

Selective electrochemical extraction of REEs from NdFeB magnet waste at room temperature

Venkatesan, Prakash; Vander Hoogerstraete, Tom; Hennebel, Tom; Binnemans, Koen; Sietsma, Jilt; Yang, Yongxiang

DOI

[10.1039/c7gc03296j](https://doi.org/10.1039/c7gc03296j)

Publication date

2018

Document Version

Accepted author manuscript

Published in

Green Chemistry

Citation (APA)

Venkatesan, P., Vander Hoogerstraete, T., Hennebel, T., Binnemans, K., Sietsma, J., & Yang, Y. (2018). Selective electrochemical extraction of REEs from NdFeB magnet waste at room temperature. *Green Chemistry*, 20(5), 1065-1073. <https://doi.org/10.1039/c7gc03296j>

Important note

To cite this publication, please use the final published version (if applicable). Please check the document version above.

Copyright

Other than for strictly personal use, it is not permitted to download, forward or distribute the text or part of it, without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license such as Creative Commons.

Takedown policy

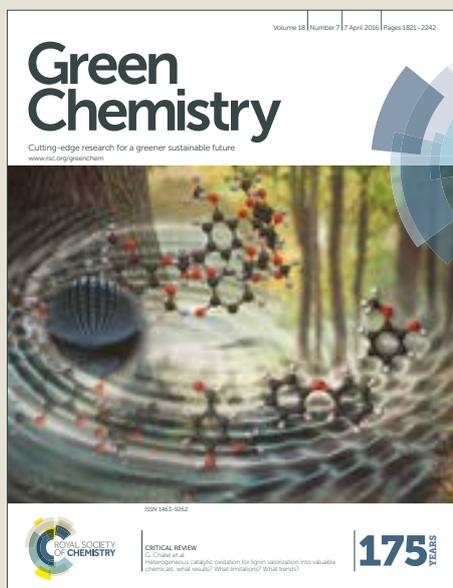
Please contact us and provide details if you believe this document breaches copyrights. We will remove access to the work immediately and investigate your claim.

Green Chemistry

Accepted Manuscript



This article can be cited before page numbers have been issued, to do this please use: P. Venkatesan, T. Vander Hoogerstraete, T. Hennebel, K. Binnemans, J. Sietsma and Y. Yang, *Green Chem.*, 2018, DOI: 10.1039/C7GC03296J.



This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the [author guidelines](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the ethical guidelines, outlined in our [author and reviewer resource centre](#), still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.



Journal Name

ARTICLE

Selective electrochemical extraction of REEs from NdFeB magnet waste at room temperature

Prakash Venkatesan^{a*}, Tom Vander Hoogerstraete^b, Tom Hennebel^c, Koen Binnemans^b, Jilt Sietsma^a, Yongxiang Yang^a

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x
www.rsc.org/

NdFeB magnet waste is one of the important secondary resources from which rare-earth elements (REEs) can be recovered. Herein we present an electrochemical route to selectively extract REEs from the magnet waste at room temperature. First, the magnet waste was partially leached with HCl. The partial leachate along with undissolved magnet waste were taken in the anolyte side of a two compartment reactor separated by an anion exchange membrane whereas the catholyte consisted of sodium chloride solution. The Fe(II) present in the leachate was oxidized and precipitated as Fe(OH)₃ while more than 95% of REEs were extracted into the solution. Subsequently, oxalic acid was used to selectively precipitate REEs as rare-earth oxalates. Hydrochloric acid liberated during the oxalic acid precipitation process could be directly reused in the partial leaching step. Sodium chloride was the only chemical consumed during the electrolysis. The effect of the NaCl concentration in the anolyte and catholyte on the extraction of metals was investigated. From magnet waste to rare-earth oxides, the developed recycling process is environmentally friendly and consumes only electricity, NaCl and oxalic acid.

Introduction

Rare earth elements (REEs) are used in variety of green technologies such as permanent magnets, electric vehicles, Ni-MH batteries and are instrumental in the progression towards a low carbon economy.^{1, 2} REEs are considered to be critical metals due to fragilities in the supply chain and increasing demand from clean energy applications.³⁻⁵ Primary mining of REEs leaves not only a large environmental footprint but also creates the “balance problem” where the more abundant cerium and lanthanum are stockpiled at the cost of neodymium, dysprosium and praseodymium.^{6, 7} Recycling REEs from end-of-life waste is one of the important strategies in addressing the balance problem, supply risks associated with REEs and in formulating a circular economic pathway for rare-earth metal production.⁸

NdFeB magnets have superior magnetic properties, consisting of 20-30 wt% of REEs and are an important secondary resource containing REEs.⁹ In 2014, 22% of rare-earth oxides produced globally were consumed for the production of NdFeB magnets

making them one of the largest applications among all REEs.¹⁰ Several reviews have summarized the recycling processes that have been developed thus far for recycling NdFeB magnets.¹¹⁻¹³ Hydrometallurgical recycling processes designed for NdFeB magnets are promising as they operate at room temperature, do not require complex setups and can be applied irrespective of the composition of the magnets.¹⁴⁻¹⁶ In hydrometallurgical processes, NdFeB magnets are completely leached with acid. These processes are unselective and iron, which is the major component of NdFeB magnets (60-70%), is co-extracted into the solution along with REEs. The leaching step is followed by precipitation step where REEs are selectively precipitated as rare-earth double sulfates or rare-earth fluorides. Complete acid dissolution of the industrial magnet waste requires around 15 moles of HCl per mole of REEs (nHCl/nREE) whereas complex end-of-life magnet waste requires 40 moles of HCl per mole of REEs.¹⁷ The whole process has many steps, consumes excess acid, alkali and other precipitation agents, that cannot be recycled.¹¹ The lack of selectivity between REEs and iron in the hydrometallurgical routes is due to the fact that iron leaches into the solution as Fe(II) which is a stable species until a pH of 6 and cannot be selectively precipitated. Recently, a chemical process¹⁵ and an electrochemical route¹⁸ were proposed to oxidize Fe(II) to Fe(III) at room temperature. After oxidation, Fe(III) was selectively and completely precipitated from the solution at a pH around 3 leaving only REEs in the solution. However, both the processes required complete and unselective dissolution of NdFeB magnets as the first step after which oxidation of Fe(II) to Fe(III) was performed.

