Ionometallurgical Leaching Process of Bauxite Residue: a Comparison between Hydrophilic and Hydrophobic Ionic Liquids

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Abstract

Bauxite residue (BR) is the solid waste generated from the Bayer process during alumina production from bauxite ore. It can be considered a secondary source of several base metals, but also critical metals such as rare earth elements (REEs). Hydrometallurgical methods have been mainly employed to extract REEs from BR. As an alternative to conventional mineral acid leaching, ionic liquids (ILs) could hold the key for developing an economical, sustainable and greener processing of low-grade REE resources. ILs are solvents consisting solely of ions and have been studied as leaching agents in metallurgical processes, hence the term ionometallurgy was coined. This paper aims to exploit two ionometallurgical approaches on treating BR, evaluating advantages and drawbacks of applying hydrophilic and hydrophobic ILs. The first leaching process involves a hydrophilic IL, $[\mathrm{Emim}][\mathrm{HSO_4}]$, which can dissolve base metals and REEs at elevated temperatures resulting to high recovery yields of scandium (up to 75 %), iron (100 %) and titanium (90 %), whereas the hydrophobic IL leaching process using $[\mathrm{Hbet}][\mathrm{Tf_2N}]$ is able to selectively dissolve REEs (up to 70 - 85 %) against iron (3 %). The findings of the studied processes provide great potential for exploiting ILs as lixiviants on low-grade REE-containing metallurgical by-products.

Keywords: Bauxite residue, rare earth elements, scandium, ionometallurgy, ionic liquids.

1. Introduction

Bauxite residue (BR) is the major by-product of the alkali leaching of bauxite, through the Bayer process, for alumina production; for each tonne of alumina, 1 – 1.5 tonnes of BR is generated [1]. It is estimated that worldwide BR production is over 150 million tonnes per year [2]. Since it consists of base metals like iron (Fe), aluminium (Al), sodium (Na), silicon (Si), calcium (Ca) and titanium (Ti) but also critical metals such as REEs, BR can be considered a valuable secondary raw material resource.

During the Bayer process, REEs along with Fe, Ti and other undissolved material remain unchanged. As a result rare earths end up in BR with an enrichment factor of approximately 2 comparing to the initial ore [3]. Therefore, the aluminum industry through the Bayer process concentrates the critical metals found in bauxite into bauxite residue.

This fact has led to escalating research with regards to recover minor elements from metallurgical wastes. Rare earth elements have been highly rated in criticality lists [4] due to their high economic value and supply risk. The main approaches on extracting REEs from BR are by hydrometallurgical or by combined pyro-hydrometallurgical processes [5]. Despite the many studies, patents and pilots scale implementations based on BR leaching for REE and particularly scandium [6], none of them yet has reach an industrial scale. Nowadays the impact of the zero-waste valorisation policy motivates the research community on finding innovative, greener and economical viable routes for metal extraction from complex polymetallic matrixes such as BR.

An innovative approach as alternative to conventional mineral acid leaching that can have significant impact to waste valorisation is ionometallurgical leaching. Ionometallurgy is the term that describes the use of ionic liquids as solvents in the field of metal processing. ILs, are room temperature molten salts, constituted by ions, generally an organic cation and an inorganic/organic anion. These solvents have superior properties against organic solvents such as negligible vapour pressure, low volatility, wide electrochemical window, non-flammability and high thermal stability. From the vast number of combinations of the cation and anion during synthesis, ILs properties can be tuned for the needs of the application rendering them as designer solvents. As such ILs have a wide range of application in extractive metallurgy since they can be used either as electrolytes for electrodeposition of reactive metals, as solvents for liquid-liquid metal extraction or separation as well as lixiviants. Several ILs have been studied as leaching agents in hydrometallurgical processes [7-9]. The driving force of applying ionometallurgical leaching on low grade secondary resources is the prospect of increasing selectivity, reduction of waste effluent and improved efficiency yields.

