

## LEACHING OF RARE EARTHS FROM BAUXITE RESIDUES USING IMIDAZOLIUM BASED IONIC LIQUIDS.

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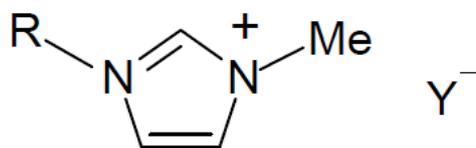
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### Abstract

*Ionic liquids are versatile solvents that can be used as alternatives in the field of hydrometallurgy. At this study, a brief review of ionic liquids utilization in metal oxides and mineral leaching will be addressed followed by investigations for direct leaching of rare earth metals from synthetic REE oxides and metallurgical by-products. In particular, leaching of pure oxides of Lanthanum, Neodymium, Dysprosium and Yttrium and also Bauxite Residues (a solid residue generated from Bayer process in the primary aluminum industry), is investigated with pure Ionic liquid 1-ethyl-3-methylimidazolium hydrogen sulfate (EmimHSO<sub>4</sub>/C<sub>2</sub>mimHSO<sub>4</sub>). Synthetic rare earth oxides totally dissolve in neat ionic liquid and high recoveries of rare earths and base metals were observed from bauxite residues.*

### Introduction

Ionic liquids (ILs) are ionic pairs which are liquid at ambient or low temperatures. Their properties include non-flammability, low vapor pressure, thermal stability, high conductivity and wide electrochemical window. Ionic liquids have been identified as alternatives to conventional solvents and are capable of enhancing the yield and selectivity of reactions<sup>[1]</sup>. Furthermore ILs are nonvolatile solvents in contrast with organic solvents and thus are safer to use in above ambient temperatures. They consist of an organic cation and an inorganic anion of different sizes (Fig. 1).



**Figure 5** Chemical structure of 1-alkyl-3-methyl-imidazolium ionic liquid

Their properties play an important role as solvents for a number of applications like catalytic reactions<sup>[2-3]</sup> separation process<sup>[4-5]</sup> and electrochemistry<sup>[6]</sup>. IL's can be used as design solvents or the so-called task specific ionic liquids, due to their ability to adjust their physicochemical properties in a variety of applications. Thus hydrophobic or hydrophilic behavior can be monitored with modifying the number or the length of alkyl chains in the cation<sup>[4]</sup> and also their miscibility with water by using different

anions <sup>[2]</sup>. Second generation ionic liquids that consist of 1-ethyl/butyl-3-methyl-imidazolium cations with discrete inorganic anions are growing in interest for exploitation in mineral processing.

In this paper a review of the use of ionic liquids in mineral processing will be addressed and also the study of applying ionic liquid 1-ethyl-3-methyl-imidazolium hydrogen sulfate (EmimHSO<sub>4</sub>) as leaching medium for rare earth oxides will be presented.

### **Dissolution of metal oxides using ionic liquids**

The first reported studies of leaching metal oxides in ionic liquids concerned the dissolution of UO<sub>3</sub> and V<sub>2</sub>O<sub>5</sub> in imidazolium chloroaluminate melt <sup>[7-8]</sup>. The solubility of UO<sub>3</sub> was found to be 1.5-2.5 10<sup>-2</sup> mol/dm<sup>3</sup> and the main species in solution was [UO<sub>2</sub>Cl<sub>4</sub>]<sup>2-</sup>. Vanadium oxide was found to be very soluble in the basic melt, 0.15 g in 1 g, but also soluble in the neutral melt. Task specific ionic liquids are ionic liquids designed for specific purposes such as betaine bis(trifluoromethylsulfonyl)imide<sup>[9]</sup>(HbetTf<sub>2</sub>N), which have been used for the dissolution of the rare earth oxides; imidazolium, pyridinium, pyrrolidinium, piperidinium, morpholinium, and quaternary ammonium bis(trifluoromethylsulfonyl)imide salts were also functionalized with a carboxyl group for the selective dissolution of metal oxides and hydroxides <sup>[10]</sup>. Oxides such as rare earth oxides, UO<sub>3</sub>, PbO, ZnO, CdO, HgO, CuO, Ag<sub>2</sub>O, NiO, PdO as well as several hydroxides were soluble in these ionic liquids whereas Co oxides, Cr<sub>2</sub>O<sub>3</sub>, FeO, Fe<sub>3</sub>O<sub>4</sub> found to be insoluble in the same experimental conditions.

