PAPER

Extraction and separation of neodymium and dysprosium from used NdFeB magnets: an application of ionic liquids in solvent extraction towards the recycling of magnets

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A procedure for the efficient extraction and separation of rare earths and other valuable elements from used NdFeB permanent magnets is presented. In a first step, an iron free leachate is prepared from an used magnet using nitric acid. Cobalt is separated through a liquid–liquid extraction in aqueous nitrate media using as organic phase the ionic liquid trihexyl(tetradecyl)phosphonium nitrate which is easily prepared from the commercially available ionic liquid trihexyl(tetradecyl)phosphonium chloride (Cyphos® IL 101). Afterwards neodymium and dysprosium are successfully separated using ethylenediaminetetraacetic acid (EDTA) as a selective complexing agent during liquid–liquid extraction with the same ionic liquid. Different parameters of the separation process such as shaking speed, time, temperature, pH effect and concentration of complexing agents were optimized. The designed process allowed the separation of these three elements efficiently in few steps. The separated rare earths and cobalt were precipitated with oxalic acid and then calcined in order to form the oxides. Nd_2O_3, Dy_2O_3 and CoO were obtained with purities of 99.6%, 99.8% and 99.8%, respectively. Recycling of the employed ionic liquid for reuse in rare earths separation was also demonstrated.

Introduction

Recycling of rare-earth elements (REEs) is of importance from an economic, industrial and environmental point of view. For instance, the mining, transportation, processing and waste disposal of REEs have very serious environmental and occupational risks,[1] besides consequences on the surrounding ecosystems and human health.[2] Indeed, most of the rare-earth deposits contain harmful radioactive elements (*e.g.* thorium and uranium).[1] Moreover, in 2010, the European Commission published a list of critical raw materials at the EU level,[3] where valuable elements such as neodymium, dysprosium (both critical at short and middle term) and cobalt (not critical at short nor at middle term) can be found.

The range of REE applications has changed over time with the design and creation of new devices and processes requiring REEs.[4] Rare-earth oxides are of high importance because they cover a wide range of applications, they are employed in the glass industry (glass components and surface polishing agents), in lamp phosphors, high-power lasers, photographic industry and as catalysts.[5] Neodymium has been used since several decades as a colorant for glass, in welding goggles and more recently also in laser crystals.[4] Presently, neodymium is mostly employed in the manufacturing of permanent magnets that are used in electric motors, wind turbines and spindles for computer hard drives.[4] Dysprosium, another REE, is currently employed as an additive to neodymium–iron–boron (NdFeB) permanent magnets to improve their high temperature performance and to increase its intrinsic coercivity.[6] Furthermore, dysprosium is being applied in the nuclear industry as component for radiation shielding,[4] while dysprosium-doped phosphors are employed as radiation detectors in clinical and environmental monitoring of ionizing radiation.[7] Additionally, some NdFeB magnets contain small but considerable quantities of cobalt since it is added to the NdFeB magnets to increase the Curie temperature of the magnet.[8] Cobalt itself is a valuable and highly demanded element due to its multiple applications in the fields of super-alloys, catalysts, pigments and batteries.[9]

In contrast to the increasing REE demand, the supply of such materials is currently experiencing a shortage. Therefore different strategies such as, reopening of old REE mines or substitutions of critical elements have been proposed to solve this issue.[10–12] Alternatively, recycling of REE can be an interesting and efficient option to overcome this situation, while reducing the impact of the balance problem and environ-

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mental issues related to mining. Indeed, through REE recycling,[13] small but representative quantities of REEs that are minor constituents in the ores but that are at the same time high in demand by the market (*e.g.* dysprosium), can be efficiently obtained. Therefore, the recovery of neodymium and dysprosium from end-of-life NdFeB magnets containing considerable amounts of these elements becomes a relevant issue at industrial level.[14] The most employed methods for the separation of REEs use organic solvents which due to their toxicity, volatility and flammability have led to the implementation of ionic liquids in an environmentally friendlier approach.[15]

Ionic liquids (ILs) are organic salts which consist entirely of ions and with a melting point that is generally lower than 100 °C.[16–18] Some of the most interesting properties of the ILs are their chemical and thermal stability, high ionic conductivity and wide electrochemical potential window. Due to their negligible vapor pressure and low flammability, ionic liquids have been usually labelled as "green solvents".[19,20] As the application of ionic liquids in different fields continuously grows, information related to their environmental, health and safety impact can already be found in the literature.[16,21,22]

Ionic liquids are often called "designer solvents", because their cation and anion can be chosen in order to obtain an ionic liquid with specific properties that fulfil the requirements needed for a given process.[23] For example, in the liquid–liquid extraction process proposed herein, hydrophobic and low viscous ionic liquids are needed. Additionally, it is important that the metal complex that is going to be extracted has a higher solubility into the ionic liquid than in the aqueous phase. Some of the most studied ionic liquid based extraction systems contain fluorinated anions such as hexafluorophosphate (PF_6^-) or bis(trifluoromethylsulfonyl)imide (Tf_2N^-) that allow the obtention of hydrophobic and low viscous ionic liquids.[24–27] However, ionic liquids containing these anions are usually expensive and hexafluorophosphate ions can undergo hydrolysis conducing to the formation of hydrofluoric acid.[28] Besides this, the extraction of charged metal ions in fluorinated ionic liquids often occurs through an ion-exchange mechanism that conduces to the partially loss of the ionic liquid by dissolution of the cation into the aqueous phase.[29] For this reason, ionic liquids with hydrophobic cations containing long alkyl chains are now selected which permits the use of less expensive and more available anions. Alternatives are the phosphonium based ionic liquids, which are good candidates for their use in liquid–liquid extractions due to their high hydrophobicity, variety and availability. Moreover, phosphonium ionic liquids are able to extract anionic complexes, instead of only metal ions. As a consequence, phosphonium ionic liquids have been applied for industrial applications and a range of phosphonium ionic liquids are commercially available on a large scale.[30,31]

In this paper, an ionic liquid was employed for the separation and recovery of rare earths from an end-of-life NdFeB magnet. We present a new, practical, efficient and environmentally friendly methodology to separate neodymium(III),

dysprosium(III) and cobalt(II) by solvent extraction using an undiluted non-fluorinated ionic liquid. The separation methods were optimized considering the main involved variables (*e.g.* loading of the organic phase, pH, shaking rate, extraction time, temperature and complexing agent concentration). Since the master alloys needed for the production of magnets are based on the respective rare-earth oxides, the separated and recovered rare earths were precipitated as their respective oxalates and then calcined to obtain the oxides. The loading capacity of the ionic liquid was determined and thus the stoichiometry of the extracted complex close to its saturation. Moreover, the recycling of the employed ionic liquid was also demonstrated.