^a Department of Materials Science and Engineering, TU Delft, 2628 CD Delft, the Netherlands

^b KU Leuven, Department of Chemistry, Celestijnenlaan 200F – P.O. Box 2404, B-3001 Heverlee, Belgium

^c Center for Microbial Ecology and Technology (CMET), Ghent University, Coupure Links 653, B-9000 Gent, Belgium

† Footnotes relating to the title and/or authors should appear here.

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

In contrast, in a pyrometallurgical process, REEs can be selectively leached from NdFeB magnet waste after a roasting pretreatment step.^{19, 20} Vander Hoogerstraete et al.²¹ designed a closed loop process in which magnets were oxidatively roasted to convert iron into Fe₂O₃ and REEs into rare-earth oxides. The roasted powder was then leached in near stoichiometric equivalent of acid for REEs ($n\text{HCl}/n\text{REE} = 3.5$) in which only REEs were selectively leached leaving out the iron as Fe(OH)₃. Subsequently, the acid used in the leaching step was recovered by precipitating REEs with oxalic acid. There was no net consumption of HCl in the whole process flow sheet. However, the roasting pretreatment step operates at 900 °C and is energy-intensive. Moreover, the selective leaching step was sluggish and required 5 days to completely extract the REEs even at 100 °C.

In this paper, we describe an electrochemical process to selectively recover REEs from NdFeB magnet waste. The proposed process happens at room temperature, with enhanced kinetics and with no net consumption of HCl. The magnet waste was treated in a simple two chamber membrane reactor separated by an anion exchange membrane. We investigated the effect of concentration of sodium chloride in both the anolyte and catholyte on the metal extraction and net energy consumption. The end product of mixed rare-earth oxides showed excellent purity (>99%) and can be directly used for metal production.

Experimental

Materials and methods

All chemicals are of analytical grade and were used without further purification. Sodium chloride (≥99%), ammonium acetate, ammonia solution (25% NH₃ in water), hydrochloric acid (37%), oxalic acid dihydrate (≥99%), ferrozine (monosodium salt hydrate of 3-(2-pyridyl)-5,6-diphenyl-1,2,4-triazine-p,p'-disulfonic acid), were purchased from Sigma Aldrich, B.V (Zwijndrecht, The Netherlands). The pH was measured by an Inolab 7310 pH meter (WTW, The Netherlands) with a Sentix 81 tip. A Universal 320R centrifuge (Hettich, The Netherlands) was used to separate the leachate from the precipitate. The magnet waste used in this study was supplied by Magneti (Slovenia). These bulk magnets are uncoated and failed the quality control step before getting magnetized. Thus, no demagnetization step was required. Ball-milling was performed at Umicore (Olen, Belgium) using a Retsch RS100 ball-mill for two hours to mill the bulk sintered magnets. Immediately after milling, the powder samples were directly divided into 3 gram subsamples and stored in a plastic vial to offset the effect of oxidation on the extraction efficiency calculations.¹⁹

Electrochemical reactor

The experiments were performed in a two compartment electrochemical reactor (two chambers each with internal dimension 8 cm × 8 cm × 2 cm with an effective volume of 128 mL). The compartments were separated by an anion exchange membrane (FAS-PET-130, anion exchange membranes, Fumatech, Germany). A stainless steel wire mesh was used as the cathode (Solana, Belgium) and a mixed metal oxide (35% Ta & 65% Ir) coated titanium electrode as the anode (Magneto Special Anodes BV, Schiedam, The Netherlands). A spacer material (ElectroCell A/S, Denmark) was placed between the surface of anode and the anion exchange membrane. The anode and cathode had a projected electrode surface area of 64 cm² each. All experiments were conducted using potentiostat Versastat 4 (Ametek, UK) and the data was obtained using Versastudio software. An Ag/AgCl (3M KCl) reference electrode was placed in the anode compartment. Both compartments were operated in batch mode at a temperature of 25±2 °C with an internal recirculation rate of 30 mL min⁻¹. The anolyte and catholyte consisted of 250 mL of leachate and NaCl solution, respectively. The liquids were pumped from two different Scott bottles that were stirred constantly at 300 rpm with a magnetic stirrer.

Analytical methods

The concentration of the elements was measured by ICP-OES (PerkinElmer Optima 3000DV). Samples (0.5 mL) withdrawn from the leachate were passed through a filter of syringe filter of 0.45 μm. The extraction efficiency (%) of any metal M was calculated by the equation:

$$\% E = \frac{M \text{ in leachate (ppm)} \times \text{Volume of leachate (ml)}}{100 \times M \text{ in magnet (\%)} \times \text{Amount of magnet used (g)}} \quad (1)$$

The chloride concentration was measured using a DX-120 Ion Chromatograph. The oxidation state of iron in the leachate was measured using the ferrozine colorimetric method.²² The concentration of Fe(II) was measured at wavelength 562 nm using UV-Vis spectrophotometer (Hitachi, U-2900). ICP-OES was used to measure the total concentration of Fe. The concentration of Fe(III) was calculated as the difference in concentration between total iron and that of Fe(II). After the electrolysis step, the precipitate was removed from the leachate by centrifugation. The iron(III) hydroxide precipitate was washed thoroughly and was completely dissolved in HCl (37%) for analysis.