Deep eutectic solvents of choline chloride mixtures with hydrogen bond donors such as carboxylic acids, amines and alcohols have been studied for dissolving metal oxides <sup>[11-15]</sup>. The solubilities of ZnO, CuO, and Fe<sub>3</sub>O<sub>4</sub> have been determined in 3 deep eutectic solvents between choline chloride and carboxylic acids at 50°C <sup>[12]</sup>. Fe<sub>3</sub>O<sub>4</sub> is more soluble in oxalic acid/ChCl system whereas 20 times less soluble in phenylpropionic acid mixture while CuO showed the opposite behavior, suggesting that deep eutectic solvents can be applied for selectively leaching of metals. In addition the solubility of 17 common metal oxides have been determined in ionic liquids of choline chloride mixtures with urea, malonic acid, and ethylene glycol <sup>[13]</sup>. At present the behavior of rare earth oxides in such deep eutectic solvents have not been studied.

The dissolution of Ca, Ni, Mn, Co, Cu, and Zn oxides in hydrophobic ionic liquid trihexyl (tetradecyl) phosphonium chloride (Cyphos IL 101) saturated with a concentrated aqueous hydrochloric acid solution have been also investigated <sup>[16]</sup>. Here the IL works as in solvent extraction, as the dissolved oxides can be in subsequent step recovered in an aqueous phase through selective stripping.

A summary of ionic liquids reported for metal oxide dissolution is shown table 1.

**Table 4** Dissolving metal oxides in ionic liquids

Ionic liquid/leaching agent	Metal oxides studied	Reference
EmimCl/AlCl <sub>3</sub>	Uranium- Vanadium	7,8
DMPIC/AlCl <sub>3</sub>		
HbetTf <sub>2</sub> N, [C <sub>6</sub> Hbet]Tf <sub>2</sub> N, [C <sub>4</sub> Hbet]Tf <sub>2</sub> N, [HbetIm]Tf <sub>2</sub> N, [HbetPy]Tf <sub>2</sub> N, [EtHbetmMor]Tf <sub>2</sub> N, [HbetmMor]Tf <sub>2</sub> N, [HbetmPip]Tf <sub>2</sub> N, ([HbetmPyr]-Tf <sub>2</sub> N),	Sc, Y, La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, U, Pb, Zn, Cd, Hg, Cu, Ag, Ni, Pd, Mn, Co, Cr, Fe, Al and Si	9,10
[Deep eutectic solvents] Choline chloride/urea /ethylene glycol/malonic acid	Ti, V, Cr, Mn, Fe, Co, Al, Si, Ca, Cu, Ni, Pb and Zn	13
(Cyphos IL 101- saturated with concentrated hydrochloric acid	Ca, Ni, Mn, Co, Cu, and Zn	16
Emim(X-), X= (Cl-), (SCN-), (DCA-), (OAc-), (Tf <sub>2</sub> N-)	Ag, Cu, Ni and Zn	17

### Ore and wastes processing with ionic liquids

Few studies have dealt also with processing ores and wastes with ILs for leaching valuable metal oxides.

**Electric arc furnace dust:** Choline chloride with urea has been applied for processing electric arc furnace dust <sup>[14], [15]</sup>. EAF dust consist mainly of metal oxides. Urea mixture had been chosen due to the low solubility of iron oxide towards high solubility of ZnO and CuO in it. Leaching of EAF with 2:1 molar ratio ChCl/urea conducted at 60°C for 48h. ZnO, Cu<sub>2</sub>O and PbO can be selectively leached and subsequently recovered from the liquid through cathodic electro-deposition. A pilot plant with a capacity of 5kg dust batches has already been built.