Experimental

Materials and methods

Trihexyl(tetradecyl)phosphonium chloride (>97%, Cyphos® IL 101) was purchased from IoLiTec (Heilbronn, Germany). $Nd(NO_3)_3 \cdot 6H_2O$ (99%) was obtained from Alfa Aesar (Karlsruhe Germany), $Dy(NO_3)_3 \cdot 6H_2O$ (99%), $Co(NO_3)_2 \cdot 6H_2O$ (99%) and Na_2EDTA (99%) were purchased from Acros Organics (Geel, Belgium), KNO_3 (99%) and NH_4NO_3 (99%) from Chempur (Karlsruhe, Germany), HNO_3 (65%), HCl (37%), NaOH (99%) and $H_2C_2O_4$ (99%) from J.T Baker, the silicone solution in isopropanol was obtained from SERVA Electrophoresis GmbH (Heidelberg, Germany) and the gallium standard (1000 mg L^{-1}) was purchased from Merck (Overijse, Belgium). All chemicals were used as received, without further purification. The concentrations of the rare earths in both the aqueous and the organic phase were determined by using a bench top total reflection X-ray fluorescence (TXRF) spectrometer (S2 Picofox, Bruker). The extraction experiments were performed in 4 mL vials and using a temperature controllable Turbo Thermo Shaker (Model: TMS-200, Hangzhou Allsheng Instrument Co. Ltd, China). After the extraction, scrubbing or stripping experiments were carried out at specific conditions for each process. The aqueous and the organic phases were separated after extraction by centrifugation using a Heraeus Megafuge 1.0 centrifuge. Then, part of the aqueous phase was removed and mixed with a gallium standard solution and MilliQ water until a total volume of 1 mL was obtained. For the organic phase (ionic liquid), the gallium standard was added to a small amount of the ionic liquid phase (15–20 mg) and was further diluted with ethanol until 1 mL. The quartz glass sample carriers were treated with 20 μL of a silicone solution in isopropanol in order to make the surface hydrophobic and obtain a concentrated drop of the aqueous phase on the center of the disk. Then the sample carriers were dried for 3 min in a hot air oven at 60 °C and 5 μL of the sample were disposed on the glass carrier. The prepared samples were dried simultaneously during 30 min. The metal concentrations were measured for 200 s. All the pH measurements were performed using an S220 Seven Compact pH/Ion meter (Mettler-Toledo) and a Slimtrode (Hamilton) electrode. The viscosity of the ionic liquid and

ionic liquid phases was measured using an automatic Brookfield plate cone viscometer (Model LVDV-II + P CP, Brookfield Engineering Laboratories, USA). Densities were measured with a 5 mL pycnometer. A Mettler-Toledo DL39 coulometric Karl Fischer titrator was used with Hydranal® AG reagent to determine the water content of the synthesized ionic liquid. ^{1}H NMR spectra were recorded in $CDCl_3$ on a Bruker Avance 300 spectrometer, operating at 300 MHz. Chemical shifts are expressed in parts per million (ppm), referenced to tetramethylsilane. The spectra were analyzed with SpinWorks software. FTIR spectra were recorded on a Bruker Vertex 70 spectrometer (Bruker Optics) equipped with a Bruker Platinum ATR accessory. The X-ray diffraction powder pattern was recorded at room temperature with a Seifert 3003 T/T X-ray diffractometer equipped with a scintillation detector. X-ray type: Cu Kα operating at 40 kV and 40 mA, scanning range: 10–80 degrees (2θ), step width: 0.02°, step scan: 2.00 s. Analysis result was progressed by "X'pert HighScore Plus" PANalytical software.

Synthesis of trihexyl(tetradecyl)phosphonium nitrate

Trihexyl(tetradecyl)phosphonium nitrate was synthesized by equilibrating 93.199 g (0.179 mol) of trihexyl(tetradecyl)phosphonium chloride with 100 mL of a 2 M potassium nitrate solution during five hours. The aqueous phase was removed and the organic phase was stirred again for five additional hours with 100 mL more of the same potassium nitrate solution in order to reduce the chloride impurities. Afterwards, the two phases were allowed to separate. The aqueous phase was removed and the organic phase was washed several times with MilliQ water and dried. The ionic liquid obtained was a colorless liquid (94.9%, 94.920 g, 0.1738 mol). ^{1}H NMR (300 MHz, $CDCl_3$, δ/ppm): 2.28 (m, 8H, 4× CH_2), 1.50 (m, 18H, 9× CH_2), 1.32 (s, 12H, 6× CH_2), 1.25 (m, 18H, 9× CH_2), 0.89 (s, 12H, 4× CH_3). The chloride concentration was measured by TXRF and it was found to be below 100 ppm.[32] Water content: 0.02 wt%, viscosity: 1437 cP (22 °C), density: 0.9132 g cm^{-3} at 22 °C Water saturated ionic liquid: water content: 3.45 wt%, viscosity 260 cP (22 °C), density: 0.9140 g cm^{-3} (22 °C).

Selective leaching and direct magnet dissolution

For the direct magnet powder dissolution and the selective leaching from roasted magnets the procedure reported by Vander Hoogerstraete et al.,[33] was followed. A magnet, obtained from the University of Birmingham, UK, and whose composition is shown in Table 1 was employed.

Magnet dissolution. Briefly, 15 g of crushed magnet (particle size < 400 μm) was put into a vial and covered with 15 mL of MilliQ water. Afterwards, 7 mL of concentrated HNO_3 (65 wt%) was carefully and slowly added; the formation of nitrogen oxides (NO_x) was observed. The vial was closed with a screw cap and heated at 80 °C during 72 h. After this time, the solution was centrifuged during 10 min at 3000 rpm. The aqueous phase was removed and its metal content was measured by TXRF. An orange solution with a pH = 0.41 was obtained. In order to remove the iron that was still present in solution,

Table 1 Composition of the employed magnet (wt%)

Element	Content (wt%)	Element	Content (wt%)
Fe	58.16	Pr	0.34
Nd	25.95	C	0.07
Co	4.22	Si	0.06
Dy	4.21	Mn	0.05
B	1.00	Cu	0.04
Nb	0.83	Ni	0.02
O	0.41	N	0.02
Al	0.34	Total	95.72

1 mL of hydrogen peroxide (35%) was added and the solution was heated at 40 °C for 1 h in order to oxidize the remaining iron(II). A small volume of this solution was poured into a vial that contained 2 mL of MilliQ water and a stirring bar. The pH was monitored with a pH electrode. The initial pH was 0.67. Slowly, under stirring, drop by drop a solution of NaOH 1 M was added to the center of the sample until a pH of 4 was reached. The sample and the solution of NaOH 1 M were gradually added to the vial trying to keep the pH all the time between 3.5 and 4. Afterwards, the sample was stirred for another hour, left to settle during one hour and then it was easily filtered. The resulted solution was pale pink. The metal content was measured by TXRF and no iron could be detected. The precipitate was filtered and analyzed quantitatively by TXRF in order to determine the rare-earth elements that might have been co-precipitated into the precipitate.

Selective leaching. The roasting was performed by placing a powder sample (<400 μm) of the magnet into a porcelain crucible and by heating to 950 °C during 15 h. A sample of the fully roasted powder (15 g) was put into a vial together with 5 mL of HNO_3 (65%) and 10 mL of MilliQ water. A stirring bar was added, the vial was closed with a screw cap and it was stirred for 72 h at 80 °C or during one month at 23 °C. Afterwards, the product was centrifuged for 10 min at 3000 rpm and the aqueous phase was removed and its metal content was measured by TXRF. With this procedure, a very intense pink colored solution of pH = 2.43 was obtained. No iron was detected in this solution. The *percentage extraction in the leachate* (%E_L) is defined as:

$$\%E_L = \frac{\text{Amount of metal in the leachate}}{\text{Total amount of metal in the leachate and precipitate}} \times 100$$

(1)

Solvent extraction

As the volume of leachate obtained was not enough to carry out all the optimization experiments, a synthetic solution mimicking the concentrations obtained in the selective leaching of rare-earth elements from the roasted NdFeB magnet was prepared. Neodymium(III) nitrate hexahydrate, dysprosium(III) nitrate hexahydrate and cobalt(II) nitrate hexahydrate were dissolved in MilliQ water and acidified with HNO_3 6.5% to pH =

2.0. The final concentrations of these solutions were: 248.54 g L^{-1} of Nd(III), 21.41 g L^{-1} of Dy(III) and 4.37 g L^{-1} of Co(II). To optimize the extraction procedure, the efficiency of the extraction was evaluated in terms of different parameters, such as temperature, concentration of ammonium nitrate, extraction time, effect of the pH, scrubbing agent, selective stripping agent, stirring rate and concentration of EDTA in the case of the separation of neodymium and dysprosium. Only one parameter was varied at the time while keeping the other variables constant.