The precipitates obtained after oxalic acid precipitation step were washed thoroughly with water and ethanol and calcined at 950 °C for 3 hours. X-ray diffraction was carried out using a Bruker D8 diffractometer with Cu Kα radiation operated at 45 kV. Rare-earth oxides obtained after calcination were dissolved in concentrated HCl (~37%) and their composition was measured with ICP-OES to determine the purity.

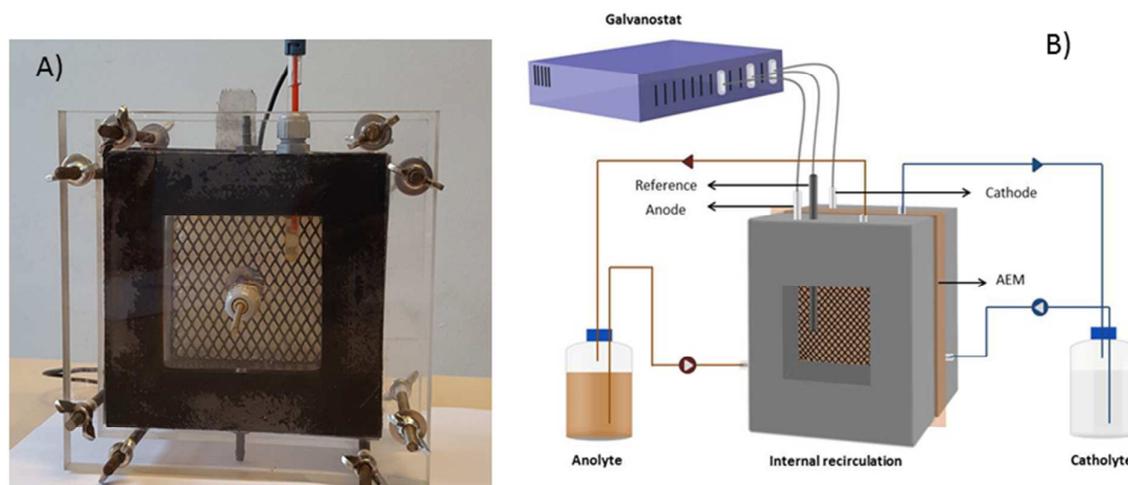


Fig.1 A) Photo and B) schematic illustration of the membrane electrochemical reactor

Results and discussion

Partial leaching of NdFeB magnets with HCl

The chemical composition of the NdFeB magnet waste is given in Table 1.

Table 1 Elemental composition of NdFeB magnets in wt%

Element	Content (wt%)	Element	Content (wt%)
Fe	63.54	Gd	0.15
Nd	22.21	Al	0.09
Dy	8.19	Cu	0.07
Co	2.99	Nb	0.06
B	1	Ni	0.04
Pr	0.76	Total	99.1

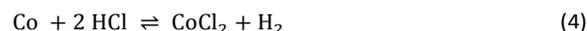
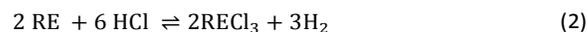
The industrial magnet waste has high dysprosium and low praseodymium content and is typically used for hybrid electric vehicles and electric motors. Neodymium, dysprosium, praseodymium, iron and cobalt form more than 98 wt% of the magnet waste, and are thus, the focus of this study. Several inorganic and even organic acids have been investigated for leaching NdFeB magnets.^{14, 16, 23} The solubility limits of rare-earth sulfates are low and thus, chlorides and nitrates are the preferred anions for downstream solvent extraction process.¹⁹ However, the oxidizing nature of nitrate anions was reported to interfere with the leaching process of NdFeB magnet waste with release of NO_x gases.²¹ Hence, HCl and a chloride system were chosen for this study.

A sample of 3 grams of magnet waste was first leached with HCl at a constant molar ratio of 3.5 between HCl to REEs ($n_{\text{HCl}}/n_{\text{REE}}$). The acid leaching was unselective and around 23±1.2 % of total magnet waste was extracted into the solution (Table 2). The partial leaching was complete within 60 minutes and was accompanied by a pH rise to 6.5±0.5. Speciation measurements of the obtained leachate with a UV-Vis spectrophotometer showed that ≥ 98.7% of iron leached was in the form of Fe(II).

Table 2 Percentage of extraction of different metals after partial leach of magnet waste with ($n_{\text{HCl}}/n_{\text{REE}} = 3.5$)

Elements	Extraction (%)
Fe	23.2
Nd	28.9
Dy	21.2
Pr	19.1
Co	36.4
Total magnet waste	23.1

The dissolution reactions of the important elements are:



Iron is the major component of the magnet waste and separation of REEs from iron forms the major part of NdFeB recycling. It is important to determine the speciation of iron in the leachate because first of all, Fe(II) remains in the solution as soluble species until a pH of 6.²⁰ Selective precipitation of

Table 3: Amount of iron extracted and % of Fe oxidized under different experimental conditions

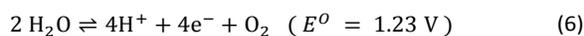
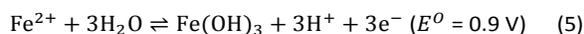
Current density (Am ⁻²)	Anolyte NaCl concentration (M)	Catholyte NaCl concentration (M)	Fe extracted (%)	Fe Oxidized (%)
40	0.2	0.6	27.1 ± 2.2	89.2 ± 1.6
50	0.2	0.6	39.2 ± 3.6	95.6 ± 0.7
75	0.2	0.6	52.3 ± 3.4	99.7 ± 0.3
125	0.2	0.6	54.1 ± 3.5	99.7 ± 0.3
125	0	0.6	56.2 ± 2.9	2.3 ± 0.6
125	0.2	0.05	0.1 ± 0.1	-
125	3.5	0.05	0	-
125	4.5	0.05	0	-

the REEs by addition of a neutralizing agent is not possible as both REEs and Fe(II) can undergo hydrolysis and co-precipitate. Secondly, addition of precipitating agents like oxalic acid is also problematic as iron(II) oxalate is also highly insoluble.^{18, 24}