This work aims to compare two ionometallurgical approaches on recovering metals by directly leaching BR. By evaluating advantages and drawbacks of applying hydrophilic and hydrophobic ILs as leaching agents, different leaching strategies can be developed. The acidic ILs studied for direct leaching BR, are the water miscible ethyl-methyl-imidazolium hydrogen sulphate (EmimHSO$_4$), and the hydrophobic betainium bis(trifluoromethylsulfonyl)imide (HBetTf$_2$N). The results of this work indicate the different leaching behaviour of metals in Greek BR for each lixiviant tested, as well as the strategies on BR utilisation that each IL promotes with respect to base and critical metal recovery.

2. Materials and Methods

Bauxite residue samples were provided by Aluminium of Greece (AoG). Samples were characterised via fusion method (1000 °C for 1 hour with a mixture of $Li_2B_4O_7/KNO_3$ followed by direct dissolution in 6.5 % HNO_3 solution). Chemical analysis was performed by Atomic Absorption Spectroscopy (AAS), Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-OES) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS). Mineralogical analysis was carried out by a Bruker D8 focus X-ray diffractometer and a quantitative analysis was performed using XDB software [10]. Particle size measurements were conducted with a Malvern Mastersizer TM laser particle size analyser. [Emim][HSO$_4$] and [Hbet][Tf$_2$N]) ionic liquids were provided by Iolitec with > 97 % purity and further characterised. Viscosity measurements were performed with a Brookfield viscometer DV-I + LV supported by a Brookfield Thermosel accessory. Infrared measurements were carried out by a Perkin Elmer FTIR spectrum 100.

Leaching experiments were conducted in a Trallero and Schlee mini reactor combined with a mechanical stirrer and a temperature controller. After filtration, the leachates from [Emim][HSO$_4$] were digested through acidic treatment (HNO_3 65 % and aqua regia) and then analysed by AAS, ICP-OES and ICP-MS. Leachates from the hydrophobic [Hbet][Tf$_2$N] were stripped with HCl where, subsequently after phase separation, the collected acidic solution was analysed for its metal content by AAS and ICP-MS.

2.1. Bauxite Residue Characterisation

Chemical analysis of the BR sample is shown in Table 1.

Table 1. Bauxite residue chemical analysis.

	Fe_2O_3	Al_2O_3	SiO_2	TiO_2	CaO	Na_2O	REO	LOI	Others
wt.%	42.34	16.25	6.97	4.27	11.64	3.83	0.19	12.66	0.06

The content of REEs in BR is shown in Table 2. It is seen that the total amount of REEs as oxides (REOs) constitute the 0.19 wt.% of BR.

Table 2. REEs content in Greek BR.

	Sc	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Dy	Er	Yb
mg/kg	134	115	156	483	32	125	25	5	22	24	14	14

The distribution of these elements in BR (Figure 1) reveals that cerium (Ce) is the most abundant element (42 %), while scandium (Sc) is 12 % of the total REEs content.

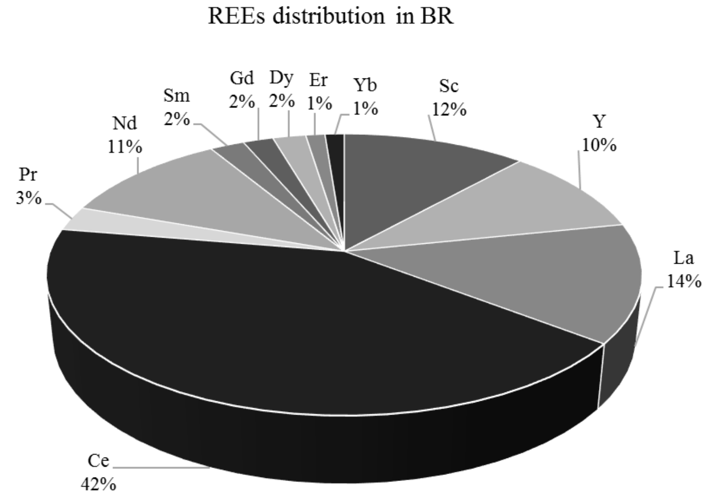

Figure 1. REEs distribution in percentages in BR [11].