Determination of the efficiency of the extraction. The concentration of Co(II), Nd(III) and Dy(III) distributed between the organic and the aqueous phases was measured using TXRF. The *distribution ratio* (D) is defined as follows:

$$D = \frac{[M]_{org}}{[M]_{aq}} = \frac{[M]_0 - [M]_{aq}}{[M]_{aq}} \times \frac{V_{aq}}{V_{org}} \quad (2)$$

where $[M]_0$ is the initial metal ion concentration in the aqueous phase. $[M]_{aq}$ is the metal ion concentration in the aqueous phase after the extraction, and V_{org} and V_{aq} are the volumes of the organic and aqueous phases, respectively. In these experiments, equal volumes of organic and aqueous phases have been employed, thus the eqn (2) can be simplified to:

$$D = \frac{[M]_0 - [M]_{aq}}{[M]_{aq}} \quad (3)$$

For poorly extracted metals, the metal concentration in the organic phase was measured and the distribution ratio (D) can be expressed as:

$$D = \frac{[M]_{org}}{[M]_0 - [M]_{org}} \times \frac{V_{aq}}{V_{org}} \quad (4)$$

The *percentage extraction* (%E) is defined as the amount of metal ion extracted to the organic phase over the initial amount of metal ion in case of equal volumes and can be expressed as:

$$\%E = \frac{[M]_0 - [M]_{aq}}{[M]_0} \times 100 \quad (5)$$

The efficiency of the separation of two metals can be described with the *separation factor* α, in which D_{M_1} and D_{M_2} correspond to the distribution ratios D of metal M_1 and M_2, respectively:

$$\alpha_{M_1 M_2} = \frac{D_{M_1}}{D_{M_2}} \quad (6)$$

For the scrubbing experiments, the *percentage recovery* (%S) can be defined as the amount of metal scrubbed from the organic phase to the total amount of metal in the organic phase before scrubbing.

$$\%S = \frac{V_{aq}[M]_{aq}}{V_{org}[M]_{org0}} \times 100 \quad (7)$$

where $[M]_{org,0}$ is the metal ion concentration in the organic phase after extraction or before stripping. This formula can be used for both scrubbing and stripping experiments.

Separation of Co(II) from Nd(III) and Dy(III). All extraction experiments were carried out with a pH = 2 water saturated trihexyl(tetradecyl)phosphonium nitrate as organic phase unless stated otherwise. Extractions were performed at 60 °C with intensive shaking (1900 rpm) during 1 h. 10 M NH_4NO_3 was used as source of nitrate ions. After the extraction, the phases were separated by centrifugation at 5000 rpm during 1 min and afterwards they were measured by TXRF. The ratio between the volumes of the organic and the aqueous phase was 1:1.

Scrubbing. The scrubbing experiments were carried out at 80 °C, during 90 min with intensive shaking (1900 rpm). A 10 M solution of NH_4NO_3 was used as scrubbing agent. The ratio between the volumes of the organic and the aqueous phase was 1:1. After the extraction, the samples were centrifuged at 5000 rpm during 1 min and the phases were separated immediately. The metal concentrations in both organic and aqueous phases were measured by TXRF.

Purification of the separated cobalt and obtention of cobalt(II) oxide (CoO). In order to remove the small impurities of neodymium and dysprosium that still could have been present after the separation, the aqueous phase was put in contact with fresh ionic liquid and shaken at 60 °C, during 1 h at 1900 rpm. After the extraction, the phases were immediately separated. Then, a stoichiometric amount of oxalic acid in solution was added to the purified aqueous phase containing the separated cobalt(II). The mixture was shaken during 10 min and then settled during 5 min, afterwards it was centrifuged at 5000 rpm for 1 minute. The white precipitate obtained was filtered and washed twice with 1 mL of water and 1 mL of ethanol. Then, transferred into a previously tared crucible and calcined at 950 °C during 4 h to obtain the corresponding CoO. The purity of the obtained oxide was measured by TXRF. XRD was carried out to confirm that the obtained oxide corresponded to CoO.

Loading. For the loading experiments, the metal concentrations in the aqueous phases were 92.0 g L^{-1} of neodymium and 91.2 g L^{-1} of dysprosium. The volume of the aqueous phase was 1 mL and the concentration of NH_4NO_3 was 10 M. The amount of organic phase was varied between 0.4 and 1.6 g for neodymium and between 0.4 and 1.8 g for dysprosium. Extractions were performed for 1 h and 30 min at 70 °C and 1900 rpm. After the extraction, the samples were centrifuged for 1 min at 5000 rpm and the aqueous phase was separated immediately and measured by TXRF.

Separation of Co(II) from Nd(III) and Dy(III)

Selective stripping of Dy(III). A synthetic solution containing only Nd(III) and Dy(III) was prepared (pH = 2). The water-saturated ionic liquid was loaded with this solution in order to obtain the following concentrations in the organic phase, 58.1 g L^{-1} for Nd and 5.5 g L^{-1} for Dy. The ionic liquid was loaded following the same procedure employed for the separation of Co(II) from Nd(III) and Dy(III). For the selective strip-

ping of Dy(III) from the organic phase containing both Nd(III) and Dy(III), a solution of Na$_2$EDTA (0.03 M) and NH$_4$NO$_3$ (10 M) was employed as stripping agent. The experiments were performed at 70 °C during 1 h with vigorous shaking (1900 rpm). After the extraction the phases were separated by centrifugation at 5000 rpm during 1 min and both, organic and aqueous phases were measured by TXRF. The selective stripping with Na$_2$EDTA (0.03 M) and NH$_4$NO$_3$ (10 M) was repeated twice in order to remove the remaining dysprosium and allow the obtention of pure neodymium.

Precipitation stripping of neodymium and obtention of Nd$_2$O$_3$. The cleaned organic phase (after the two scrubbing steps) was put in contact with 1 mL of a solution 76 g L^{-1} of oxalic acid and shaken for 10 min at 22 °C. As soon as the oxalic acid solution was put in contact with the ionic liquid phase the formation of a white precipitate was observed. After the stripping precipitation, the samples were centrifuged and the organic phase was carefully removed. The aqueous phase, containing the precipitate, was filtered and the solid was washed twice with 1 mL of water and then with 1 mL of ethanol. The solid was put into a previously tared crucible and then calcined at 950 °C during 4 h. A light blue powder was obtained and it was analyzed by TXRF and XRD.

Purification of the selectively stripped Dy(III). The aqueous phase containing dysprosium after the selective stripping with EDTA also contains a considerable amount of neodymium, this is inevitable due to the high percentage of neodymium that is present in the magnet and the low amount of dysprosium. In order to purify this dysprosium, 50 μL of 16% HNO$_3$ was added to the aqueous phase and it was put in contact with 1 mL of fresh ionic liquid and shaken at 70 °C during 1 h at 1600 rpm. In order to achieve a purity of dysprosium higher than 99% this procedure had to be repeated three times.

Obtention of Dy$_2$O$_3$. Once the dysprosium has been purified, the aqueous phase can be treated with a stoichiometric amount of oxalic acid in order to precipitate dysprosium(III) oxalate and recover the supernatant that contains the EDTA which can be reused in the system as stripping agent. The white precipitate corresponding to the dysprosium oxalate was filtered, washed with 1 mL of water and 1 mL of ethanol and then calcined at 950 °C during 1 h. A white powder was obtained and it corresponded to Dy$_2$O$_3$ according to XRD.