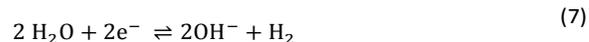
In contrast to Fe(II), Fe(III) can undergo hydrolysis at a pH of about 2 whereas REEs are stable until a pH of 6. To study the oxidation of Fe(II) under ambient conditions, a control experiment of leaching was performed where air was purged into the leachate for 24 hours. The leachate turned green over time with slight precipitation of Fe(OH)₂ and air oxidation did not result in oxidation of Fe(II) or further extraction of metals. This is due to the fact that oxidation of Fe(II) by air is an extremely sluggish reaction with its kinetics heavily dependent on the pH.²⁵ Thus, electrochemical oxidation of Fe(II) to Fe(III) was formulated as the basis for removal of iron from the leachate.

Electrochemical extraction of REEs

Membrane electrolysis has been successfully employed in various fields including metal recovery.²⁶⁻²⁸ For all the electrolysis experiments, 3 grams of magnet waste was first partially leached with HCl at (*n*HCl/*n*REE = 3.5). In this study, a membrane electrochemical reactor with two chambers separated by an anion exchange membrane was used to treat the magnet waste (Fig.1). The partially leached solution (Table 2) was passed into the anolyte compartment while the undissolved magnet particles stayed in the Scott bottle along with the magnetic stirrer. The catholyte consisted of sodium chloride solution. Both the catholyte and anolyte were internally recirculated. The following reactions are possible at the anode:



The cathodic reaction is reduction of water to produce hydroxide ions.



The anion exchange membrane not only prevented migration of Fe(III) to the catholyte where it can be reduced to Fe(II) but also ensured capture of acid released from reaction (5) to be utilized for leaching undissolved magnet particles. In all the electrolysis experiments, the metals were leached exclusively inside the anolyte loop. ICP-OES analysis of catholyte after the electrolysis showed no presence of metals and thus, it can be concluded that the anion exchange membrane served as an effective physical barrier.

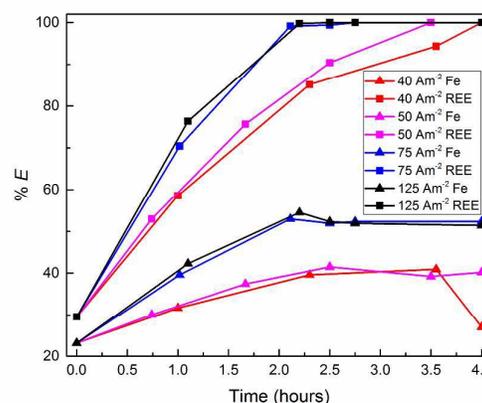


Fig. 2 Influence of current density on percentage extraction of REEs and iron with 0.2 M NaCl in the anolyte and 35 g/L NaCl in the catholyte a) 40 Am⁻² b) 50 Am⁻² c) 75 Am⁻² d) 125 Am⁻²

Influence of current density over metal extraction

To investigate the kinetics of magnet leaching under different current densities, an artificial brine solution (0.6 M, 35 g/L

NaCl) was used as a catholyte and 0.2 M NaCl was added to the anolyte as a supporting electrolyte. The kinetics of REEs leaching into the solution increased with increase in current density (Fig. 2). At current densities above 50 Am^{-2} , more than 97% REEs and cobalt were extracted into the solution within three hours. Around 50% of iron was removed from the leachate as $\text{Fe}(\text{OH})_3$ due to electrochemical oxidation of $\text{Fe}(\text{II})$. In acidic pH, the kinetics of oxidation of $\text{Fe}(\text{II})$ by dissolved oxygen is very sluggish²⁵ and direct anodic oxidation of $\text{Fe}(\text{II})$ was found to be the predominant mechanism.²⁹ However, $\geq 30\%$ of iron was also co-extracted into the leachate. This is due to formation of acid by migration of chloride ions to anolyte.



Chloride anions migrated from catholyte to the anolyte through the anion exchange membrane and reacted with protons produced from water electrolysis (eqn (5)) to form HCl thereby leaching metals unselectively.³⁰ Loss of around 3.5 ± 1 wt % of chloride ions from catholyte was measured by ion chromatography. After complete treatment of the waste, water electrolysis and subsequent acid formation happens at the anolyte which was also observed as a drop in pH.

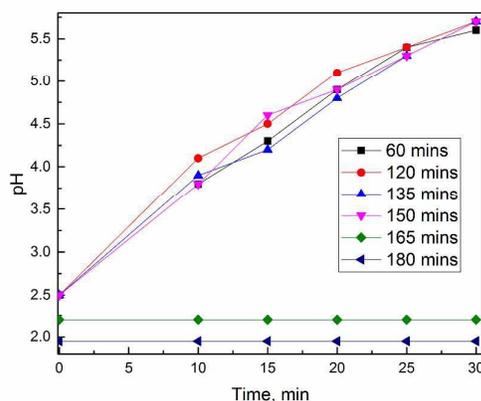


Fig. 3 Evolution of pH of the anolyte in time after electrolysis reactor is switched off at various intermittent time intervals with 0.2 M NaCl in anolyte, 0.6 M NaCl in catholyte and at 50 Am^{-2} .

