



Leaching of rare earth elements from ‘Rödberg’ ore of Fen carbonatite complex deposit, using the ionic liquid HbetTf2N



Panagiotis Davris*, Danai Marinos, Efthymios Balomenos, Alexandra Alexandri, Maria Gregou, Dimitrios Panias, Ioannis Paspaliaris

National Technical University of Athens (NTUA), School of Mining and Metallurgical Engineering, Laboratory of Metallurgy, Heroon Polytechniou 9, 15780 Zografou, Greece

ARTICLE INFO

Keywords:

Rödberg
Rare earth
Ionic liquids
HbetTf2N
Fen carbonatite

ABSTRACT

In this study, the ionic liquid betainium bis(trifluoromethylsulfonyl)imide (HbetTf2N), has been applied directly as a leaching agent on a low-grade rare earth element (REE) ore called Rödberg, from the Fen carbonatite complex ore deposit located in Norway. REE in Rödberg are mainly present in the form of fluoro-carbonates of bastnäsite group minerals. Factors studied during leaching were water ratio into ionic liquid, leaching temperature, pulp density (%w/v) and retention time. Leaching of Rödberg ore with HbetTf2N resulted to 65–100% recovery of light REE and 40–60% recovery of heavy REE. Additionally > 80–90% of Ca and Mg content dissolves, whereas the HbetTf2N is selective against iron and silicon resulting in a Fe/Si rich residue. The metals dissolved into HbetTf2N after leaching are stripped with an aqueous acidic solution, regenerating the ionic liquid for reuse. Through acid stripping, REE concentration is doubled in the aqueous acidic solution, for further purification. The carboxylic acid functional group attached to the cation side of HbetTf2N is capable of dissolving bastnäsite thus enabling the development of new alternative methods for treating low-grade REE primary resources.

1. Introduction

Rare-earth elements (REEs) are a group of metals consisting of scandium, yttrium and lanthanides exhibiting similar chemical properties. REE global demand grows with an annual rate of 5% (Dutta et al., 2016), due to their increasing usage in a wide range of applications, particularly renewable energy technologies and electronic devices (Krishnamurthy and Gupta, 2015). REE are essentials towards a cleaner, greener future (Binnemans et al., 2013), with an estimated increasing demand of Nd and Dy (being indispensable in the manufacture of high strength permanent magnets) by 700% and 2600% in the next 25 years, respectively (Alonso et al., 2012). The European Commission (ERECON, 2015; EU, 2014) and the US Department of Energy (US, 2011) labeled REEs among the most critical raw materials, in terms of supply risk and economic importance.

Extractive metallurgy of REE is industrially applied to minerals such as monazite, bastnäsite and ion-adsorption clays, with China being the main producer (Gambogi, 2015; Habashi, 2013; Jha et al., 2016; Krishnamurthy and Gupta, 2015). Current exploitation of European REE deposits (Goodenough et al., 2016) can tackle REE regional supply issues derived from the major producers. Among the studied European

REE ore deposits (Balomenos et al., 2017) the Fen carbonatite complex located in south Norway is an enriched REE/Th deposit. It is reported to contain 486 million tonnes, of sövite rock type, grading about 0.9% TREO, and is therefore considered among the largest REE deposits in the world. REEs of the Fen Carbonatite Complex deposit are found in synchysite-parasite minerals of the bastnäsite group and low-thorium monazite minerals (Mitchell and Brunfelt, 1975; Schilling, 2013). Rödberg ore is a hematite-calcite-dolomite carbonatite rock type of the Fen complex deposit, that has been formed from ferrocarnatite transformation occurred by the action of groundwater oxidizing hydrothermal solutions (Andersen, 1984; Andersen, 1987). Comparing to other rock formations present in Fen complex, Rödberg ore is enriched in light REE (La to Eu in the lanthanide series) (Mitchell and Brunfelt, 1975) resembling well exploited REE carbonatite deposits. LREE enrichment is caused by fine-grained dissemination of monazite, bastnäsite, parasite and/or synchysite minerals (Ihlen et al., 2014). REE hydrometallurgical extraction from bastnäsite is industrially applied through different hydrometallurgical routes depending on purity. Caustic soda cracking, sulfuric acid baking or a combination of roasting and HCl leaching are the main industrial methods for bastnäsite treatment (Kul et al., 2008; Lucas et al., 2015; Krishnamurthy and Gupta,

* Corresponding author.

E-mail address: panosdavris@metal.ntua.gr (P. Davris).

2015).

As alternatives to conventional hydrometallurgical treatment, ionic liquids (IL's) could hold the key to develop a sustainable and greener processing of low-grade REE resources. ILs, are room temperature molten salts, constituted by ions, generally an organic cation and an inorganic/organic anion. From a broad range of applications that IL's have, hydrometallurgical processes have a small share but with great potential. (Abbott et al., 2011; Tian et al., 2010). The driving force of applying ionometallurgical leaching on low-grade resources is the prospect of increasing selectivity, reduction of waste effluent and improved efficiency yields (Binnemans and Jones, 2017).

HbetTf2N is an ionic liquid functionalized with a carboxylic group attached to its cation side. Studies show that HbetTf2N and its similar derivatives dissolve a range of synthetic metal oxides including REE, yet Fe, Si and Al oxides are insoluble (Nockemann et al., 2008b; Nockemann et al., 2006). Additionally, HbetTf2N exhibits a switching thermomorphic behavior as upon mixing with an aqueous solution having low pH, it was found to be immiscible at temperatures below 55 °C, whereas above 55 °C or high pH is fully miscible. Metals dissolved into HbetTf2N can be stripped with an acidic solution regenerating the IL through hydrogen-metal exchange and phase separation. The difference in the volume ratio of the IL and aqueous acid phase can lead to higher metal concentration of the resulting aqueous solution similarly to solvent extraction techniques. HbetTf2N leaching process and its advantages on generating an enhanced REE solution, have been studied in low-grade REE resources such as Bauxite residue, as well as on recycling of phosphor lamps waste powder and neodymium magnets where selective dissolution of the REE against other metals has been successfully proven (Davris et al., 2016; Dupont and Binnemans, 2015a; Dupont and Binnemans, 2015b).