**Brass ash:** BmimHSO<sub>4</sub> has been investigated for leaching of industrial brass ash in order to recover copper and zinc. Parameters such as dissolution time, IL concentration and oxidizing agents have been studied <sup>[18]</sup>. 99% dissolution efficiency has been achieved for Zn and 24.82% for Cu after 4h of leaching at 70°C with 50% v/v BmimHSO<sub>4</sub> in water. To increase the extraction ratio of Cu oxidizing agents were added to the leaching solution. With H<sub>2</sub>O<sub>2</sub> addition up to 82% of Cu was leached at 70°C after 5h.

**Sulphidic ores containing gold and silver:** The first reported study of BmimHSO<sub>4</sub> utilization in metal leaching concerned the extraction of Au and Ag from a complex gold bearing ore <sup>[19]</sup>. The leach solution was prepared by dissolving thiourea in BmimHSO<sub>4</sub> in the presence of Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>. Leaching was carried out at 50°C resulting in 85% Au recovery and 60% Ag recovery. The remaining base metals copper, lead, zinc and iron had low extraction yields. Furthermore recycling of BmimHSO<sub>4</sub> has been studied by stripping the leach liquor with activated carbon. Altering IL organic cation while maintaining the HSO<sub>4</sub><sup>-</sup> anion revealed that as the alkyl chain of the alkyl-methylimidazolium hydrogen sulphate increases from butyl to octyl, the extraction of gold

decreases. This may be attributed to the corresponding rise of the viscosity of the IL solution. Except from the cation alteration, different anions have been studied keeping the butyl chain of the cation constant. BmimCl, BmimBF<sub>4</sub>, BmimN(CN)<sub>2</sub> and BmimCH<sub>3</sub>SO<sub>3</sub> were studied for gold extraction. Significant recoveries occur for the BmimCH<sub>3</sub>SO<sub>3</sub> and BmimHSO<sub>4</sub> for gold, silver and base metals. Moderate recoveries occur for BmimBF<sub>4</sub> and low recoveries for BmimN(CN)<sub>2</sub> and BmimCl. These observations suggest that the anion in the ionic liquid plays an active role during the dissolution process. Furthermore leaching of gold and silver was studied in the presence of (peroxomonosulfate HSO<sub>5</sub><sup>-</sup>) or Fe(III) oxidants, and complexing agents such as thiourea, Cl<sup>-</sup>, Br<sup>-</sup> and I<sup>-</sup> using BmimHSO<sub>4</sub> and BmimCl as solvent medium [21]. Over 85% of gold was leached and significant amount of silver recovered in the presence of HSO<sub>5</sub><sup>-</sup>/ thiourea at 25–50 °C in both BmimHSO<sub>4</sub> and BmimCl. HSO<sub>5</sub><sup>-</sup>/ thiourea system had the same leaching efficiency as the Fe(III) thiourea system. Recoveries of gold and silver were significantly higher than in an aqueous medium and negligible recoveries of base metals obtained in ionic liquids.

**Chalcopyrite:** Chalcopyrite leaching was studied with 1:1 water: Bmim(BF<sub>4</sub>) volume ratio in the presence of Fe(BF<sub>4</sub>)<sub>3</sub> [22]. 90% of copper extraction was achieved after 8 h at 100 °C. BmimHSO<sub>4</sub> and its aqueous solution were used for leaching chalcopyrite [23] concentrate in temperature range from 50 to 90°C. Copper extraction increased from 52% to 88% as ionic liquid concentration increased from 10% to 100% at 70°C for 24h. 1-alkyl-3-methyl-imidazolium ionic liquids were studied as solvent medium either in neat or in aqueous mixtures, in the presence of thiourea and iron (III) as an oxidant [20]. Initially the leaching behavior of pure pyrite was studied in pure BmimHSO<sub>4</sub>, leading to poor results. Chalcopyrite ore concentrate behaved differently during its leaching in the same medium. 85% recovery of copper and less than 8% iron dissolution were achieved after leaching of chalcopyrite at 60°C with 20%w/v in water. The metal extraction increases with temperature. Moreover increasing the concentration of BmimHSO<sub>4</sub> also lead to higher extraction yields for copper. In comparison to leaching the same chalcopyrite ore concentrate with an aqueous 1M H<sub>2</sub>SO<sub>4</sub> solution, the abovementioned BmimHSO<sub>4</sub> solution achieves 62% higher Cu leaching efficiency.