Recycling of the ionic liquid. Once the process is finished and neodymium is removed from the ionic liquid by precipitation stripping, the ionic liquid can be equilibrated with MilliQ water and reused in a new cycle of separations. If an excess of oxalic acid is employed during the precipitation stripping of neodymium, the ionic liquid has to be pre-treated before its reutilization. An easy and green way to purify the ionic liquid is to precipitate the excess of oxalic acid with calcium nitrate. 1 mL of a 1 M solution of calcium nitrate was put in contact with the ionic liquid and shaken during 20 min at 70 °C and 1600 rpm. Afterwards, a white precipitate was obtained and removed after centrifugation. The ionic liquid was then equilibrated with water and reused again without losing its efficiency.

Results and discussion

Obtention of the leaching solution

Two different methods were employed in order to carry out the extraction of rare earths from used NdFeB magnets: leaching of pristine magnets and leaching of roasted magnets The selective leaching from the roasted magnet led to solutions rich in rare earths in which iron was not detected. Table 2 shows the %E obtained with the two proposed methods, where it can be seen that the magnet dissolution process is not as efficient and convenient as the selective leaching starting from the roasted magnet. The standard reduction potential for iron(III) is more positive than for iron(II),[34] thus during the dissolution of the magnet alloy, iron will go in solution as Fe(II). Indeed, the presence of iron(II) into the solution leads to the formation of NO during the dissolution process. The overall reaction is described as follows

$$3Fe^{2+} + 4H^+ + NO_3^- \rightleftharpoons 3Fe^{3+} + 2H_2O + NO \qquad (8)$$

Different nitrogen oxides, besides NO can be formed during the process: NO$_2$, N$_2$O$_4$, and N$_2$O$_3$.[35] NO$_2$ is a reddish brown toxic gas and air pollutant. NO and NO$_2$ are known for being ozone-depleting substances.

The possibility to obtain iron-free leachates from the roasted NdFeB magnets has been already discussed in detail by Vander Hoogerstraete et al.[33] Briefly, as a result of the magnet roasting process, iron is present immediately as Fe(III) and will go into solution as Fe(III), then it will be hydrolyzed to Fe(OH)$_3$ when the pH of the leachate rises to pH values above 2. The latter precipitates easily at this pH whereas the rare-earth metal ions stay in solution. In contrast, the dissolution of the non-roasted magnet leads to the formation of hydrated Fe^{2+}, which is more difficult to hydrolyze than hydrated species of Fe^{3+} and thus it remains in solution with the rare-earth metal ions.

The presence of iron in the leachate obtained from the non-roasted magnet represents an interference for the proposed extraction method with ionic liquids because it leads to the formation of undesired precipitates. For instance, after the

Table 2 Percentages extraction in the leachate (%E_L) of the different metals from the dissolution of the non-roasted magnet and the selective leaching of the roasted magnet

Process	Temperature (°C)	Time	%E_L			
			Fe(III)	Co(II)	Nd(III)	Dy(III)
Selective leaching from the roasted magnet	80.0	72 h	N.D.[a]	14.6	83.3	78.3
	22.5	2 weeks	N.D.[a]	3.72	47.5	42.2
	22.5	6 weeks	N.D.[a]	12.7	85.5	77.9
Dissolution of the non-roasted magnet	80.0	72 h	23.1	20.7	37.7	21.0
	22.5	2 weeks	6.8	4.9	19.9	14.7

[a] N.D. Non detected.

extraction procedure from the solution obtained by dissolution of the magnet, the presence of a yellowish precipitate was observed at the liquid–liquid interface making it difficult to obtain two clean and separated phases. Formation of iron (hydr)oxide precipitates during extraction processes with ionic liquids have been previously reported and confirmed by TXRF analysis, this is due to acid extraction by the ionic liquid which conduces to an increase of the pH.[29] In order to overcome this issue, it was required to precipitate the iron present in the solution before carrying out the liquid–liquid extraction.

In a first approach, the iron was precipitated by the direct addition of an ammonia solution to the leachate obtained from the non-roasted magnet powder. This led to a brown gelatinous precipitate that was difficult to filtrate and manipulate. Alternatively, many different procedures for the precipitation of iron oxides have been described in detail.[36,37] Different factors such as temperature, pH, the employed base and its concentration, stirring rate, precipitation and ageing times play a key role in the obtention of easily filterable precipitates. The solution was oxidized with hydrogen peroxide and taken to a final pH of 4 with NaOH. The precipitate formed was then removed by filtration and the resulted pink diluted solution was employed for the extraction of rare-earth ions with positive results as no precipitate was observed between the phases. Synthetic iron oxides are of importance because they have a wide range of applications in industry, as pigments, catalysts, sensors and biomedicine, among others.[36] Thus, it is useful to identify the iron oxide phases present in the obtained precipitate. The precipitated iron was analyzed by XRD, founding that it consisted of amorphous goethite (α-FeOOH) and probably iron hydroxide.

It is well known that iron(III) oxyhydroxides have large surface areas and can be effective scavengers of metal ions and oxyanions.[37–39] For this reason, the rare earths that may have been adsorbed onto the precipitate were quantified. The loss of rare earths and cobalt during the precipitation of iron from the dissolution of the non-roasted magnet was equal to 1.5% for Nd, 1.9% for Dy and 1.2% for Co. Even though these are not critical losses, the precipitation of iron by the slow addition of 1 M NaOH requires large volumes of NaOH, and as a consequence dilutes the sample to concentrations that are not of interest for this study.

Taking into account that the oxides of the magnet alloy are less reactive than the magnet powder, it is easier, safer and environmentally friendlier to carry out the selective leaching of roasted magnets rather than the dissolution process with nitric acid. Even though the selective leaching procedure from roasted magnets can be energy consuming (72 h at 80 °C or 1 month at room temperature), it allows the production of iron-free leachates rich in rare earths that can be directly employed in a solvent extraction process without the need of adding extra steps for the separation of iron by solvent extraction or by precipitation prior the separation of rare earth elements into individual elements. Therefore, iron-free leachates obtained from roasted magnet powder were used for testing the optimized separation system in Co(II), Nd(III) and Dy(III) separation.

Separation of Co(II) from Nd(III) and Dy(III)

The effect of different variables such as, feed solution concentration, extractant concentration, extraction time, shaking speed, pH and time, were optimized by the "one variable at a time" method. This optimization was carried out with solutions that mimicked the concentration of rare-earth ions in the obtained iron-free leachates. The first parameter studied was the effect of the concentration of the feed solution. Fig. 1 shows the variation of the extraction percentage with respect to the dilution of the initial concentrated feed of Co(II), Nd(III) and Dy(III). At very high concentrations (as the obtained leachate) and where no dilution was carried out, the efficiency of the extraction is relatively low, 80.5% for Nd(III) and 76.4% for Dy(III). When the synthetic solution is diluted with MilliQ water (dilution factor of two), the extraction efficiency increases (i.e. 96.9% and 94.6% for Dy(III) and Nd(III), respectively, $\alpha_{Nd/Co}$: 590, $\alpha_{Dy/Co}$: 500). However, as for industrial applications it is more interesting to work with concentrated feed solutions rather than diluted ones, the synthetic solution was diluted only twice for the rest of the optimization experiments even though more diluted solutions presented higher rare-earth extraction percentages.