In this study, the ionic liquid HbetTf2N is applied for leaching REE from Rödberg ore, a low grade bastnäsite deposit of Fen complex. Several factors were studied during leaching followed by stripping experiments of the loaded ionic liquid pregnant solution for metals recovery and IL regeneration. By taking advantage of HbetTf2N properties a new treatment of low-grade REE resources is proposed providing several benefits such as high REE recoveries, regeneration of the ionic liquid for reuse and low acid input in the process leading to pre-concentration of REE in the final aqueous solution for further purification.

2. Materials and methods

Betainium bis(trifluoromethylsulfonyl)imide supplied from Iolitec with > 97% purity. Solid samples of Rödberg ore were provided by REE minerals AS, located in south Norway. HCl, NaOH and Na₂CO₃ reagents of laboratory grade were used. Mineralogical characterization using X-Ray diffraction (XRD) was made by a Bruker D8 focus X-ray diffractometer. Scanning Electron Microscope analysis (SEM) made with a Jeol 6380 LV. The particle size measurement conducted with a MALVERN Laser particle size analyzer. Infrared measurements conducted with a Perkin Elmer FTIR spectrum 100. ¹H NMR measurements conducted with a Varian V300 MHz spectrometer using DMSO-*d*₆ as a solvent at 25 °C. Chemical analysis of solid samples obtained by total dissolution with fusion using a mixture of Li₂B₄O₇/KNO₃ at 1000 °C, followed by nitric acid dissolution. Dissolved metals into solutions were measured by inductive coupled plasma mass spectroscopy (ICP-MS) and atomic absorption spectroscopy (AAS). Carbon analysis in solids made with LECO furnace CS200. Total Organic Carbon, Direct TNT Method (20.0 mg/L) was used to measure organic carbon concentration into aqueous solutions, using a HACH DR/2500 spectrophotometer. Organic carbon concentration into aqueous solutions indicates IL losses that occur during acid stripping of the loaded ionic liquid solution. Measurements of pH were made with a Metrohm 826 pH meter mobile.

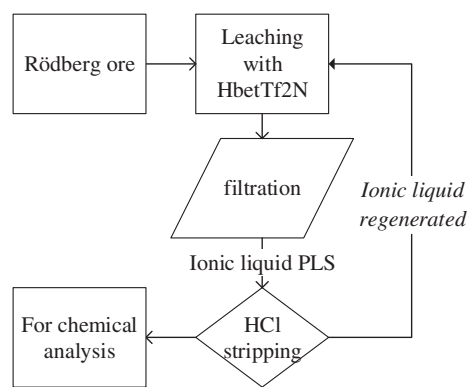


Fig. 1. Experimental procedure followed for leaching experiments.

2.1. Experimental

Leaching experiments conducted in a mini reactor setup incorporated with temperature controller, mechanical stirrer and a vapor condenser. Filtration of the pulp made via suction filtration using Whatman GF/C glass microfiber filters of 1 µm pore size. Factors studied during Rödberg ore leaching with HbetTf2N were water addition into HbetTf2N, %w/v pulp density, retention time and leaching temperature. Mechanical stirring rate of 400 rpm applied to all experiments. Acid stripping of the metal loaded ionic liquid solution performed with an excess of HCl at ambient temperature applying intense stirring for 30 min and separate the immiscible phases in separating funnels. Repeated stripping cycles were applied until metal content in the aqueous phase measured below detection limits < 50 µg/L. Metal concentration in ionic liquid pregnant solution was measured by dissolving 5 mL of pregnant solution to 100 mL of 10% HNO₃ solution. Experimental setup upon leaching can be seen in Fig. 1.

3. Results and discussion

3.1. Characterization of Rödberg ore

Chemical analysis of Rödberg ore in the form of oxides can be seen in Table 1.

Rare earth elements (as oxides) in Rödberg samples found to be 1.04% wt. Individual REE content is shown in Table 2. REE distribution of Rödberg indicate that 93% are light REE (from La to Eu) represented mainly by La, Ce and Nd.

Mineralogical analysis with XRD identified minerals such as calcite [CaCO₃], dolomite [CaMg(CO₃)₂], hematite [Fe₂O₃], quartz [SiO₂] and clinocllore [(Mg₅Al)(AlSi₃)O₁₀(OH)₈]. Samples tested for leaching, were crushed, pulverized and passed through a 420 µm size sieve resulting to a fine powder having D₅₀ = 21.5 µm. SEM image of back-scattered electrons combined with Energy-dispersive X-ray spectroscopy (EDS) analysis, reveals white areas rich in REE, combined with Ca and F indicating the bastnäsite's mineral group, whereas gray areas consist mainly of Ca, Fe and Si (Fig. 2).

3.2. Chemistry of HbetTf2N during dissolution and IL regeneration

The molecular structure HbetTf2N can be seen in Fig. 3. Its viscosity significantly decreases by increasing temperature or by the addition of water. Its structure is described elsewhere (Davris et al., 2016). HbetTf2N can crystallize in ambient temperature and absence of water.

Protonated carboxyl functionalized HbetTf2N is able to dissolve a range of metal oxides including REE, whereas Fe, Al and Si metal oxides were found to be insoluble (Nockemann et al., 2008b; Nockemann et al., 2006). The acidity of the carboxylic group (pKa 1.83) attached to the cation side of the ionic liquid (Fig. 3), facilitates metal dissolution

Table 1
Chemical analysis of Rödberg sample.

Element	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MnO	MgO	ThO ₂	TREO	CO ₂	Other
% wt.	10.00	1.63	30.10	27.06	1.41	6.34	0.05	1.04	22.00	0.37

Table 2
REE, concentration (mg/kg) found in Rödberg.

Element	Sc	La	Ce	Pr	Nd	Sm	Eu	Gd
mg/kg	89.82	1566.78	3355.32	525.56	2292.25	329.10	69.24	192.59
+/-	1.17	22.88	77.82	4.68	52.06	9.09	0.91	3.40
Element	Tb	Dy	Ho	Er	Tm	Yb	Lu	Y
mg/kg	15.08	50.25	8.56	27.07	— ^a	17.74	— ^a	269.79
+/-	0.10	0.54	0.00	0.37	—	0.15	—	5.72

^a Below 1 mg/kg.