A summary of the research works that have studied the use of ionic liquids as solvents in mineral processing can be seen in Table 2.

**Table 5** Ionic liquids in mineral processing

Ionic liquid/leaching agent	Minerals	Target Metals	Reference
[Deep eutectic solvents] Choline chloride:urea	Electric arc furnace dust (oxidic form)	Zn, Cu, Pb	14,15
BmimHSO <sub>4</sub> /H <sub>2</sub> O <sub>2</sub> or potassium peroxymonosulfate	Industrial brass ash (oxidic form)	Zn, Cu	18
BmimHSO <sub>4</sub> /thiourea and Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	sulphidic ores containing Au,Ag	Au, Ag	19
Bmim <sup>+</sup> X <sup>-</sup> , (X <sup>-</sup> = Cl <sup>-</sup> , CH <sub>3</sub> SO <sub>3</sub> <sup>-</sup> , N(CN) <sub>2</sub> <sup>-</sup> , BF <sub>4</sub> <sup>-</sup> , HSO <sub>4</sub> <sup>-</sup> )/thiourea and Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	sulphidic ores containing Au,Ag / pyrite, sphalerite chalcopryrite		20
BmimHSO <sub>4</sub> or BmimCl /peroxomonosulfate (HSO <sub>5</sub> <sup>-</sup> ) or iron (III), and complexing agents thiourea, chloride, bromide and iodine	sulphidic ores containing Au,Ag		21
Fe(BF <sub>4</sub> ) <sub>3</sub> in water:Bmim(BF <sub>4</sub> ) at 1:1	chalcopryrite	Cu	22
BmimHSO <sub>4</sub>			23

### Leaching rare earth oxides using ionic liquids

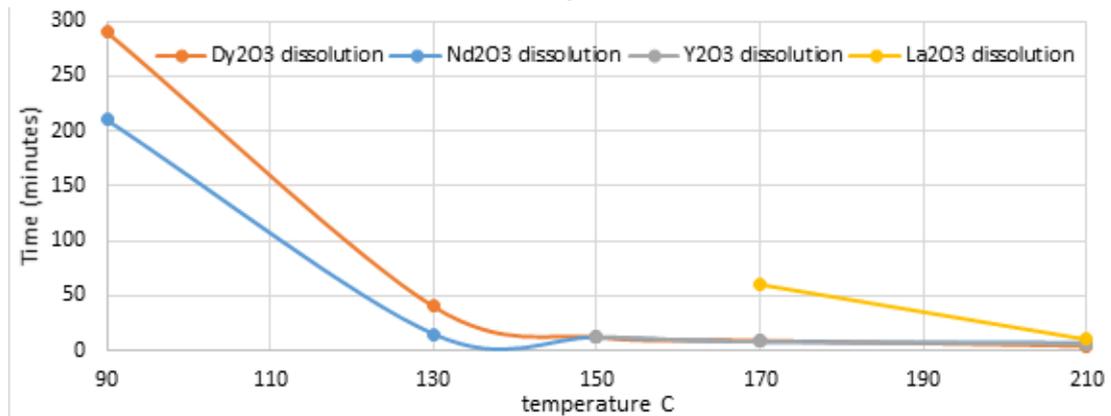
This study will present preliminary results for utilizing ILs in leaching Rare Earth oxides from both synthetic oxides and REE containing metallurgical wastes.

**Synthetic rare earth oxides:** Preliminary experiments investigated the dissolution behavior of synthetic rare earth oxides in neat IL EmimHSO<sub>4</sub>. Ionic liquid EmimHSO<sub>4</sub> with purity 95% was obtained from Sigma Aldrich and was used without any further purification. The oxides studied were yttrium oxide, neodymium oxide, dysprosium oxide and lanthanum oxide which were obtained from Alfa Aesar with 99.9% purity.