It is important to notice that when using low feed solution concentrations, the percentage extraction of cobalt into the ionic liquid increases. The latter occurs when the ionic liquid is not saturated with rare-earths ions and part of the cobalt can be solubilized in the water-saturated ionic liquid. Still the small percentage of cobalt that can be solubilized into the ionic liquid can be removed afterwards during the scrubbing step.

The separation of Co(II) from Nd(III) and Dy(III) was also performed at different temperatures, ranging from 40 °C to 80 °C, to determine the influence of the temperature on the extraction process (Fig. 2). Higher temperatures provided better
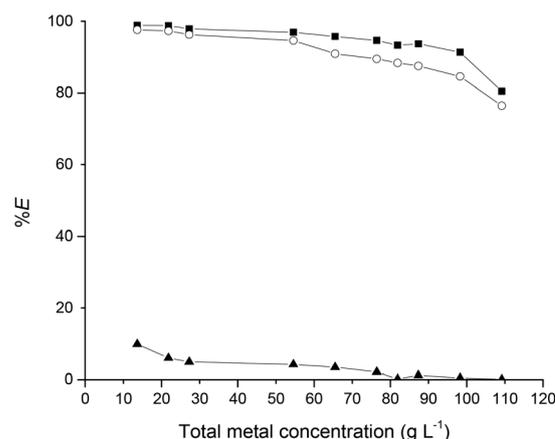
Fig. 1 Percentage extraction (%E) of cobalt (▲), neodymium (■) and dysprosium (○) as a function of the total concentration of cobalt(II), neodymium(III) and dysprosium(III) together in the aqueous phase. Conditions of extraction: NH_4NO_3 8 M, equilibrium pH = 2, 1900 rpm, 60 min, 60 °C.
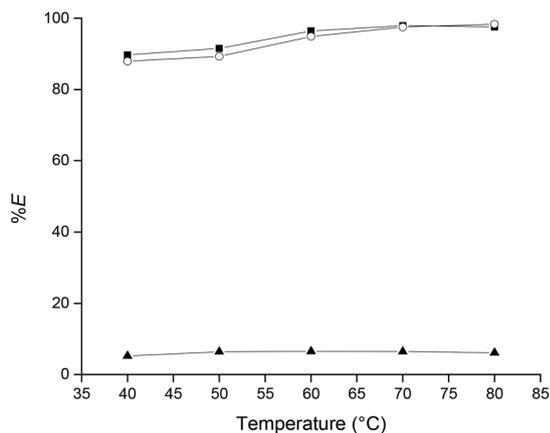
Fig. 2 Variation of the percentage extraction (%*E*) of cobalt (▲), neodymium (■) and dysprosium (○) as a function of the temperature. Conditions of extraction: equilibrium pH = 2, 1900 rpm, 60 min, concentration of NH_4NO_3 8 M.

extraction percentages for Nd(III) and Dy(III) as they shift the equilibrium of endothermic reactions to the right. On the other hand, high temperatures decrease the viscosity of the ionic liquid and facilitate the transfer of rare earth complexes into the organic phase. A value of 70 °C was chosen as optimal.

Furthermore, the ammonium nitrate concentration was evaluated for concentrations up to 10 M (Fig. 3). As expected, a higher amount of complexing agent led to a higher extraction percentage for both Nd(III) and Dy(III). The addition of concentrated NH_4NO_3 not only has a positive effect on the extraction percentage of the rare earth metals, but also avoids the formation of emulsions after the vigorous shaking during the extraction. An optimum value of 10 M NH_4NO_3 was chosen to carry out the further optimization experiments. Larger concen-

trations of NH_4NO_3 could not be obtained because it was not possible to solubilize the salt.
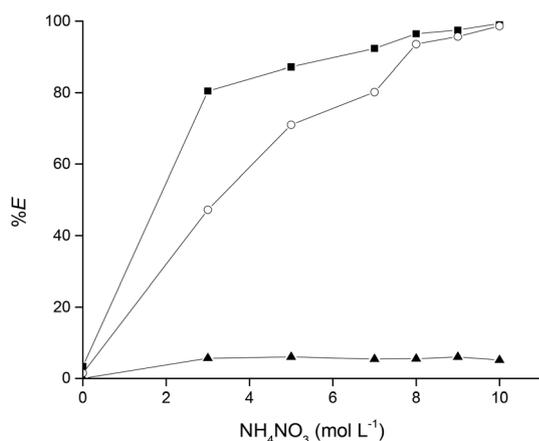
For the study of the pH effect on the extraction percentage of Nd(III) and Dy(III), different pH values between 0.25 and 6 were evaluated. The pH did not have a significant effect in the percentage extraction. However, it is important to remark that at pH values higher than 5.8, the rare earths were precipitated and therefore could not be separated and extracted. The influence of the extraction time was evaluated in the range of 10 to 120 min. The results show that by increasing the extraction time from 0 to 40 min, the percentage of extraction is considerably increased (Fig. 4). However, since only after an extraction time of 60 min equilibrium was reached, a time of 60 min was kept as optimal value.

In general, an increase in the shaking speed generates an improvement in the extraction rate of a process that involves mass transport features. The effect of the shaking speed was evaluated in the range of 0 to 2400 rpm. The extraction percentage becomes higher as the stirring speed increases. Still without mechanical shaking at high temperatures (70 °C), the ionic liquid can get dispersed into the aqueous phase favoring the diffusive processes and mass transport through the phases and thus relatively high percentages of extraction can be obtained. A shaking speed of 1600 rpm was chosen as the optimum value for this extraction process since at higher speeds no improvement of the extraction percentage was observed.

The viscosity of the water-saturated trihexyl(tetradecyl)phosphonium nitrate ionic liquid is 260 cP (at 22 °C), whereas the viscosity of the dried ionic liquid is 1440 cP (at 22 °C). Fig. 5 shows the variation of the water-saturated ionic liquid viscosity as a function of the metal loading at two different temperatures. It can be observed how the temperature has a dramatic effect on the viscosity of the ionic liquid. In this system, the viscosity can be decreased in almost a factor of 10 even at high metal loadings (109.2 g L^{-1}), while increasing the temperature