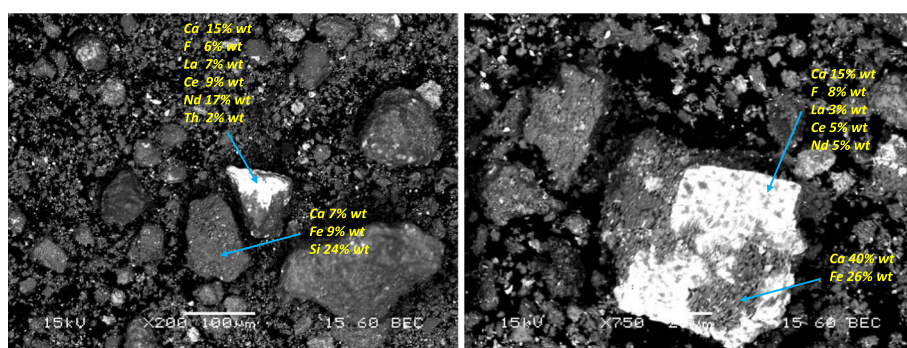


Fig. 2. SEM backscattered image of Rödberg having REE enriched bastnäsite type particles.

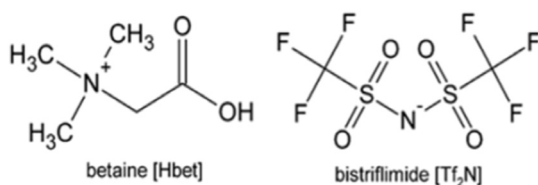


Fig. 3. HbetTf2N molecular structure.

and complex formation with the deprotonated zwitterionic betaine (Nockemann et al., 2008a; Nockemann et al., 2009). Additionally the anion Tf2N[−] does not participate in the reaction but is essential on providing physical properties such as hydrophobicity, low viscosity and good thermal stability (Jagadeeswara Rao et al., 2009). Based on the carbonatite feeding material the dissolution equations of calcite and bastnäsite with HbetTf2N ($T > 55^{\circ}\text{C}$) proposed are:

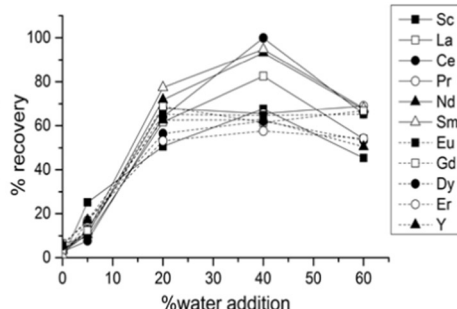
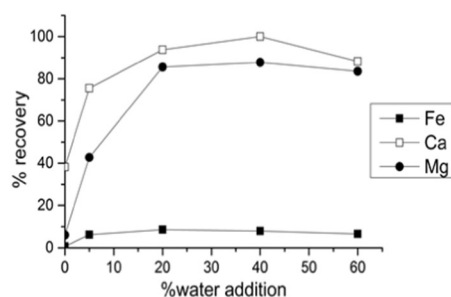
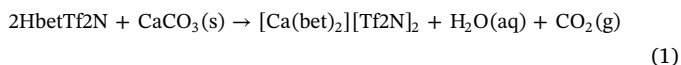


Fig. 4. Base elements and REE recoveries upon water addition (%v/v) into HbetTf2N during Rödberg leaching. Conditions used 90°C for 24 h 5% pulp density (%w/v).

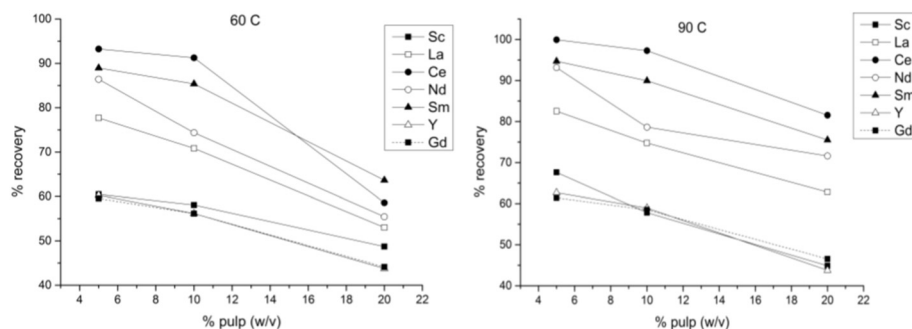


Fig. 5. % recoveries of selected REE upon Rödersberg leaching with HbetTf2N, at 60 °C and 90 °C and different pulp densities. Conditions used 24 h, 40% v/v water ratio.

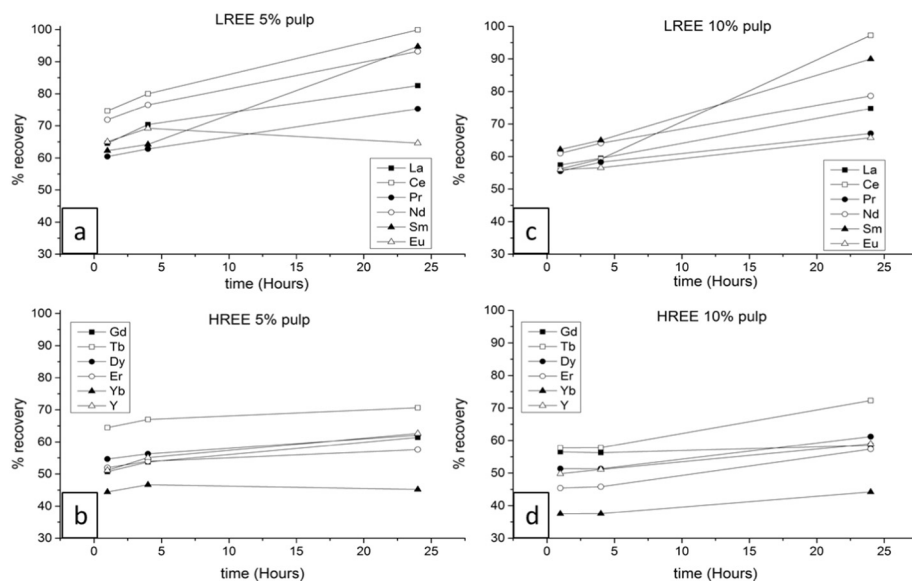


Fig. 6. Kinetics of LREE (a, c) and HREEs (b, d) recoveries after Rödersberg leaching with HbetTf2N at 5% pulp density (%w/v) and 10% pulp density. Conditions used 90 °C, 40% v/v water ratio.