Although this value is low, Sc concentration is 134 ppm, and is much higher than the abundance in the Earth's crust (22 ppm on average) and that means a notable enrichment of Sc in BR. Due to the high market price (Sc_2O_3 - 3200 $/kg, 99.9 % purity) [12], Sc represents 95 % of the economic value of rare earths in bauxite residue [3, 13]. This fact has led to the development of several metallurgical schemes for the complete BR valorisation incorporating the extraction of REEs and especially of Sc (as in the case of Greek BR).

Mineralogical phases identified are hematite (Fe_2O_3), goethite ($Fe_2O_3 \cdot H_2O$), boehmite (AlOOH), diaspore (AlOOH), gibbsite ($Al(OH)_3$), calcite ($CaCO_3$), anatase (TiO_2), rutile (TiO_2), perovskite ($CaTiO_3$), cancrinite [$Na_6Ca_2(AlSiO_4)_6(CO_3)_2$], calcium aluminium iron silicate hydroxide [$Ca_3AlFe(SiO_4)(OH)_8$] [14] . Particle size analysis of the sample showed a $D_{0.5}$=1.87 µm.

2.2. [Emim][HSO_4] Characterisation

[Emim][HSO_4] molecular weight is 208.24 g/mol and density (ρ) at room temperature is 1367.9 kg/m^3. The molecular structure of the IL is presented in Figure 2.

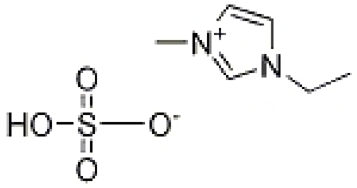

Figure 2. [Emim][HSO_4] molecular structure.

Viscosity measurements, given in Figure 3, reveal that by increasing temperature, viscosity of this IL dramatically decreases.

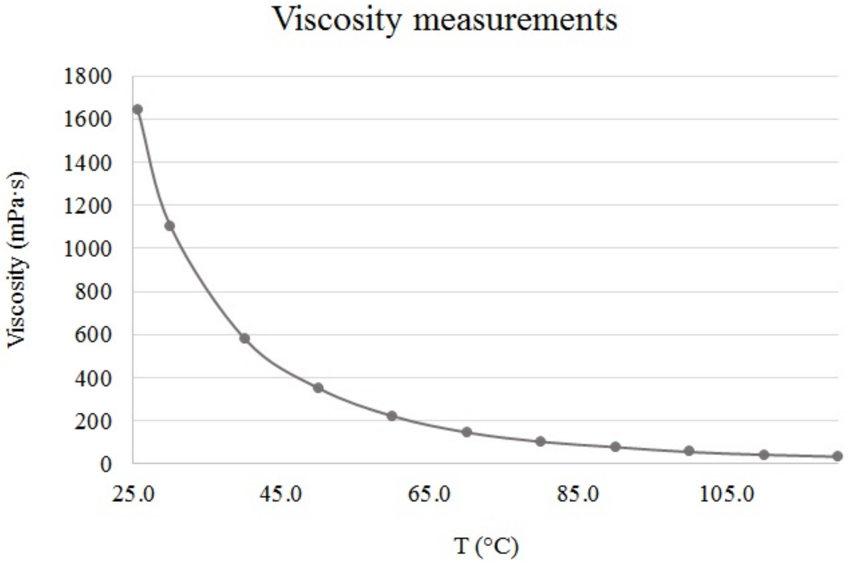

Figure 3. Viscosity measurements of [Emim][HSO_4] versus temperature.