The pH of the anolyte served as an important parameter for indicating the end point of the electrolysis. During the electrolysis, a constant pH of 2.5 ± 0.2 was observed. This constant pH reflects the dynamic equilibrium existing between two competing reactions in the anolyte, chemical dissolution of the magnet (eqn (2)-(4)) and $\text{Fe}(\text{II})$ oxidation (eqn (5)). The

cell was switched off at intermittent time intervals and the pH of the anolyte was subsequently monitored over time when no energy was supplied. Two distinct profiles of the anolyte pH were observed. In a first profile, at intermittent time intervals 60, 120, 135 and 150 minutes, the pH gradually increased to 6 ± 0.5 (Fig. 2). This increase of pH when the cell was turned off indicates that there were still magnet particles that remained undissolved and reaction was still incomplete. In the second profile, at intermittent time intervals 165, 180 minutes the pH of the anolyte remained stable at 2 ± 0.2 and continuation of the electrolysis resulted in a further decrease of pH. This stable profile can be attributed to complete treatment of all magnet waste and further acid formation resulting from migration of chloride ions from catholyte.

Despite co-extraction of iron, $\geq 99\%$ of the iron that was extracted into the leachate existed in $\text{Fe}(\text{III})$ state (Table 3). It has to be noted that this $\text{Fe}(\text{III})$ from these leachates can easily be removed by neutralization and precipitation to obtain a REE-rich solution.¹⁵ Thus, ammonia was added dropwise to increase the pH of the leachate to 4.5 ± 0.2 . Table 4 presents the composition of leachate after electrolysis and after neutralization. It can be seen that the electrolysis step removes around 50 % of iron from the original magnet. The neutralization step resulted in precipitation and complete removal of iron in the form of iron(III) hydroxide precipitate. The obtained iron(III) hydroxide precipitate was filtered and the XRD of the precipitate showed that it consisted of $\beta\text{-FeO}(\text{OH})$, akagenite.

Despite complete removal of iron from the leachate, co-extraction of iron into the leachate during electrolysis can be problematic as it requires the additional step of neutralization. Thus, to limit the co-extraction of iron and to further understand the effect of chloride ions in both compartments on the extraction as well as speciation of iron into the solution, experiments were performed with a) complete absence of NaCl in the anolyte and b) with very low concentration of NaCl (0.05 M) in the catholyte.

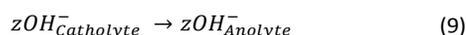
Effect of catholyte NaCl concentration

To understand the migration of chloride ions from the catholyte, the effect of catholyte NaCl concentration on the extraction of different metals was investigated first at a constant current density of 50 Am^{-2} (Fig. 4.). No NaCl was added to the anolyte. Low concentration of NaCl (0.05 and 0.01 M) in the catholyte resulted in incomplete leaching of the metals. A saturation point for extraction was reached at 2-3 hours and further electrolysis resulted even in a slight decrease of the metal concentration signifying possible

Table 4: Composition of leachates after electrolysis at 125 Am⁻² and neutralization with ammonia

Elements	Nd (mg/L)	Dy (mg/L)	Pr (mg/L)	Co (mg/L)	Fe (mg/L)
Completely leached magnet waste	2652.0	982.8	91.2	358.7	7624.5
Leachate after electrolysis	2643.0	979.1	90.7	358.3	4284.9
After neutralization	2551.2	943.4	89.4	347.9	<0.1
Retention [%]	95.0 ± 2	95.5 ± 1	98.0 ± 0.5	98.5 ± 0.5	-

precipitation of metals due to migration of hydroxide ions to the anolyte.



However, complete extraction of REEs was observed at a NaCl concentration similar to that of brine solution and higher (0.6 M and 1 M NaCl). Nevertheless, more than 40% of iron was still co-extracted into the leachate. However, in contrast to the previous experiments where 0.2 M NaCl was present in the anolyte, almost all of the iron extracted into the leachate was Fe(II) in the absence of NaCl in the anolyte (Table 2). This shows that the presence of sodium chloride additive salt in the anolyte plays a role in Fe(II) oxidation.

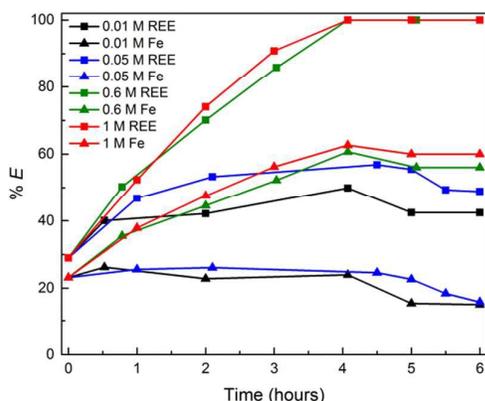


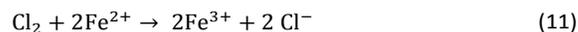
Fig 4 Percentage extraction of REE and iron over different concentrations of sodium chloride in catholyte at constant current density of 50 Am⁻², after initial leaching at (nHCl/nREE = 3.5).

Influence of anolyte NaCl concentration

The role of NaCl concentration in anolyte on the speciation and extraction was investigated further at a constant current density of 125 Am⁻². The catholyte concentration of NaCl was kept constant at 0.05 M to minimize the influx of chloride ions into the anolyte. Similar to the previous set of experiments, in the absence of NaCl in the anolyte, the leach was incomplete and unselective with co-extraction of iron. However, with the addition of NaCl in the anolyte, around 94 ± 2 % REEs and cobalt

were selectively extracted into the leachate with almost complete removal of iron (Fig. 5). This selective extraction of REEs and cobalt can be attributed to two different factors. First, by reducing the NaCl amount in the catholyte (0.05 M), the excess acid formation by migration of chloride ions was prevented.