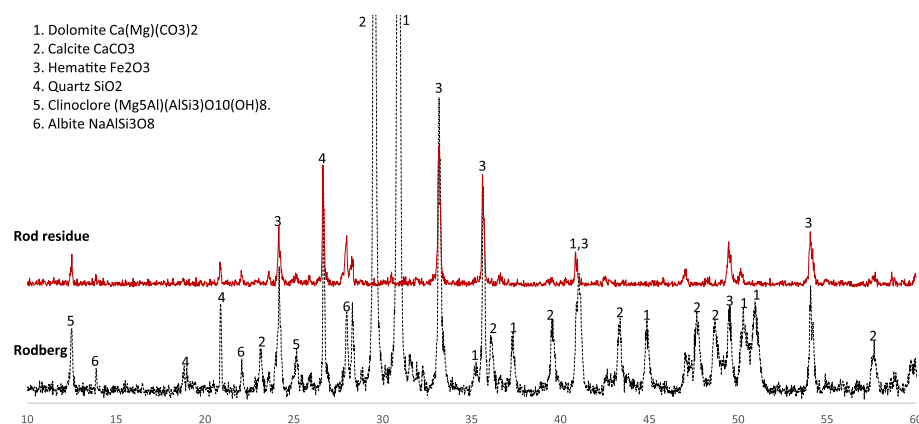
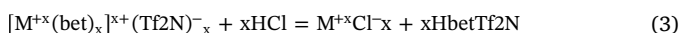


Fig. 7. XRD comparisons of Rödersberg ore and residue after leaching.

HbetTf2N PLS and regeneration of the IL:



where x is the oxidation number of the individual metal ions i.e. Fe^{3+} , REE^{3+} , Ca^{2+} etc. During acid stripping of the loaded ionic liquid solution, protonated betaine and metal chlorides are produced (Eq3).

3.3. Leaching factors studied on Rödersberg with HbetTf2N

3.3.1. Effect of water addition into HbetTf2N

In order to study the effect of water addition in HbetTf2N during Rödersberg leaching, a series of experiments were conducted in a range of 0 up to 60%v/v water addition to HbetTf2N, at conditions of 90 °C for

24 h retention time, and 5%(w/v) pulp density. As can be seen in Fig. 4, pure HbetTf2N does not facilitate REE dissolution, whereas increasing water content beyond saturation point (~20%v/v) and up to 40% v/v results to a significant increase of REE recoveries (Fig. 4). Particularly LREE such as La, Ce and Nd, which are the main representatives of Rödersberg ore, reach 80–100% leaching efficiency with their maximum yields being at 40% v/v water addition in HbetTf2N. Additionally, HREE recoveries provide moderate yields in the range of 50–60%. Si dissolution is negligible and Fe dissolution remains steady at low leaching yields 7–8%, whereas high dissolution of Mg (80%) and Ca (90%) occurs. Water content of 5%v/v in HbetTf2N provides low dissolution of REE but a significant amount of Ca dissolves. Water addition in HbetTf2N has a significant positive effect on REE recovery as in the

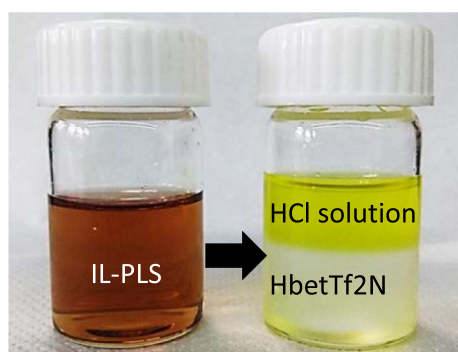


Fig. 8. HCl metal stripping on ionic liquid pregnant leach solution.

presence of water, metal dissolution is facilitated due to H^+ dissociation and viscosity reduction (Davris et al., 2016). Therefore, during Rödberg leaching, 40%v/v water addition into HbetTf2N kept steady, in order to further study factors such as temperature, pulp density as well as kinetics.

3.3.2. Effect of temperature at different pulp densities

Temperature effect was studied at 60 °C and 90 °C at different pulp densities of 5–10–20% (w/v). Leaching conditions of 24 h with 40% v/v water addition applied. REE recoveries at different pulp densities for two leaching temperatures can be seen in Fig. 5. Increasing pulp density from 5 to 20 (%w/v) resulted to a small reduction of REE recoveries due to the consumption of leaching agent by gangue material. LREE recoveries significantly reduced at leaching temperature of 60 °C and 20% pulp density, while to a less extent at 90 °C, whereas HREE recoveries exhibit small reduction respectively. Particularly La, Ce, Nd and Sm recoveries at 90 °C, reduce from a range of 80–100% at 5% w/v pulp density, to a range of 65–85% at 20% w/v pulp density. Additionally, at both leaching temperatures Sc, Y and Gd recoveries are in a range of 60–70% at 5% w/v pulp while their recoveries reduce to ~45% as pulp density increases. Increasing temperature from 60 °C to 90 °C at a steady pulp density results to an overall increase of REE recoveries with temperature's positive effect being more apparent for LREE at higher pulp densities.