Mid-infrared spectrum have shown bands (cm^{-1}) at 3452 (OH), 3151 (aromatic/imidazole CH), 3106 (imidazole ring), 2985 (CH), 2944 (CH), 2881 (($(CH_2)_n$–CH_3), 2583–2497 (HOSO•••HOSO), 1636 (OH), 1572 (C=C, C=N, C–N), 1454 (CH_3), 1431 ($S=O_2$), 1389 (CH_3), 1211 ($S=O_2$), 1160 (S–O attached to C_2H_5), 1089 (HSO_4^-), 1023 (C–N–C), 960 (O–S–O), 832 (imidazole ring), 757 (CH of imidazole ring) and 701 (C–H–C) [15]. 1H NMR (500 MHz, DMSO) δ ppm: 1.36 (t, 3H, CH_3), 3.85 (s, 3H, CH_3), 4.19 (q, 2H, CH_2), 7.75 (d, 2H, CH=CH), 9.19 (s, 1H, N-CH-N), 9.45 (s, 1H, HSO_4^-).

2.3. [Hbet][Tf_2N] Characterisation

[Hbet][Tf_2N] molecular weight is 398 g/mol, density (ρ) is 1531 kg/m^3. FTIR (cm^{-1}) 1750 (COOH), 1477 (CH_2), 1418 (SO_2), 1346 (SO_2), 1325 (SO_2), 1176 (CF_3), 1127 (SO_2), 1051 (SO_2), 740 (CF_3). ^{1}H NMR (300 MHz, DMSO) δ ppm: 4.27 (s, 2H, CH_2), 3.20 (s, 9H, 3CH_3). Molecular structure is shown in Figure 4.

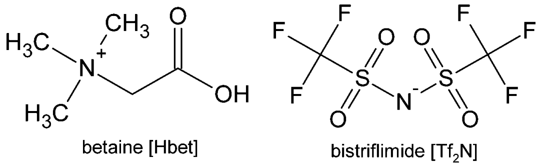

Figure 4. [Hbet][Tf_2N] molecular structure.

Its viscosity significantly decreases either by increasing temperature from 350 mPa·s at 50 °C to 8 mPa·s at 170 °C (Figure 5) or by addition of water. [Hbet][Tf_2N] can crystallise at room temperature. Although IL is hydrophobic, it has a switching thermomorphic behaviour, as at temperature > 55 °C it can form one homogeneous mixture, whereas upon cooling it separates forming two separate phases. Protonated carboxyl functionalized [Hbet][Tf_2N] is able to dissolve metal oxides including REE, whereas Fe, Al and Si metal oxides were found to be insoluble [16, 17]. Water addition to [Hbet][Tf_2N] facilitates dissolution due to H^+ dissociation and viscosity reduction [11] at temperatures > 55 °C where a homogenous solution of [Hbet][Tf_2N] is present.

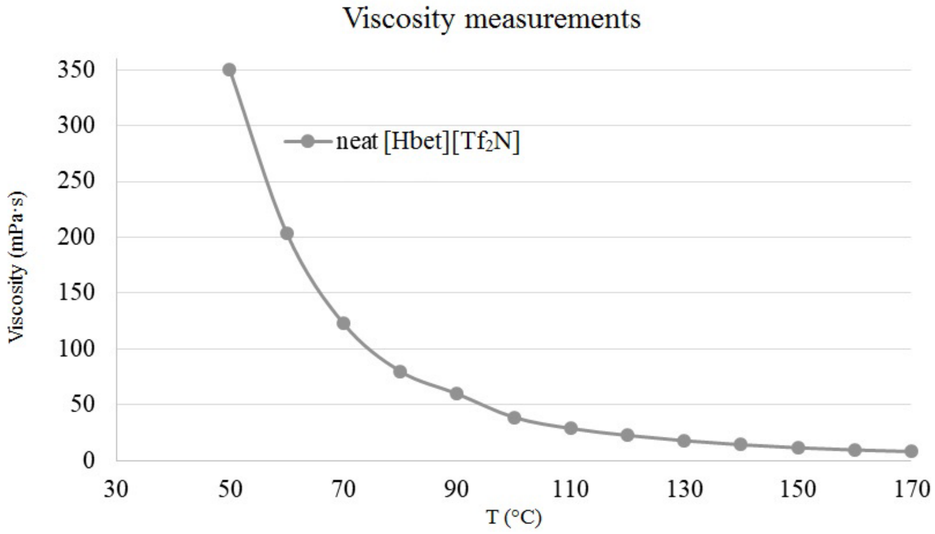

Figure 5. Viscosity measurements of [Hbet][Tf_2N] versus temperature.