Fig. 3 Variation of the percentage extraction (%*E*) of cobalt (▲), neodymium (■) and dysprosium (○) as a function of the concentration of ammonium nitrate. Conditions of extraction: equilibrium pH = 2, 1900 rpm, 60 min, 70 °C.
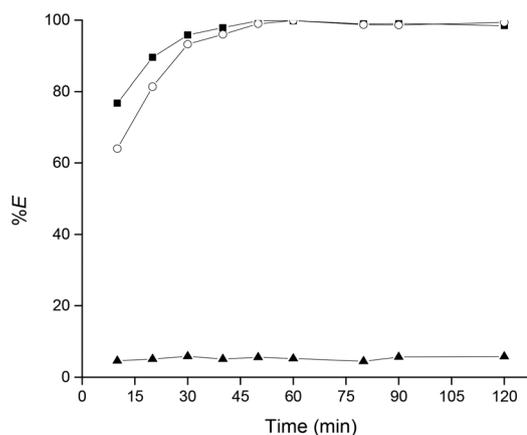
Fig. 4 Effect of the extraction time on the percentage extraction (%*E*) of cobalt (▲), neodymium (■) and dysprosium (○). Conditions of extraction: equilibrium pH = 2, 1900 rpm, 70 °C. NH_4NO_3 10 M.
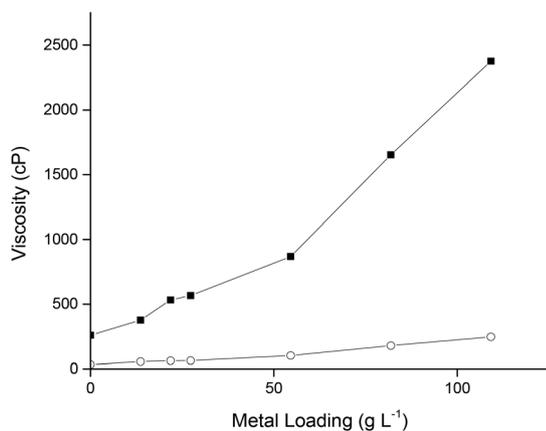
Fig. 5 Viscosity of the water-saturated ionic liquid trihexyl(tetradecyl)-phosphonium nitrate as a function of the total metal loading (Nd(III) and Dy(III)) at 23 °C (■) and at 70 °C (○).
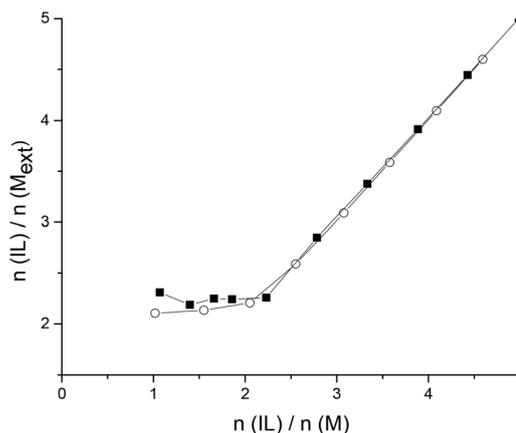
Fig. 6 The number of moles of IL over the number of moles of extracted metal (n(IL)/n(M_{org})) as a function of the number of ionic liquid equivalents added, at constant initial metal concentrations of neodymium, 1900 rpm, 120 min, 70 °C. Symbols: neodymium (■), dysprosium (○).

to 70 °C. This highlights the importance of working not only with water-saturated ionic liquids, but also at high temperatures in order to decrease the viscosity of the ionic liquid without the need of adding molecular solvents.

The principle of separation between Nd(III), Dy(III) and Co(II) is based on the fact that the trivalent rare-earth ions can form anionic complexes with bidentate nitrate ligands. Even though anionic complexes of cobalt with the above mentioned ligands can also be formed in organic solvents,[40] these are more labile to experience water exchange and form the more stable pink hexaaqua complex.[41] For this reason, negative charged complexes formed between the rare earths and the nitrate ions can be extracted into the ionic liquid. The general extraction mechanism for lanthanide extraction can be written as:

$$\mathrm{Ln^{3+} + 3NO_3^- + } n\overline{[P_{66614}][NO_3]} \rightarrow \overline{[Ln(NO_3)_{3+n}][P_{66614}]_n} \quad (9)$$
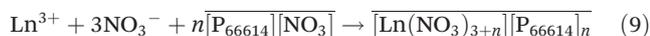
The maximum metal loading experiments (Fig. 6) were carried out for the individual elements. The concentration of Nd(III) and Dy(III) was kept constant and the amount of ionic liquid was increased. When the number of ionic liquid equivalents in the separation system is less than two, the molar ratio of the ionic liquid over the number of moles of neodymium or dysprosium extracted in the ionic liquid phase remained almost constant at a value of two. This means that the anionic nitrate complexes of Nd(III) and Dy(III) are extracted formed by two molecules of ionic liquid at maximum loadings, as indicated in eqn (10) and (11).

$$\mathrm{Nd(NO_3)_3 + } \overline{2[P_{66614}][NO_3]} \rightarrow \overline{[P_{66614}]_2[Nd(NO_3)_5]} \quad (10)$$

$$\mathrm{Dy(NO_3)_3 + } \overline{2[P_{66614}][NO_3]} \rightarrow \overline{[P_{66614}]_2[Dy(NO_3)_5]} \quad (11)$$
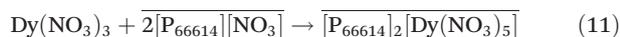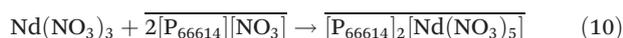
As it can be seen in Fig. 4, a low percentage of cobalt(II) is still extracted into the ionic liquid together with Nd(III) and Dy(III). Thus, the implementation and optimization of a scrubbing step for the removal of the remaining cobalt is necessary.

The following parameters have been optimized for the scrubbing step: shaking speed, concentration of ammonium nitrate, scrubbing time and pH effect. The effect of the NH₄NO₃ concentration in the scrubbing step is shown in Fig. 7. An increase in the concentration of the salting-out agent generates higher extraction percentages for the back-extraction of the remaining Co(II) present in the organic phase. These percentages of extraction remained almost constant when the NH₄NO₃ concentration was varied between 7 and 10 M. However, when using high concentrations of NH₄NO₃ less Dy(III) and Nd(III) were back-extracted. For this reason, all further scrubbing experiments were carried out using 1 mL of a 10 M NH₄NO₃ solution. Under optimum conditions, Nd(III) and Dy(III) were only back-extracted in extraction percentages of 0.38% and 0.35%, respectively.
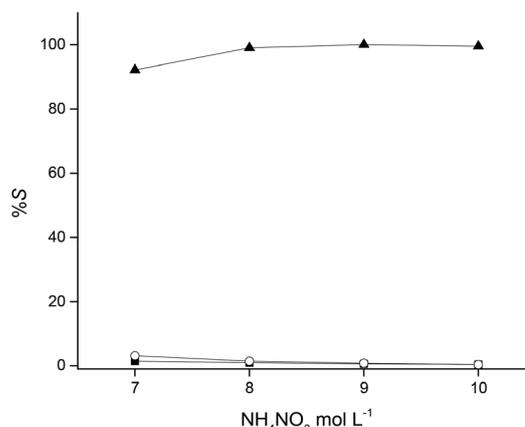
Fig. 7 Percentage scrubbing of cobalt (▲), neodymium (■) and dysprosium (○), during the scrubbing step as a function of the concentration of ammonium nitrate. 120 min, 70 °C, 1600 rpm.
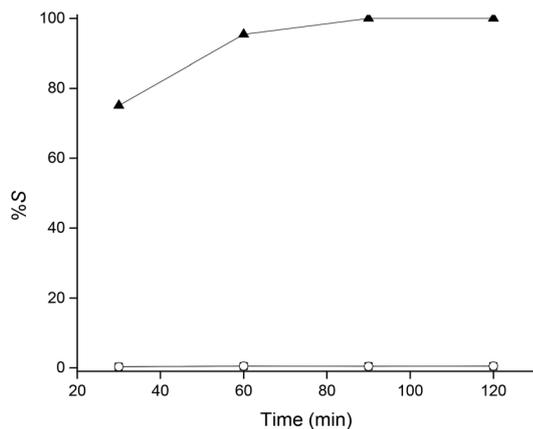
Fig. 8 Percentage scrubbing of cobalt (▲), neodymium (■) and dysprosium(○) from the ionic liquid during the scrubbing as a function of the scrubbing time. 70 °C, 1600 rpm. NH_4NO_3 10 M.

Moreover, the purity of the cobalt extract can be further increased by putting the scrubbing aqueous solution containing Co(II) in contact with fresh ionic liquid. Thus a complete removal of Nd(III) and Dy(III) can be achieved. As shown in Fig. 8, longer times are required to achieve the total removal of cobalt(II) from the ionic liquid. This can be explained due to the fact that the viscosity of the ionic liquid loaded with big amounts of Nd(III) and Dy(III) is higher than for the free ionic liquid. Higher temperatures can also be employed, in order to reduce scrubbing times. However, this is not convenient for the scaling up of the process because it would be ideal to have all the extractors working at the same temperature (*e.g.* for simplicity and to avoid losses of heat due to fluctuations in the temperature). A time of 90 min was chosen as the optimum value for the removal of Co(II) from the organic phase.