3.3.3. Effect of retention time during leaching at different % w/v pulp densities

Kinetics was studied comparing LREE and HREE recoveries at 5 and 10% pulp density and 90 °C (Fig. 6). Increasing retention time has a major effect in LREE during leaching compare to HREE. From 1 h to 24 h retention time and low pulp density (Fig. 6a), the dissolution range of LREE increases from 60 to 75% to 65–100%. However, retention time during leaching seems to have minor effect on HREE leaching with a slight increase in their recoveries between 1 h and 24 h leaching (Fig. 6b,d). As pulp density increases the REE recoveries exhibit slower kinetics. This is mainly attributed to the large co-dissolution of Ca (84%) and Mg (73%) after 1 h, leading to extensive consumption of the leaching agent and prohibiting REE recovery (Fig. 6c).

3.3.4. Residue after HbetTf2N leaching

Mineralogical analysis with XRD in the leaching residue indicate

almost total dissolution of calcite and dolomite whereas mineral phases such as hematite, clinocllore and quartz remain undissolved as can be seen in Fig. 7. The generated residue after leaching with HbetTf2N at 24 h 5% pulp density at 90 °C, found to have 55% of Fe_2O_3 and 25% SiO_2 composition.

3.4. Metal recovery from the leachate by acid stripping and IL regeneration

An ionic liquid pregnant solution (PLS) is obtained after leaching and solid liquid separation. The PLS solution obtained is a reddish clear liquid (Fig. 8) having a pH of ~2.5 and upon cooling to ambient temperature remains as a homogeneous liquid phase (Fig. 8). Chemical analysis of selected REE and base metals in PLS at leaching conditions 4 h retention time, 90 °C at 5% pulp density (%w/v) and 40%v/v water addition, is provided in Table 3. It should be noted that despite the high recovery yields of REE achieved during leaching against Fe, the final metal concentration of Fe is much higher than that of REE. Upon stripping of the PLS with an acidic HCl solution, metal ions are extracted along with water, forming two immiscible phases, the metal loaded aqueous solution and the regenerated hydrophobic ionic liquid (Fig. 8).

The stoichiometric amount of HCl needed for total metal extraction and IL regeneration was calculated from chemical analysis of the PLS (Table 3) and Eq3, and found to be 0.65 mmol HCl/mL of PLS. Taking into account the small volume of the acidic solution to be used and the IL losses during stripping, 8N HCl concentration is suitable for stripping metals efficiently providing good phase separation and low IL losses to the aqueous phase. Therefore a series of stripping experiments were conducted using 8N HCl solution at the stoichiometric amount as well as 10%, 20%, 50% and 100% of acid excess (Fig. 9). Addition of 100% acid excess, using 8N HCl solution, resulted to > 90% metal recovery from PLS into one step producing a final aqueous solution with double the metal concentration (Table 3).

3.4.1. Acid stripping based on pH

During metal stripping from the loaded ionic liquid solution, it was found that all metals could be easily extracted, except Th, Sc and Fe which appear to form strong complexes with the HbetTf2N and more acid consumption is needed to increase their recovery yield (Fig. 9). This assumption was verified by a series of experiments to study the stripping behavior of metals at a pH range from 2.5 to 0 (Fig. 10). Upon contact of IL-PLS with HCl it was found that a final pH > 2 in the aqueous phase provides high recovery yields of Ca, and Mg along with moderate REE-Fe recovery. Yet at pH ~1.6, REE are recovered with 65–85% efficiency whereas recoveries of Th (< 10%), Sc (below the detection limit in aqueous phase i.e. < 40%) and Fe (< 60%) are significantly lower. As pH reduced close to zero all metals are efficiently recovered (Fig. 10). This differentiation upon stripping efficiency signifies that Sc, Th and Fe ions form more stable complexes than the other REE and base metal ions. Especially Sc and Fe high affinity with HbetTf2N has been also confirmed by previous studies (Davris et al., 2016; Dupont and Binnemans, 2015b; Hoogerstraete et al., 2013; Onghena and Binnemans, 2015) and can be utilized in the process through consecutive stripping steps of the PLS for achieving a bulk group separation of REE, Ca, Mg and Fe against Sc and Th.

A significant drawback of the proposed process is the IL losses

Table 3
Metal concentration measured into solutions.

Metal concentration (mg/L)															
	Sc	La	Ce	Nd	Sm	Dy	Y	Er	Gd	Pr	Eu	Th	Fe	Ca	Mg
PLS	3	66	118	89	13	1	7	1	7	18	2	25	865	9310	1700
8N HCl stripping (100% excess.)	5	125	248	178	25	3	15	1	13	37	4	56	1690	17,865	3255

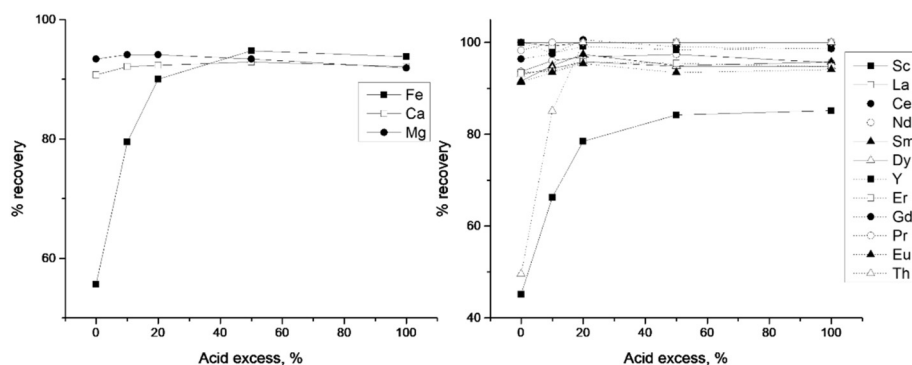


Fig. 9. Stripping metals from ionic liquid pregnant leach solution adding % excess of stoichiometrically HCl at 8N concentration.