3. Results and Discussion

The direct leaching of BR experiments using [Emim][HSO_4] were carried out at 200 rpm, 200 °C, 12 hours retention time and 5 % w/v pulp density were conducted. Results shows (Figure 6) high recovery yields of Sc (78 %), this is due to the fact that it occurs in the same mineralogical phases of Fe (hematite and goethite) and Ti (perovskite) [18].

As shown in Figure 6, Ti recovery is 92 % whilst Fe is almost totally dissolved. Additionally, Al and Na are extracted (about 40 %); Ca is transferred to the pregnant solution, but it is precipitated as anhydrite ($CaSO_4$), while Si extraction is limited to the level of 9 %. Among REEs, neodymium (Nd) reaches 30 % recovery yield whereas lanthanum (La), yttrium (Y) and Ce dissolutions are below 3 %.

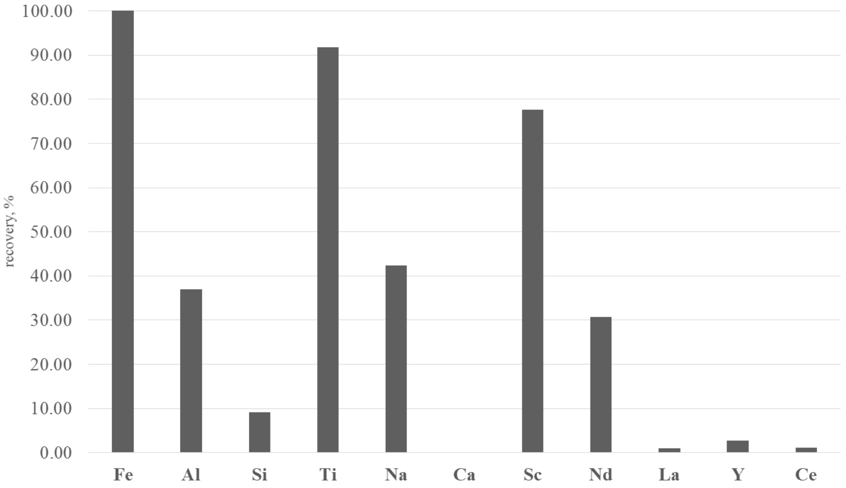

Figure 6. Metal recovery yields after [Emim][HSO_4] leaching of BR at 200 rpm, 200 °C, 12 hours and 5 % w/v pulp density.

Leaching experiments with [Hbet][Tf2N] at 400 rpm, 4 hours retention time and 5 % w/v pulp density at 40 % v/v water addition into IL were carried out at atmospheric (90 °C) and pressure leaching (180 °C) conditions. Metals dissolved into the IL were stripped using an acidic solution whereas the ionic liquid is regenerated for reuse.

This ionic liquid is able to dissolve REEs (Figure 7) in a range of 35 - 52 %, at low temperatures selectively against Fe, Ti and Si whereas Al has moderate recovery with Ca and Na providing high leaching yield. As the temperature rises to 180 °C under autoclaving conditions, there is an increase in REE selectivity reaching at the range of 60 - 80 % with Sc remaining at moderate extraction yields (about 39 %) revealing the different mineral association that Sc has against the other REEs present in BR.