Secondly and most importantly, chlorine gas was generated from the oxidation of chloride ions at the anode. Subsequently, Fe(II) is oxidized also by reaction with chlorine. It has to be noted that even in the experiments where no NaCl was presented in the anolyte, more than 50% of iron present in the magnet was removed as Fe(OH)₃. Thus, Fe(II) oxidation at the anolyte happens directly at the anode surface as well as by electrochlorination. Generation of chlorine gas by *in-situ* electrochlorination has been used in water disinfection as a safe alternative to transporting chlorine gas to the sites of water treatment.^{31, 32}



Chlorine gas is also used in organic industries to oxidize Fe(II) to Fe(III).³³ Electrogenerated chlorine was reported to play a dual role of oxidizing Fe(II) as well as leaching metals from the waste.^{34, 35} High concentrations of chloride ions (3.5 M and 4 M) were investigated here mainly because they can be used as salting agents for environmentally friendly downstream solvent extraction processes to separate different REEs from each other.²¹ The whole extraction process was complete within 3 hours. This is marked improvement over other selective leaching processes which required 5-7 days for complete extraction of REEs.^{21, 36} Prolonging the reaction time further decreased the extraction of REEs due to possible precipitation of REEs as hydroxides due to migration of hydroxide ions from the catholyte (eqn. 8). On average, the leachate contained 3600 mg/L of REEs and 310 mg/L of cobalt. The concentration of REEs can be remarkably increased by treating a large amount of magnet waste in a single batch or by reusing the leachate obtained at the end of the electrolysis over and over again in the subsequent electrolysis runs.

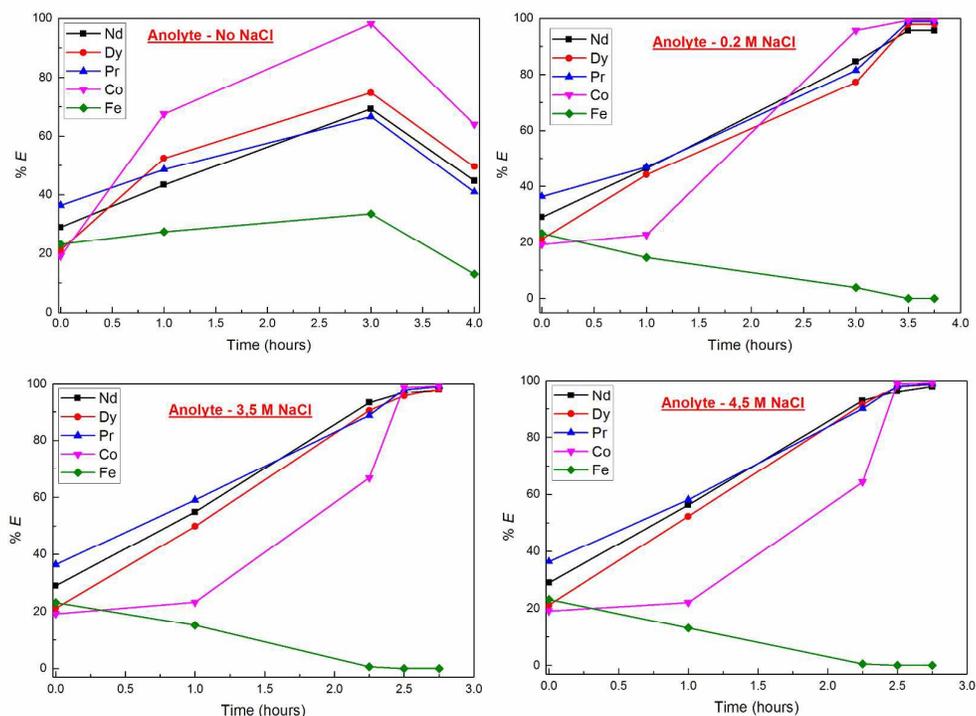
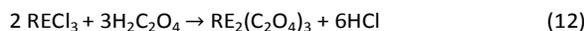


Fig. 5 Percentage of extraction of metals (Nd, Dy, Pr, Fe and Co) over different concentrations of NaCl in the anolyte at constant current density of 125 Am^{-2} .

Selective oxalate precipitation of REEs

Oxalic acid is often used as the precipitation agent to recover REEs in the solid form as rare-earth oxalates and to regenerate the acid.³⁷



Rare-earth oxalates are highly insoluble ($K_{\text{sp}} = 1.3 \times 10^{-31}$ for neodymium oxalate)³⁸ in comparison to cobalt(II) oxalate ($K_{\text{sp}} = 6.3 \times 10^{-8}$)³⁹ and thus oxalic acid was added to the leachate to selectively precipitate the REEs. As in Fig.6, at the ratio of moles of oxalic acid to REEs of 2:1, almost all REEs were precipitated while only less than 1% of cobalt was precipitated. The obtained rare-earth oxalates were calcined further at 950°C to obtain rare-earth oxides. The XRD pattern of the obtained rare-earth oxides showed the pattern of two different phases of Nd_2O_3 (Fig.7). The obtained oxides were dissolved in HCl and analysed with ICP-OES. The oxide was found to be quite pure (99.5 % of REEs) with only minor impurities from cobalt and aluminium. The remnant leachate was rich in cobalt. Recently we demonstrated that the remnant leachate can be directly used, after possible up concentration step, in an electrowinning process to recover the valuable cobalt metal.¹⁸

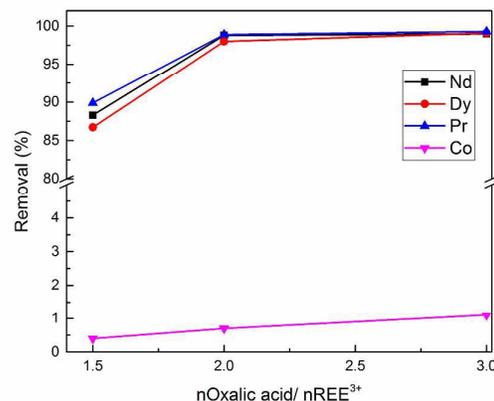


Fig. 6 Removal of REEs as rare-earth oxalates by addition of oxalic acid.