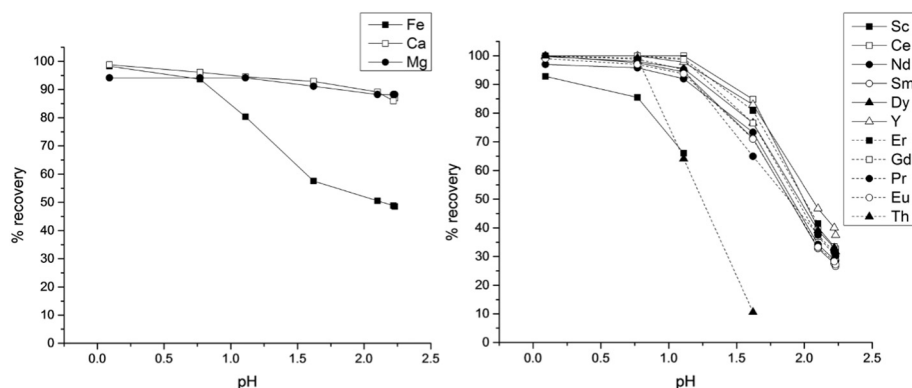


Fig. 10. Metal stripping from IL-PLS using HCl at different pH and 1:1 volume ratio.

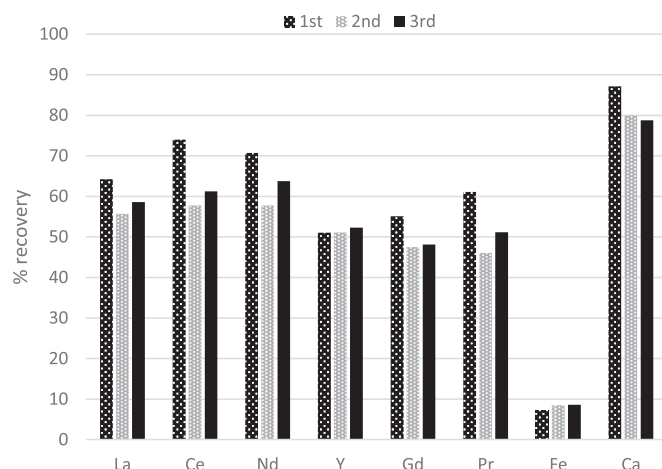


Fig. 11. Repeated leaching cycles of the same HbetTf2N to new Rödberg ore portion.

obtained during acid stripping upon liquid/liquid interaction. During HCl stripping in Table 3 an overall 7% IL losses occurred. These losses can be significantly increased by applying multi stripping steps. The reason of IL losses mainly lies to IL solubility in pure water (despite being hydrophobic) which has been found to be 14%wt.(Dupont et al., 2015). This solubility can be significantly reduced by using salting out agents (salting out is the term used to suppress the IL solubility into an aqueous solution). Different choice of a salt cation and anion, as well as increasing salt concentration in aqueous solution, can have a drastic impact on IL solubility. Particularly the addition of sulfate anions that promote salting out of the IL, is an effective way to minimize IL losses (Dupont et al., 2015; Freire et al., 2009), and can be applied efficiently in contaminated IL aqueous streams for IL recovery (Neves et al., 2012). On the other hand addition of salting out agents such as Na_2SO_4 despite decreasing IL solubility generates CaSO_4 precipitate due to the presence of high concentration of Ca into solution that eventually entraps REE

leading to scattering between the solution and the precipitate. Therefore the side effects of salting out agents should be taken under consideration. Future work is focused on two main approaches to solving this issue. Finding the most suitable salting out agent or apply other functionalized bistriflimide IL's with different cations and length chains exhibiting similar chemical behavior to HbetTf2N with reduced water solubility. The metals selective behavior during stripping along with minimizing IL losses and acid consumption will be further explored in a future study to reveal the full benefits of the HbetTf2N leaching process.

3.4.2. Repeated leaching cycles with the regenerated HbetTf2N

In order to evaluate leaching performance of the regenerated IL, repeated leaching cycles using the same IL conducted (after acid stripping and regeneration) to a new portion of Rödberg ore based on the experimental procedure in Fig. 1. Steady conditions applied for each cycle of 20% v/v water addition to HbetTf2N, 5% pulp density at 90 °C for 1 h. Metal recoveries (Fig. 11) exhibit similar yields after conducting 3 leaching cycles with the same IL on new portions of Rödberg ore. FTIR measurements (Fig. 12) and consistent leaching yields (Fig. 11) indicate that regenerated HbetTf2N doesn't lose its leaching performance.

Using FTIR analysis (Fig. 12) it is evident that upon acid stripping the IL is fully regenerated. This can be easily visualized through comparison of the $\nu(\text{C}=\text{O})$ of the carboxylate group attached to the cation side of pure IL, PLS and IL after 3 cycles of leaching and regeneration (Fig. 12). The $\nu(\text{C}=\text{O})$ of PLS has been significantly decreased due to metal complex formation on the carboxylate group whereas upon acid stripping the carboxylate vibration is identical (and even better) to pure HbetTf2N.

3.4.3. Preliminary REE precipitation from the resulting HCl solution

The resulting HCl solution obtained after stripping (Table 3) has main co-dissolved metals such as Fe, Ca and Mg and can be further treated by neutralization for REE purification. Some precipitation techniques include phosphate, carbonate, oxalate and hydroxide precipitation (Beltrami et al., 2015; Jha et al., 2016) to obtain an