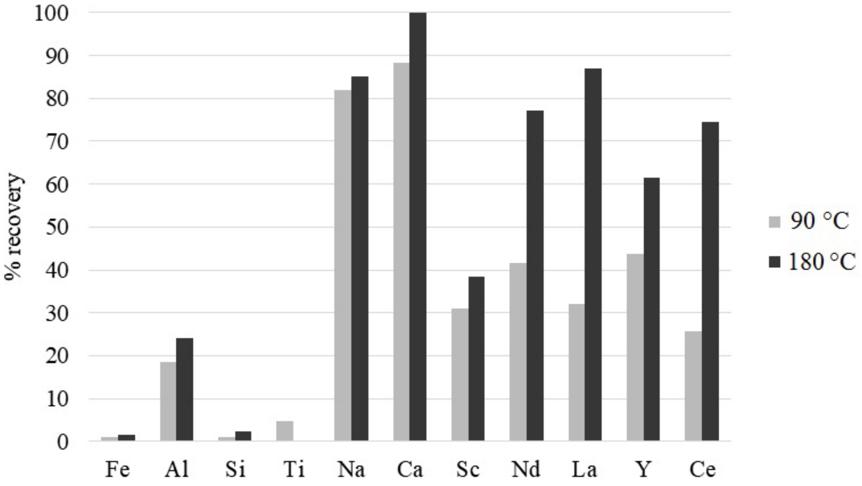

Figure 7. Metal recovery yields after [Hbet][Tf_2N] leaching of BR at 400 rpm, 90 -180 °C, 4 hours, 40 % water addition and 5 % w/v pulp density.

Combining the results obtained, the hydrophilic IL [Emim][HSO_4] is very promising leaching agent for the recovery of Sc (78 %) and also for Ti (92 %). However the main drawbacks of this system are that it is not selective against iron, which is almost totally dissolved and secondly that there are IL losses due to Ca precipitation as anhydrite. On the other hand, [Hbet][Tf_2N] cannot achieve high recovery yields of Sc (39 %), but it is able to leach the rest of the REEs selectively whereas Fe, Si and Ti are poorly leached.

A short overview of the ILs leaching remarks can be shown in the following Table 3.

Table 3. ILs comparisons and remarks.

[Emim][HSO_4] BR leaching	**[Hbet][Tf_2N] BR leaching**
High metal extraction yields in water free system especially Fe, Ti and Sc	High selectivity of REE against Fe, Ti and Si. Water needed to facilitate dissolution
Relatively cheap compared to other ILs	Too expensive
Very viscous at high metal concentrations making the S/L separation a quite demanding process.	Easy regeneration for reuse

4. Conclusions

In this study a comparison between two ionometallurgical processes on treating BR have been presented. The first method concerns a hydrophilic IL, [Emim][HSO_4], whereas the second one involved a hydrophobic IL, [Hbet][Tf_2N].

From the results obtained [Emim][HSO_4] is able to achieve high recovery yields of Sc (78 %) and Ti (92 %) together with base metals (Fe, Al, Na) at elevated temperature (200 °C). Meanwhile, [Hbet][Tf_2N] provides a good selectivity of REEs (up to 70 - 85 %) against Fe, Si and Ti, while Sc has moderate recovery.

Analysing the two approaches, it is possible to conclude that [Hbet][Tf_2N] gives a desirable selectivity of REEs without reaching high recovery of Sc. On the other hand, [Emim][HSO_4] is a good lixiviant for Sc and Ti but it is not selective towards Fe. Furthermore it should be noted that [Emim][HSO_4] is cheaper as a reagent to hydrophobic IL. That is mostly due to the fluorinated anion of the [Hbet][Tf_2N] structure to obtain its hydrophobicity. From this analysis it is evident that an acidic hydrophobic ionic liquid that can be produced with better cost efficiency can have even greater potential for its up scaling on treating low grade secondary critical metal resources.

This study emphasises ionometallurgical approaches as an alternative to conventional hydrometallurgy, showing a considerable capability for exploiting ILs as lixiviant in metallurgical processes. ILs can be considered an eco-friendly replacement for volatile organic solvents and mineral acids supporting an economical, sustainable and greener processing of low-grade REE resources.

5. Acknowledgements

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