As it was previously described in the Experimental section, the separated and purified cobalt was recovered by precipitation with oxalic acid and posterior calcination to the corresponding CoO, as it was corroborated by XRD. The purity of the obtained oxide, measured by TXRF was 99.8%, with a yield of 99.4% and Nd as the main impurity.

Separation of Nd(III) and Dy(III)

After having separated and purified cobalt from the magnet leachate, the selective separation between the remaining Dy(III) and Nd(III) has to be performed. With this aim, one can take advantage of the difference in the stability constant that Dy(III) and Nd(III) have for the formation of complexes with EDTA (*i.e.* logarithms of stability constants: 18.0 for Dy(III) and 16.2 for Nd(III))[42] Indeed, as the affinity of Dy(III) for the EDTA is slightly higher than for Nd(III) this can be used to carry out the stripping of Dy(III) from the organic phase. Chelation with EDTA has been employed for the extraction and separation of rare earths.[15,43–45] To explore this possibility, the concentration of EDTA (dissolved as the disodium salt) was varied between 0 and 0.1 M (based on the stoichiometric amount of Dy(III)

present in the ionic liquid), while keeping the concentration of NH_4NO_3 constant at 10 M. The presence of NH_4NO_3 avoided the back-extraction of the Nd(III) into the aqueous phase. As depicted in Fig. 9, Dy(III) can be selectively stripped from the organic phase at an EDTA concentration of 0.03 M (and 10 M of NH_4NO_3) with an efficiency of 58.9%. It is important to notice that only a 2.3% of Nd(III) is back-extracted during this procedure.

When only EDTA is employed in absence of NH_4NO_3, no selectivity is achieved for the back-extraction of the rare earths ions. Similar results are observed when only NH_4NO_3 is present at different concentrations and no EDTA is employed.

The temperature effect on the selective stripping of Dy(III) was also studied in the range of 50 to 80 °C. A temperature of 70 °C was chosen since it allowed the obtention of relatively high and low stripping percentages for Dy(III) (79.8%) and Nd(III) (4.0%), respectively. As 70 °C is also the optimized temperature for the other steps, an easier temperature control can be envisaged at a scaled up stage. Another parameter studied for the stripping of Dy(III) was the initial pH in the aqueous phase, which was varied between 0.75 and 7.5. The obtained results show that the pH does not have any direct effect in the selective stripping of dysprosium(III) when working with a pH from 2.5 to 7. Moreover, it was observed that at pH values higher than 7.5, the extraction could not be carried out because of the formation of a large amount of precipitate. At pH values lower than 2.5, no formation of precipitate was observed, but the stripping efficiency decreased due to the competition of H^+ ions with the rare-earth metal ions for the EDTA.

The stripping time was also evaluated within the range of 5 to 80 min. As the complexation of rare earths with EDTA is fast, it is only required an extraction time of 30 min to carry out this step efficiently (Fig. 10).
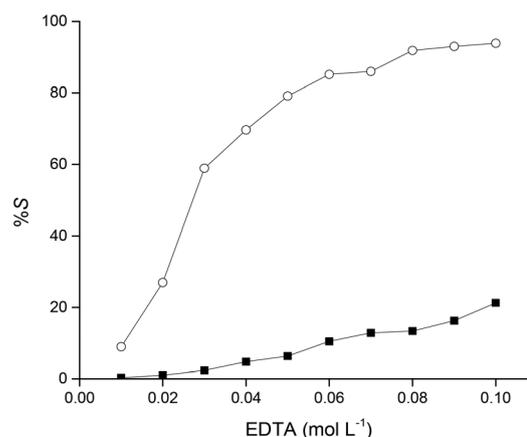
Fig. 9 Selective stripping percentage of neodymium (■) and dysprosium (○) as a function of the concentration of EDTA. NH_4NO_3 10 M, shaking speed: 1400 rpm, pH = 5 (initial pH in the aqueous phase) 60 °C.
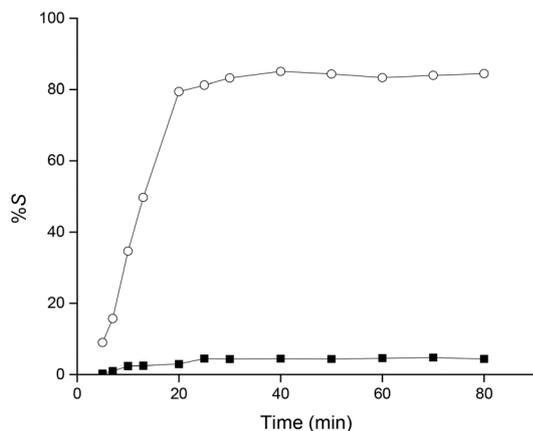
Fig. 10 Effect of the scrubbing time in the percentage of selective stripping of Dy(III) (○) and Nd(III) (■). EDTA 0.03 M, NH$_4$NO$_3$ 10 M, Shaking speed: 1400 rpm, pH = 5 (initial pH in the aqueous phase), 70 °C.

In order to remove the remaining Dy(III) present in the ionic liquid, two more selective stripping steps have to be performed with EDTA and NH$_4$NO$_3$. Once the ionic liquid only contains Nd(III), it can be recovered by adding an oxalic acid solution that leads to the formation of a light pink precipitate. Indeed, in only 8 min (at room temperature) the Nd(III) is quantitatively precipitated as the respective oxalate.

$$2Nd^{3+} + 3H_2C_2O_4 \rightarrow Nd_2(C_2O_4)_3 + 6H^+ \qquad (12)$$
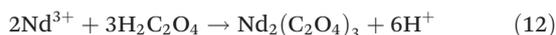
It was found that a stoichiometric amount of oxalic acid is required (*i.e.* $n(C_2O_4^{2-})/n(Nd^{3+}) = 1.5$) to carry out an effective precipitation of Nd(III) (Fig. 11).

The obtained precipitate was washed and calcined. The purity of Nd$_2$O$_3$ was determined by TXRF and it was found to be 99.6% with the dysprosium as the only impurity. The yield corresponded to 99.3% and it was calculated once the whole process was carried out and all the fractions of neodymium were collected and put together.
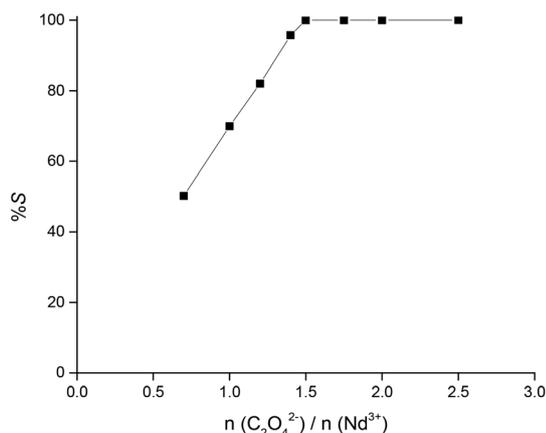
Until this point, two of the three major elements in the original leachate have been purified and isolated as oxides. Then Dy(III) remains in the aqueous phase as an EDTA complex. As the magnet is rich in neodymium and has a low amount of dysprosium, it is inevitable that some neodymium also gets back-extracted during the stripping of dysprosium. Even though the stripping percentage of neodymium is low, as it is shown in Fig. 10, this is relative because the initial amount of neodymium in the ionic liquid phase is 1000 times larger than the amount of dysprosium. This means that the aqueous phase obtained after the stripping of dysprosium contains a mixture of dysprosium and neodymium that has to be separated through another solvent extraction process. As [Nd(EDTA)]$^-$ is a less stable complex than [Dy(EDTA)]$^-$, it can be dissociated by the addition of HNO$_3$ to the aqueous phase, and the Nd(III) that is released can be complexated by the nitrate ions that are present in the ionic liquid. As a result, neodymium(III) can be re-extracted into fresh ionic liquid. This process was optimized in terms of time, concentration of HNO$_3$ and volume of HNO$_3$. The optimum conditions found were 20 minutes of extraction time, 16% wt/wt HNO$_3$, and 50 μL of HNO$_3$. Fig. 12 shows the effect of the volume of HNO$_3$ added to the aqueous phase on the extraction percentage of Nd(III) and Dy(III).