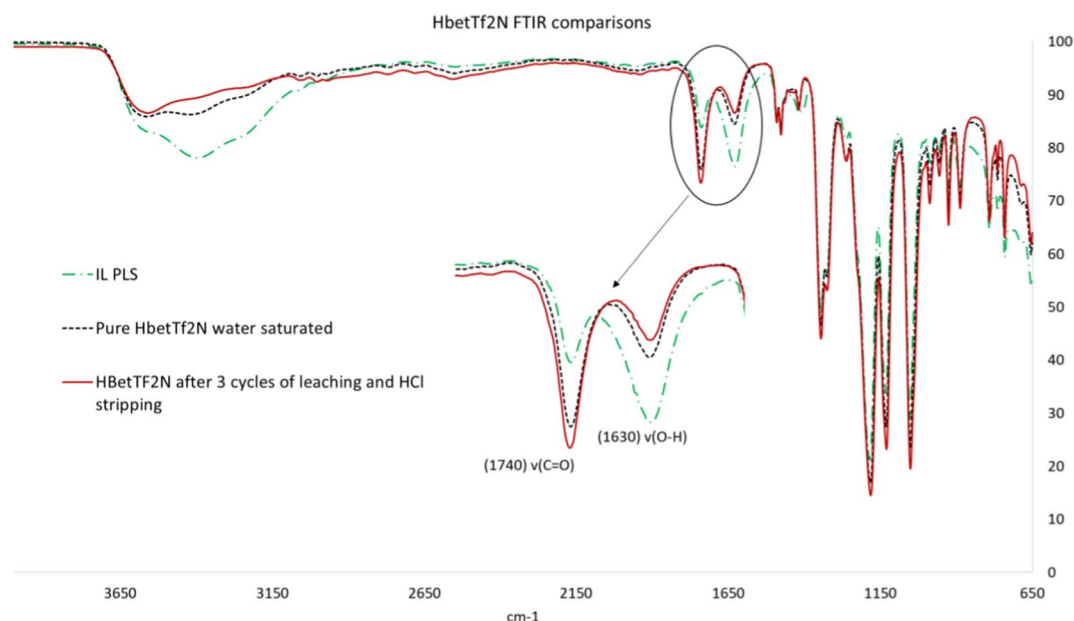


Fig. 12. FTIR comparisons of Pure HbetTf2N- HbetTf2N pregnant solution PLS- HbetTf2N after 3 cycles of leaching and acid stripping.

Table 4
selected REE and base elements concentration in the precipitate at pH 6.5 and the solution.

Element	Sc	Y	La	Ce	Pr	Nd	Eu	Gd	Si	Al	Fe	Ca	Mg
% wt in precipitate	0.12	0.40	3.22	7.35	0.90	4.29	0.09	0.30	0.83	5.08	14.30	7.02	0.37
ppm in solution	— ^a	—	0.05	0.08	—	0.05	—	—	—	—	14.65	6400.00	1270.00

^a Below 50 µg/L.

intermediate REE concentrate for REE separation through solvent extraction technics. Preliminary tests for REE precipitation included neutralization with NaOH up to pH 3 followed by further neutralization with Na₂CO₃ up to pH 6.5. Consumption of NaOH and Na₂CO₃ were found to be of 40.24 g and 12 g per liter of the aqueous pregnant solution respectively. The resulting precipitate at pH 6.5 has a total 16.5% wt. REE content (Table 4), resulting to almost total REE precipitation from solution along with small amounts of Fe, Ca and Al as main co-precipitated elements. The metal concentration of the remaining solution can be seen in Table 4.

The resulting REE precipitate can be further purified in order to minimize the main metal impurities such as Fe, Al and Ca. Additionally further trials will be made using a range of conventional precipitate reagents (oxalates, carbonates, phosphates) with main goal to produce a less contaminated REE precipitate suitable for further REE separation by means of solvent extraction techniques.

4. Conclusions

In this study, the functionalized ionic liquid HbetTf2N found to be able of dissolving bastnäsite, which is the main REE bearing mineral present in Rødberg ore. Factors studied during leaching indicate that water addition into HbetTf2N had a positive effect on REE leaching whereas increasing temperature at 90 °C and decreasing pulp density to 5% w/v, resulted in 65–100% LREE recoveries with HREE recoveries range from 40 to 60% after 24 h retention time. Kinetics at low pulp density indicate high recovery yields (60–70% LREE) after 1 h of leaching yet REE recovery has slower kinetics at higher pulp density. HbetTf2N leaching is selective against Fe and Si mineral phases, while high dissolution yields obtained for Ca and Mg resulted to an almost total dissolution of calcite and dolomite phases from Rødberg ore. Metals dissolved into the IL-PLS were almost totally extracted through

acid stripping using 100% excess of stoichiometric HCl, where HbetTf2N is regenerated for reuse. The regenerated HbetTf2N doesn't lose its leaching performance after 3 leaching cycles. It was found that Sc, Fe and Th form strong complexes with HbetTf2N and a bulk separation from the rest REE, Ca and Mg can be achieved. Yet IL losses should be taken into account and action on further minimizing IL losses must be implemented. Neutralization of the HCl solution after stripping resulted to a precipitate having 16.5% wt. REE content. It can be concluded that ionic liquids have great potential to be applied in low-grade REE carbonate primary resources providing good leaching efficiency, regeneration of the leaching agent and production of an enhanced REE solution for further purification by known methods.

Acknowledgments

"The research leading to these results has received funding from the European Community's Seventh Framework Programme ([FP7/2007–2013]) under grant agreement no 309373. This publication reflects only the author's view, exempting the Community from any liability". Project web site: www.eurare.eu

References

- Abbott, A.P., Frisch, G., Hartley, J., Ryder, K.S., 2011. Processing of metals and metal oxides using ionic liquids. *Green Chem.* 13 (3), 471–481.
- Alonso, E., et al., 2012. Evaluating rare earth element availability: a case with revolutionary demand from clean technologies. *Environ. Sci. Technol.* 46 (6), 3406–3414.
- Andersen, T., 1984. Secondary processes in carbonatites: petrology of "Rødberg" (hematite-calcite-dolomite carbonatite) in the Fen central complex, Telemark (South Norway). *Lithos* 17, 227–245.
- Andersen, T., 1987. Mantle and crustal components in a carbonatite complex, and the evolution of carbonatite magma: REE and isotopic evidence from the Fen complex, southeast Norway. *Chem. Geol.* 65 (2), 147–166.
- Balomenos, E., et al., 2017. The EURARE project: development of a sustainable exploitation scheme for Europe's rare earth ore deposits. *Johnson Matthey Technol.*