The experiments were conducted by introducing 1g of dried rare earth oxide powder into 10ml of pure ionic liquid (10% w/v pulp density). Temperatures were varied from 90 to 210<sup>o</sup> C, where EmimHSO<sub>4</sub> remains stable and liquid. The end point of the leaching experiments was determined by optical observation (fig. 2), at the point where a clear solution was obtained. The hot solution was then filtered using fiber glass filters and the resulting filter paper washed with deionized water. Atomic absorption spectroscopy was used to measure the metal content in the pregnant solution and thus to determine the total dissolution of the REE oxide. The time needed to achieve the complete dissolution of different rare earth oxides under different temperature is shown in figure 3.



**Figure 6** Neodymium (left) and Lanthanum (right) oxide dissolving in neat EmimHSO<sub>4</sub> at elevated temperatures. The solution becomes clear in less than 5 minutes at 210 °C.



**Figure 7** Time needed for total dissolution of 1 g of various rare earth oxides in 10 ml of neat EmimHSO<sub>4</sub> at different temperatures.

At elevated temperature rare earth oxides dissolve in very short times. At lower temperature lanthanum and yttrium oxide didn't dissolve and their solution formed a highly viscous gel-like phase. The trend here shows that dissolution is highly effected with temperature, which can be related to the significant decrease in the viscosity of EmimHSO<sub>4</sub>, shown in table 3, leading to better wettability of the solids and faster dissolution rates.

**Table 6** Viscosity of neat EmimHSO<sub>4</sub> at different temperatures <sup>[24]</sup>.

Temperature	20 °C	100 °C	150 °C	200 °C
Viscosity (mPa*s)	1354	55	13	4

**Bauxite residue (red mud):** Bauxite Residue, also known as red mud, is the major solid waste generated during the primary alumina production with the Bayer process. For each tone of alumina produced, almost 1 tone of residue is generated. This amounts to approximately 120 million tons of bauxite residues that are produced worldwide each year. Significant research effort takes place for the effective utilization of Bauxite Residues <sup>[25-27]</sup>, while it's potential as a source for REE production has also been proposed <sup>[28-30]</sup>.

In the present study bauxite residues provided by ALSA S.A in Greece were used. Chemical analysis of the sample was performed after total dissolution with a fusion method and rare earth elements were measured using inductively coupled plasma mass spectroscopy (ICP-MS) while base metals with atomic absorption spectroscopy (AAS). Calcium and sodium were determined with XRF method. The results are presented in table 4.

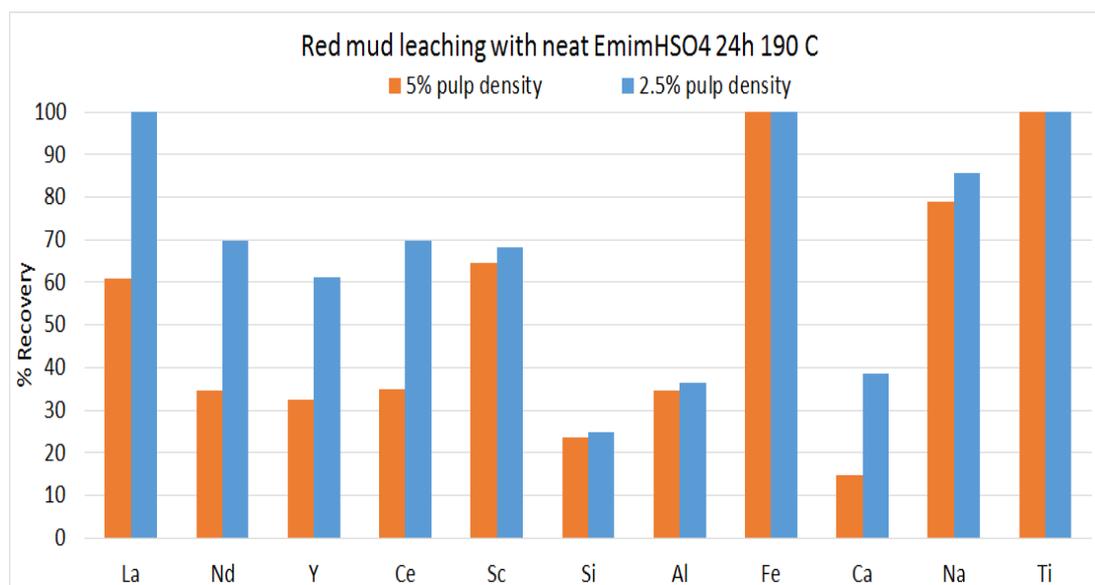
**Table 7** Chemical analysis of ALSA's Bauxite residues sample