This process was carried out three times (in total) in order to remove all the remaining Nd(III), which was further precipitated from the ionic liquid and calcined as described above. The purified Dy(III) in the aqueous phase was precipitated as oxalate and calcined as well. After all the fractions were collected and reunited, Dy$_2$O$_3$ was obtained, as confirmed by XRD. The purity of the oxide was analysed by TXRF (99.8%) and the yield of the process was 99.1%.

Finally, free-iron leachates obtained from roasted NdFeB magnets were employed as feed solutions for the separation of

Fig. 11 Effect of the ratio $n(C_2O_4^{2-})/nNd^{3+}$ on the percentage of precipitation stripping of Nd(III) from the ionic liquid phase. Shaking speed: 1600 rpm, 23 °C, time: 10 min.
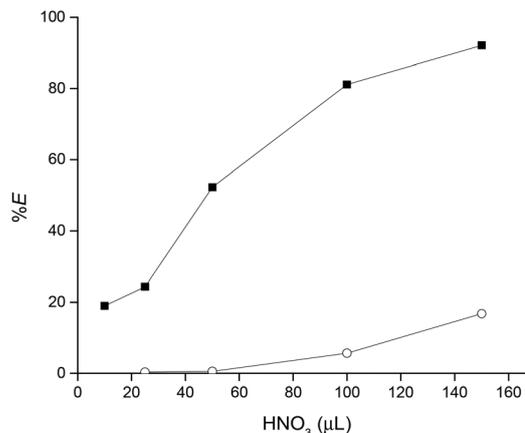
Fig. 12 Effect of the volume of nitric acid (16 wt%) added to the aqueous phase on the percentage of extraction of Dy(III) (○) and Nd(III) (■). Shaking speed: 1600 rpm, 70 °C, 40 min.

Table 3 Percentage of extraction and purity of the oxides obtained when applying the optimized system to leachate samples

Leachate	Yield Nd_2O_3 (%) (purity %)	Yield Dy_2O_3% (purity %)	Yield CoO % (purity %)
Selective leachate at 80 °C	99.2 (99.7)	99.1 (99.8)	99.6 (99.6)
Selective leachate at 22.5 °C	99.3 (99.6)	99.2 (99.6)	99.4 (99.8)

rare earths by using the herein implemented liquid–liquid extraction process. The employed experimental conditions corresponded to the optimum ones determined previously with the synthetic solution. The obtained results are summarized in Table 3. High extraction percentages and high rare-earth metal oxide purities were obtained when using the iron-free leachates. For instance, no other impurities were detected on the obtained final oxides, as the concentration of other metals in the starting material was considerably low.

Recycling and recirculation of solvents and reagents is of importance in the industry from both environmental and economic points of view. With this aim, the ionic liquid was recovered and recycled. Once the metals present in the ionic liquid were precipitated with a stoichiometric amount of oxalic acid, then the ionic liquid was washed once with MilliQ water and equilibrated at the desired pH. Table 4 summarizes the results obtained for the recycling of the ionic liquid. Three cycles were carried out for the separation of cobalt(II), neodymium(III) and dysprosium(III), the ionic liquid was recovered almost completely after each extraction and it was successfully employed in new cycles of separation without affecting the extraction percentages.

It has to be mentioned that when excesses of oxalic acid are used for the precipitation stripping, the oxalic acid has to be removed first from the ionic liquid in order to avoid precipitation of the rare earths once a new cycle of separations is started. Two methods were tested for the purification of the ionic liquid; the first one comprehends the dilution of the ionic liquid into dichloromethane or toluene and the posterior acid–base extraction with sodium hydroxide. In the second one, the excess of oxalic acid is precipitated with calcium nitrate and then removed after centrifugation. Even though both ways allow the recuperation of the ionic liquid and its reuse without affecting its efficiency, the second option is easier to carry out and offers an environmentally friendlier approach since it does not involve the use of molecular solvents.

After the precipitation of dysprosium with oxalic acid, the solution containing EDTA and ammonium nitrate can be recycled. The extraction percentages varied (4.2% for Nd(III), 79.1% for Dy(III) with fresh solution) and (4.5% for Nd(III), 73.8% for Dy(III) with recycled solution). In the same way, the nitric acid employed for the preparation of the leachate can be recovered for its utilization in a new leaching once the cobalt has been precipitated.

Recycling of magnets has a lower environmental impact than mining.[46] Even though the separation of transition metals and rare earths is just a part of the process of the complete recycling chain of NdFeB magnets, it constitutes an important step that can be performed efficiently with more environmental friendly ionic liquids and precipitation stripping methods. Moreover, ionic liquids can be reused without affecting considerably the overall process efficiency. Additionally, phosphonium ionic liquids with nitrate anions, as the one employed in the present work, are not expensive (in comparison to other ionic liquids) and for instance have already been produced in large quantities.[31] With the proposed processes, elements that are required by the industry and usually end up in landfills can be recovered and processed for its use again in NdFeB magnets or any industry requiring of rare-earth elements.

Conclusions

The ionic liquid trihexyl(tetradecyl)phosphonium nitrate was employed successfully for the liquid–liquid separation of cobalt, neodymium and dysprosium. An efficient and easy to carry out process herein proposed, allowed the recovery of highly valuable metal oxides with high purities, CoO (99.8%), Nd_2O_3 (99.6%), Dy_2O_3 (99.8%). This process was successfully tested in the separation of cobalt(II), neodymium(III) and dysprosium(III) from iron-free leachates in nitric acid. Therefore, it is compatible with the current industrial processes for the separation of rare earths that employ nitric acid leachates and also allows the convenient production of oxalates that can be calcined to produce the respective oxides.

The stripping precipitation consuming only oxalic acid is convenient for the posterior calcination of the products and the obtention of the oxides, as well as, the reuse of the ionic liquid. These oxides are key elements in the recycling chain of permanent magnets because they are the precursors of the alloys needed for the production of the recycled magnets.

The presented process for the separation and recovery of neodymium, dysprosium and cobalt opens the door for the exploration of new and greener systems for the recycling of rare earths in less steps than the currently employed without the use of harmful molecular solvents.

Acknowledgements

Table 4 Recycling of the ionic liquid and efficiency of the separation process using recycled ionic liquid

Recycle #	Yield Nd_2O_3 (%) (purity)	Yield Dy_2O_3% (purity)	Yield CoO % (purity)	Recovery of IL (%)
1	99.2 (99.7)	99.1 (99.8)	99.6 (99.6)	97.8
2	99.3 (99.7)	99.1 (99.6)	99.7 (99.5)	97.2
3	98.9 (99.6)	98.7 (99.6)	99.7 (99.6)	96.8

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