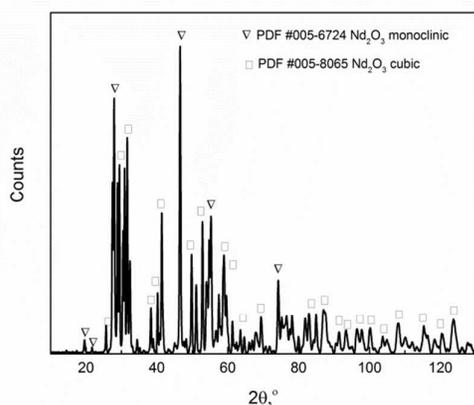


Fig 7: XRD pattern of the obtained rare-earth oxide.

Overall process and energy consumption

The overall recycling process for NdFeB magnet waste contains five distinctive steps (Fig. 8). First, the NdFeB magnet was partially leached with HCl at a ratio of (n HCl/ n REE = 3.5) with 3.5 M NaCl as an additive salt.

Then, the leachate was fed into the anolyte compartment of the two chambered electrochemical reactor separated by an AEM while the unreacted magnet powder stuck to the magnetic stirrer in the anolyte Scott bottle. The catholyte contained a NaCl solution of low concentration (0.05 M). Upon electrolysis, iron was oxidatively precipitated as $\text{Fe}(\text{OH})_3$ while $\geq 95\%$ REEs and cobalt were extracted into the leachate. The pH played an important role in indicating the end point of the electrolysis process. During the electrolysis, the pH was constant at 2.5 ± 0.2 and was a result of competing reactions of magnet dissolution by acid and oxidative precipitation of $\text{Fe}(\text{II})$. The electrolysis process was switched off intermittently and as long as unreacted magnet waste remained, the pH raised to 6.5 ± 0.3 . Complete treatment of NdFeB magnet waste resulted in decrease of pH to a value below 2. Thus the pH served as an effective indicator for the end point of the reaction. At the end of electrolysis step, the leach residue was removed by filtration. Subsequently, the leachate was treated with oxalic acid to further precipitate REEs as rare-earth oxalates. The acid that was consumed in the partial leaching step was regenerated in this precipitation step. The rare-earth oxalates were further calcined at 950°C to produce rare-earth oxides. The acid along with cobalt ions and a highly concentrated NaCl solution can be fed again into the anolyte resulting in a closed-loop process without net consumption of HCl. Cobalt can be separated using a solvent extraction step⁴⁰ or it can be recovered as cobalt metal through an electrowinning step.⁴¹ For the 3 grams of magnet waste treated in the process, 1.2 ± 0.1 grams of rare-earth oxides was obtained as the main product. The iron hydroxide residue (3.6 ± 0.2 grams) produced was found to be in the form of β - $\text{FeO}(\text{OH})$ akaganeite and can be potentially used in pigment industries, ion exchangers and

gas sensors.⁴² Residual cobalt (0.09 grams) present in the solution can be used in the subsequent electrolysis step to increase the cobalt concentration until it is suitable for direct electrowinning.

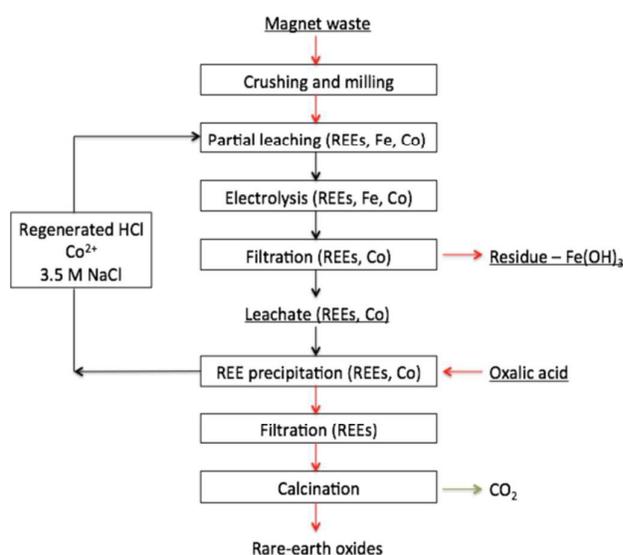


Fig. 8 Flow chart of the recycling process. Red arrows: solid stream, black arrows: aqueous stream, green arrow: gaseous stream

The average cell voltage and energy consumption (kWh/kg) calculated per kilogram of magnet for different experimental conditions are tabulated in Table 5. Increase in concentration of NaCl in the catholyte decreases the energy consumption significantly. However, at high concentration of NaCl in the catholyte almost half of the iron present in the magnet waste was co-extracted into the leachate. The speciation of the extracted iron into the solution depended upon the presence of NaCl in the anolyte. Nevertheless, the best suited conditions for selective extraction of REEs with iron removal are 3.5 M of anolyte NaCl and 0.05 M of catholyte NaCl (condition G). Both conditions C and G can provide iron-free leachates rich in REEs and cobalt. However, condition C requires an additional neutralization step for iron removal. In terms of energy consumption, condition G requires almost 3.5 times more energy than condition C. At an energy cost of €0.12, these results indicate that the magnet waste can be processed at an energy cost of €0.7/kg in a scaled up set-up. Assuming an average of 30% of REEs in magnet waste, the power cost of the developed electrochemical process to produce a kilo gram of rare-earth oxides would be less than three euros. In 2014, the price of Nd_2O_3 was €50 per kilogram.¹⁰ Thus, despite additional capital and operational costs, the developed recycling process is still commercially attractive. Although the focus of this manuscript is on treatment of NdFeB magnet waste, the concept of *in-situ* electrochemical oxidative-precipitation of iron from waste feed can be extended and used in treatment of ferrous fraction of a generic WEEE stream (Waste Electrical