<b>Red mud oxides</b>	$Fe_2O_3$	$Al_2O_3$	$CaO$	$TiO_2$	$SiO_2$	$Na_2O$	REO	Loss of ignition
<b>Chemical analysis %wt.</b>	43%	25%	9%	5%	5%	2%	0.14%	10%
<b>Rare earths in Bauxite Residues (mg/Kg)</b>								
<i>Ce</i>	512			<i>Pr</i>	30			
<i>La</i>	193			<i>Sm</i>	26			
<i>Sc</i>	135			<i>Dy</i>	24			
<i>Nd</i>	129			<i>Gd</i>	21			
<i>Y</i>	114			<i>Yb</i>	13			
				<i>Er</i>	13			

Scandium oxide is 0.02% wt. in the red mud analyzed, a concentration considered to be exploitable <sup>[30]</sup>. Overall the REE concentration in the ALSA red mud is in the same levels of concentrations reported in previous studies <sup>[31]</sup>.

Minerals that have been identified by XRD in red mud are mainly hematite [ $Fe_2O_3$ ], gibbsite [ $Al_2O_3 \cdot 3H_2O$ ], diaspore [ $Al_2O_3 \cdot H_2O$ ], cancrinite [ $Na_6Ca_2(Al_6Si_6O_{24})(CO_3)_2$ ], katoite [ $Ca_3Al_2(SiO_4)(OH)_8$ ] and rutile [ $TiO_2$ ]. Measurements on grain size distribution indicate an average grain size of 12  $\mu m$ .

Direct leaching of red mud with  $EmimHSO_4$  at different pulp densities was contacted at elevated temperatures. After 24h of leaching at 190°C, filtration at high temperatures and washing the resulting filter cake with deionized water the filtrate was analyzed in ICP-MS and AAS. Experiments at 5% and 2.5% pulp density (w/v) were carried out. The metal recoveries are shown in figure 4.



**Figure 8** Recovery of rare earths and base metals from red mud after leaching with neat EmimHSO<sub>4</sub> at 190 °C for 24h.

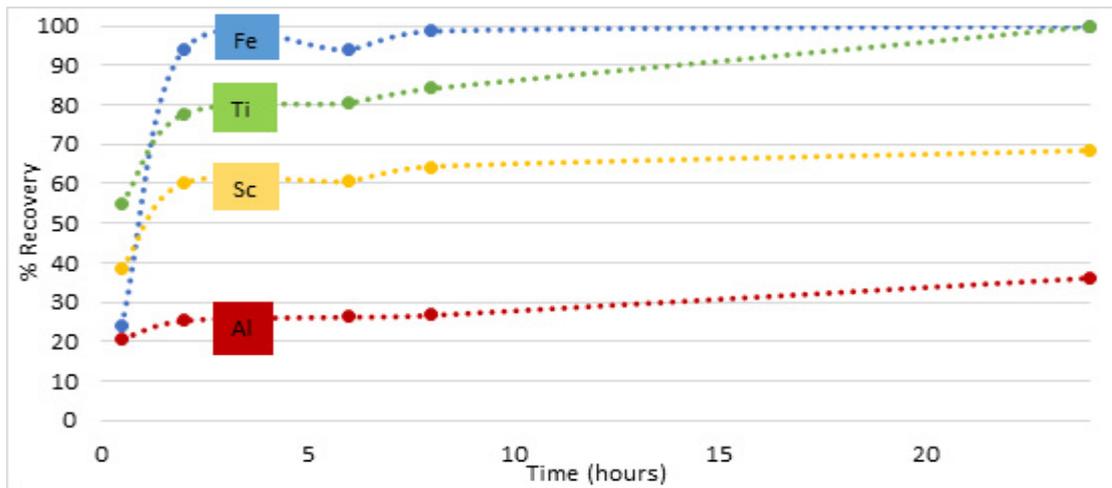
At these leaching conditions almost total dissolution of iron and titanium was observed while the residue consisted mainly of aluminum and silicon. EmimHSO<sub>4</sub> showed no particular leaching selectivity between rare earths and base metals. The average recovery yield of rare earths increased with decreasing pulp density, reaching a 60-70% at the 2.5% pulp density. The resulting concentration of the pregnant leach solution is given in table 5.