- Rev. 61 (2), 142–153.
- Beltrami, D., Deblonde, G.J.P., Bélair, S., Weigel, V., 2015. Recovery of yttrium and lanthanides from sulfate solutions with high concentration of iron and low rare earth content. *Hydrometallurgy* 157, 356–362.
- Binnemans, K., Jones, P.T., 2017. Solvometallurgy: an emerging branch of extractive metallurgy. *J. Sustain. Metall.* 3, 570. <http://dx.doi.org/10.1007/s40831-017-0128-2>.
- Binnemans, K., et al., 2013. Recycling of rare earths: a critical review. *J. Clean. Prod.* 51, 1–22.
- Davris, P., Balomenos, E., Panias, D., Paspaliaris, I., 2016. Selective leaching of rare earth elements from bauxite residue (red mud), using a functionalized hydrophobic ionic liquid. *Hydrometallurgy* 164, 125–135.
- Dupont, D., Binnemans, K., 2015a. Rare-earth recycling using a functionalized ionic liquid for the selective dissolution and revalorization of Y₂O₃:Eu³⁺ from lamp phosphor waste. *Green Chem.* 17 (2), 856–868.
- Dupont, D., Binnemans, K., 2015b. Recycling of rare earths from NdFeB magnets using a combined leaching/extraction system based on the acidity and thermomorphism of the ionic liquid [Hbet][Tf₂N]. *Green Chem.* 17 (4), 2150–2163.
- Dupont, D., Depuydt, D., Binnemans, K., 2015. Overview of the effect of salts on biphasic ionic liquid/water solvent extraction systems: anion exchange, mutual solubility, and thermomorphism properties. *J. Phys. Chem. B* 119 (22), 6747–6757.
- Dutta, T., et al., 2016. Global demand for rare earth resources and strategies for green mining. *Environ. Res.* 150, 182–190.
- ERECON, 2015. Strengthening the European Rare Earths Supply Chain: Challenges and Policy Options.
- EU, 2014. Report of the Ad Hoc Working Group on Defining Critical Raw Materials.
- Freire, M.G., et al., 2009. Ion specific effects on the mutual solubilities of water and hydrophobic ionic liquids. *J. Phys. Chem. B* 113 (1), 202–211.
- Gambogi, J., 2015. U.S. Geological Survey, Mineral Commodity Summaries.
- Goodenough, K.M., et al., 2016. Europe's rare earth element resource potential: an overview of REE metallogenetic provinces and their geodynamic setting. *Ore Geol. Rev.* 72 (Part 1), 838–856.
- Habashi, F., 2013. Extractive metallurgy of rare earths. *Can. Metall. Q.* 52 (3), 224–233.
- Hoogerstraete, T.V., Onghena, B., Binnemans, K., 2013. Homogeneous liquid–liquid extraction of metal ions with a functionalized ionic liquid. *J. Phys. Chem. Lett.* 4 (10), 1659–1663.
- Ihlen, P.M., Schiellerup, H., Gautneb, H., Skår, Ø., 2014. Characterization of apatite resources in Norway and their REE potential — a review. *Ore Geol. Rev.* 58, 126–147.
- Jagadeeswara Rao, C., Venkata Krishnan, R., Venkatesan, K.A., Nagarajan, K., Srinivasan, T.G., 2009. Thermochemical properties of some bis(trifluoromethyl-sulfonyl)imide based room temperature ionic liquids. *J. Therm. Anal. Calorim.* 97 (3), 937–943.
- Jha, M.K., et al., 2016. Review on hydrometallurgical recovery of rare earth metals. *Hydrometallurgy* 165, 2–26.
- Krishnamurthy, Nagaiyar, Gupta, C.K., 2015. The Rare Earths, Second ed. CRC Press, Extractive Metallurgy of Rare Earths, pp. 1–84.
- Kul, M., Topkaya, Y., Karakaya, I., 2008. Rare earth double sulfates from pre-concentrated bastnasite. *Hydrometallurgy* 93 (3–4), 129–135.
- Lucas, J., Lucas, P., Le Mercier, T., Rollat, A., Davenport, W., 2015. Chapter 4 - Extracting Rare Earth Elements from Concentrates, Rare Earths. Elsevier, Amsterdam, pp. 47–67.
- Mitchell, R.H., Brunfelt, A.O., 1975. Rare earth element geochemistry of the Fen alkaline complex, Norway. *Contrib. Mineral. Petrol.* 52 (4), 247–259.
- Neves, C.M.S.S., Freire, M.G., Coutinho, J.A.P., 2012. Improved recovery of ionic liquids from contaminated aqueous streams using aluminium-based salts. *RSC Adv.* 2 (29), 10882–10890.
- Nockemann, P., et al., 2006. Task-specific ionic liquid for solubilizing metal oxides. *J. Phys. Chem. B* 110 (42), 20978–20992.
- Nockemann, P., Thijs, B., Hecke, K.V., Meervelt, L.V., Binnemans, K., 2008a. Polynuclear metal complexes obtained from the task-specific ionic liquid betainium bistriflimide. *Cryst. Growth Des.* 8 (4), 1353–1363.
- Nockemann, P., et al., 2008b. Carboxyl-functionalized task-specific ionic liquids for solubilizing metal oxides. *Inorg. Chem.* 47 (21), 9987–9999.
- Nockemann, P., et al., 2009. Speciation of rare-earth metal complexes in ionic liquids: a multiple-technique approach. *Chem. Eur. J.* 15 (6), 1449–1461.
- Onghena, B., Binnemans, K., 2015. Recovery of scandium(III) from aqueous solutions by solvent extraction with the functionalized ionic liquid betainium bis(tri-fluoromethylsulfonyl)imide. *Ind. Eng. Chem. Res.* 54 (6), 1887–1898.
- Quagliano, J., Kida, S., Fujita, J., 1962. Preparation and infrared studies of metal complexes containing the zwitterion ligand betaine, (CH₃)₃NCH₂COO. *J. Am. Chem. Soc.* 84 (5), 724–729.
- Schilling, J., 2013. Petrography, mineralogy and whole-rock data of the major lithologies of the Fen Complex. 2013.034. In: Norges Geologiske Undersøkelse.
- Tian, G.-c., Li, J., Hua, Y.-x., 2010. Application of ionic liquids in hydrometallurgy of nonferrous metals. *Trans. Nonferrous Metals Soc. China* 20 (3), 513–520.
- US Department of Energy, 2011. Critical Materials Strategy.