of leaching bauxite residue with EmimHSO₄ at 190 °C indicated that almost total dissolution of Fe, Ti and 70 % REE occurs while the individual REE showed similar extraction yields.⁴ Therefore in order to study the selectivity of REE against iron and other base elements, different leaching temperatures were applied, and also the effect of water addition was studied (Figure 2). For clarity the results for REE are provided in terms of Sc extraction.

![EmimHSO₄ + Bauxite residue leaching](image3)

![EmimHSO₄ solution + Bauxite residue](image4)

**Figure 2:** Recovery of metals: neat EmimHSO₄, time 4 h, pulp density 2.5 % w/v (left), EmimHSO₄-water solution 2.5 % pulp density w/v, Temp. 80 °C, Time 4 h (right).
Iron dissolution from bauxite residue is very small at low temperatures and as temperature rises there is a significant increase of the iron dissolution from 4 % at 130 °C to 10 % at 150 °C and up to 80 % at 170 °C. On the other hand Sc recovery was moderate at low leaching temperatures at 37-40 % and reached 66 % at 170 °C. Aluminium showed a small increase of its recovery with temperature, while titanium recoveries reached up to 62 % at 170 °C. It is evident that in neat EmimHSO₄ system temperature plays an important role to the selective leaching of REE and Ti over Fe. The extraction yields seems to be in agreement with the results obtained from the synthetic oxides. Upon addition of water selectivity of REEs against iron exist. Particularly Sc extraction found to be between 41-43 % regardless the addition of water and iron extraction remain low at 5-6 %. Issues to deal with the EmimHSO₄ system are handling issues due to high viscosity of the IL which hampers working at higher pulp densities and also for the downstream process, several processes must be taken into consideration for effectively regenerate the hydrophilic IL.

**The case of HbetTf₂N:**

HbetTf₂N is a functionalised hydrophobic IL which is capable of dissolving a wide range of metal oxides including REO yet Fe, Al and Si oxides found to be poorly or not soluble into this IL⁵ Additionally the metals dissolved can be stripped with an acidic solution and the ionic liquid regenerates and separates from the aqueous solution for reuse. Preliminary experiments on leaching Bauxite residue with HbetTf₂N indicate that major effect on REE extraction is the water addition into the IL whereas also higher temperatures increase the metal recovery. Furthermore the IL structure remains intact after regeneration.⁶ In this study different volumes of water have been added ranging from 20 to 60 % into IL whereas different pulp densities ranging from 2.5 % up to 10 % have been used. Experiments conducted for 4h and the results for 40 % addition of water can be seen in Figure 3:

![Figure 3: Recovery of individual REE (left), Recovery of Base metals and Sc (right). Conditions: Temp. 90 °C, Time 4 h, 400 rpm, 40 % v/v water at 2.5-5-10 % pulp.](image-url)
Moderate extraction has been found for REE, low recovery for Fe and total dissolution of Ca and Na observed. Repeated kinetic experiments were conducted at 10 % pulp density and 40 % water v/v addition (Figure 4).

**Figure 4**: kinetic leaching for recovery of individual REE, Conditions: Temp. 90 °C, 400 rpm, 40 % v/v water at 10 % pulp.

The subsequent stripping step of the metals dissolved after leaching is a crucial step for a metal stepwise extraction in order to produce a more concentrated REE stream and recycle the IL back to the leaching process (Figure 5). The concentration of metals in the acidic pregnant solution after separating the washings and stripping with 1:1 and 1:2 volume ratio of 4M HCl: HbetTf2N can be seen in Table 1:

**Figure 5**: stripping of the dissolved metals from HbetTf2N with 4 M HCl. The ionic liquid regenerates and separates from the aqueous solution due to hydrophobicity.
Table 1: Metal concentrations after stripping with HCl at different volume ratios. Leaching conditions, 90 °C 40 % v/v water, 10 % pulp, 4h, 400 rpm

<table>
<thead>
<tr>
<th>Stripping 4 M HCl:HbetTf2N</th>
<th>Volume ratio:</th>
<th>1:1</th>
<th>1:2</th>
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<tbody>
<tr>
<td>Sc</td>
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</table>

Overall the leaching efficiency of the REE extraction is about 20-50 % whereas the Fe dissolution remain at 2 %. Also the Al dissolution is steady to 18-20 % whereas Ca and Na are totally dissolved. In contrary to the overall metal recoveries observed, the metal with the highest concentration in the final pregnant solution are Al, Ca, Na and Fe.

Conclusions

In this study two ionic liquids were studied. EmimHSO₄ showed a temperature depended selectivity between REE and Fe. As temperature rises to 170 °C the Sc recovery reach up to 70 % but with large Fe, Ti dissolution. At 130 °C Sc yields are 35 % and Fe about 5 %.

HbetTf2N provide also selectivity 20-50 % REE and 2 % Fe but has greater potential due to the stripping step and its recycling back to the leaching process. Adjusting the volume ratio of the acid in the stripping step generates a more concentrated REE
stream, enhancing a subsequent purification step with known methods such as solvent extraction or ion exchange.

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References