**Table 5** Concentration of metals in EmimHSO<sub>4</sub> after leaching bauxite residue (2.5% w/v pulp density at 190°C, 24h).

Elements	% recovery	~mg/L solvent	Elements	% recovery	~mg/L solvent
La	100	5	Al	36	1205
Nd	70	2	Fe	100	7650
Y	61	2	Ca	39	627
Ce	70	9	Na	86	318
Sc	68	2	Ti	100	700

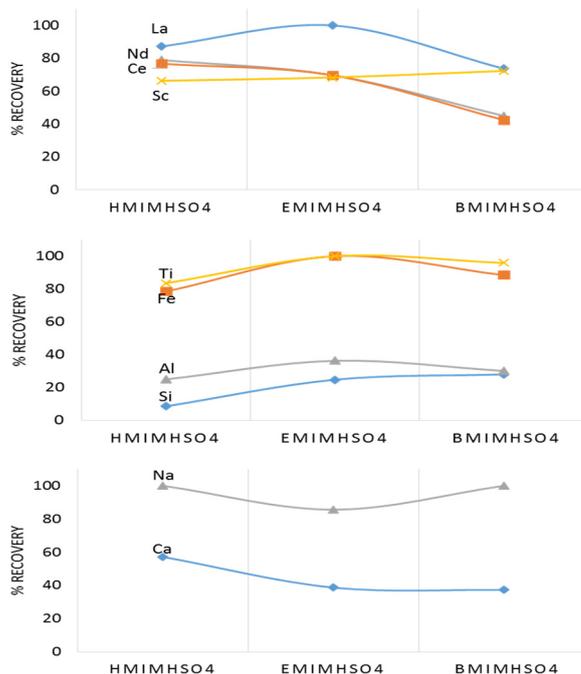
#### Kinetic experiments:

Keeping temperature constant at 190°C and pulp density at 2,5%(w/v), kinetic experiments were conducted with neat EmimHSO<sub>4</sub> for ½, 2,6 ,8, and 24h. The metal recoveries are shown in figure 5.



**Figure 9** Recoveries of selected metals versus time after leaching with EmimHSO4 at 190 °C for ½, 2, 6, 8, 24h.

After 2 hours retention time high recoveries for Fe and Ti were achieved. Iron is totally recovered within the first 2 hours of leaching. Titanium is dissolved fast during the first two hours, reaching a recovery of 80% and then its leaching rate is decelerated necessitating 24 hours retention time in order to achieve 100% recovery. Scandium (as a proxy for all REE) reaches also almost it’s maximum recovery in 2 hours and prolonging the leaching time does not seem to have a significant effect as in the case of Ti leaching. Aluminum follows a very slow dissolution process and its recovery doesn’t exceed 35% after 24 hours retention time.



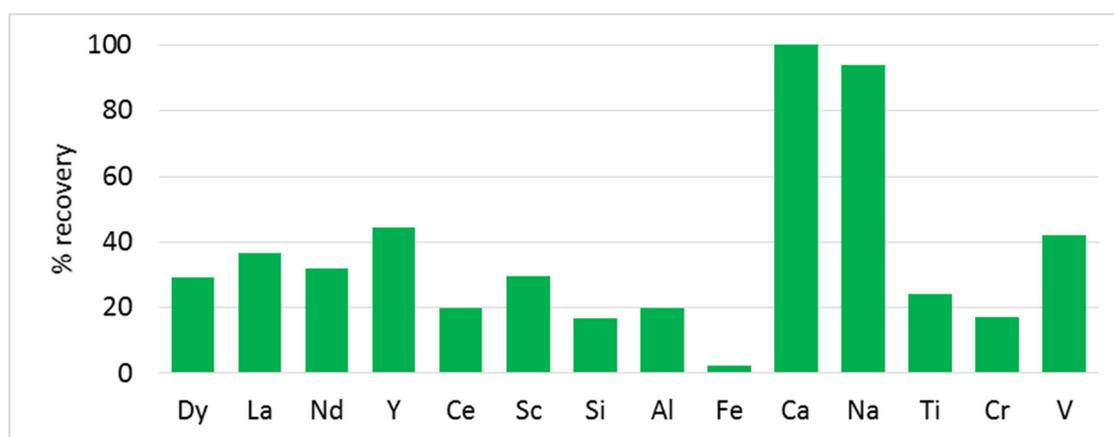
**Figure 10** Metal recoveries with different cations in imidazolium hydrogen sulfate ionic liquid (190°C 24h, 2.5% pulp density).

**Effect of altering the alkyl chain in 1-alkyl-3methyl-imidazolium hydrogen sulfate:**

Altering the alkyl chain in imidazolium cation by using the ionic liquids 1-butyl-3methyl-imidazolium hydrogen sulfate (BmimHSO4 >95% purity), and 1-methylimidazolium hydrogen sulfate (HmimHSO4 >95% purity) resulted to small differences on metal recoveries from Bauxite residues as seen in figure 6. Separating the metals in three different groups, it can be concluded that base elements reach their maximum recovery in EmimHSO4 while Na and Ca follow an opposite trend. Rare earth elements such as La, Nd and Ce

present their lowest recoveries in BmimHSO<sub>4</sub> whereas Sc recovery is practically unaffected by the alteration of cations. Overall small changes occur with the variation of the IL cation.

**Preliminary results with task specific ILs:** Despite the high recoveries of rare earths achieved with the imidazolium - hydrogen sulfate ILs, the pregnant solutions produced contain large amounts of dissolved Fe and Ti, making the extraction of the REE from such solutions impractical. Thus future investigations should be focused to exploit ionic liquids for selective dissolution between critical metals and iron as the latter is the most abundant in red mud. As an indication for this potential, in figure 7 the results of a preliminary leaching test of Bauxite Residue with the task specific IL betaine bis(trifluoromethylsulfonyl)imide (HbetTf<sub>2</sub>N) is shown. The results indicate that the specific IL favours the dissolution of Ca, Na, REE and other minor elements while the iron of the Bauxite Residue remains practically undissolved.



**Figure 7** Direct leaching of red mud with 50% v/v HbetTf<sub>2</sub>N in water at 60 C with 10% pulp density for 24h.

## Conclusions

In the present study direct dissolution of synthetic rare earth oxides and red mud has been made with ionic liquid EmimHSO<sub>4</sub>. Preliminary experiments with pure ionic liquid EmimHSO<sub>4</sub> and synthetic rare earth oxides prove that dissolution process is feasible and occur at shorter times as temperature rises. Neat EmimHSO<sub>4</sub> provides the acidity needed for the metal oxides to dissolve and form metal complexes as other studies with imidazolium ionic liquids proposed <sup>[17]</sup>. Bauxite residue also dissolve in EmimHSO<sub>4</sub>. Small dissolution of silicon and aluminum occur and high recoveries of rare earth elements such as yttrium, lanthanum, cerium, neodymium and scandium have been obtained in the range of 60-70%. Alteration of the cation in imidazolium hydrogen sulfate ionic liquid has little effect in the metals recovery. Preliminary results show that utilizing different ILs, such as the HbetTf<sub>2</sub>N may even achieve selective leaching of the REEs. Thus from these studies and literature investigations ionic liquids seem to be promising alternative solvents for primary and secondary raw materials processing.

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