Table 5: Average cell voltage and energy consumption per kg of magnet waste under different conditions

Condition	Current density (Am ⁻²)	Anolyte NaCl concentration (M)	Catholyte NaCl concentration (M)	Cell Voltage (V)	REE extraction (%)	Energy consumption (kWh/kg)
A	40	0.2	0.6	2.79	99.1±0.3	0.95
B	50	0.2	0.6	2.91	99±0.4	1.24
C	75	0.2	0.6	3.1	99±0.5	1.65
D	125	0.2	0.6	3.31	99±0.5	2.2
E	125	0	0.6	3.89	45.3±0.7	4.15
F	125	0.2	0.05	6.45	95.3±0.3	6.02
G	125	3.5	0.05	6.24	97.5±0.5	5.82
H	125	4.5	0.05	6.1	98.1±0.6	5.7

and Electronic Equipments) which contains substantial amount of REEs.⁴³⁻⁴⁵ The electrochemical oxidative-precipitation process not only removes iron from the leachate but also simultaneously regenerates the acid that can be used by other metals present in the feed to dissolve into the solution.

Conclusions

An environmentally friendly electrochemical process was developed to selectively recover REEs from NdFeB magnet waste at room temperature. REEs were selectively extracted from NdFeB magnet waste by partial leaching followed by membrane electrolysis. Fe(II) was oxidized in the anolyte and precipitated as Fe(OH)₃. The acid liberated from oxidation of Fe(II) was captured in the anolyte *in-situ* and was used in leaching the undissolved magnet waste further until ≥95% REEs were leached into solution and all iron was removed as iron(III) hydroxide precipitate. The concentrations of sodium chloride in the anolyte and catholyte were shown to play an important role in the recovery process. The kinetics of metal extraction was shown to increase with increase in current density. Oxalic acid was used as a selective precipitating agent to separate REEs from cobalt. The whole process consumes only sodium chloride, oxalic acid, current and produced rare-earth oxides with a purity ≥99%.

Acknowledgement

The research leading to these results has received funding from the European Community's Seventh Framework Programme ([FP7/2007-2013]) under grant agreement n°607411 (MC-ITN EREAN: European Rare Earth Magnet Recycling Network). This publication reflects only the author's view, exempting the Community from any liability. Project website: www.erean.eu. Prof. Korneel Rabaey, Synthia Maes and Kristof Verbeeck from the University of Ghent (Belgium) are acknowledged for the useful discussions and for providing

the components necessary for the experimental work. The authors thank Magneti (Slovenia) for providing the magnet waste used in this study.

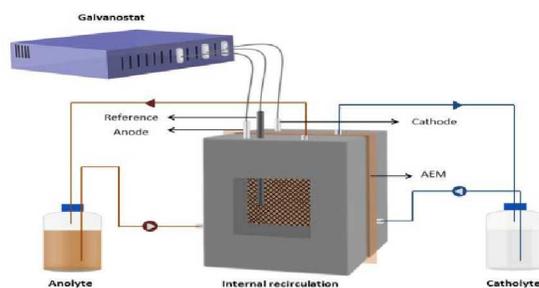
References

1. E. Alonso, A. M. Sherman, T. J. Wallington, M. P. Everson, F. R. Field, R. Roth and R. E. Kirchain, *Environmental Science & Technology*, 2012, **46**, 3406-3414.
 2. K. Nansai, K. Nakajima, S. Kagawa, Y. Kondo, S. Suh, Y. Shigetomi and Y. Oshita, *Environmental Science & Technology*, 2014, **48**, 1391-1400.
 3. K. M. Goodenough, F. Wall and D. Merriman, *Natural Resources Research*, 2017, DOI: 10.1007/s11053-017-9336-5.
 4. E. D. Gemechu, C. Helbig, G. Sonnemann, A. Thorenz and A. Tuma, *Journal of Industrial Ecology*, 2016, **20**, 154-165.
 5. E. C. European Commission, *Report on the critical raw materials for EU, report of the Ad hoc working group on defining critical raw materials.*, European Commission, Enterprise and Industry, Brussels
- Available at <http://ec.europa.eu/growth/sectors/raw-materials/specific-interest/critical/> [Sept. 2017]), 2017.
6. Z. Weng, N. Haque, G. M. Mudd and S. M. Jowitt, *Journal of Cleaner Production*, 2016, **139**, 1282-1297.
 7. J. C. K. Lee and Z. Wen, *Journal of Industrial Ecology*, 2016, DOI: 10.1111/jiec.12491.
 8. B. Sprecher, I. Daigo, W. Spekkink, M. Vos, R. Kleijn, S. Murakami and G. J. Kramer, *Environmental Science & Technology*, 2017, **51**, 3860-3870.
 9. O. Gutfleisch, M. A. Willard, E. Bruck, C. H. Chen, S. G. Sankar and J. P. Liu, *Adv Mater*, 2011, **23**, 821-842.
 10. J. Gambogi, *2014 Minerals Yearbook: Rare earths*, U.S Geological Service, Reston

ARTICLE

Journal Name

- https://minerals.usgs.gov/minerals/pubs/commodity/rare_earths/myb1-2014-raree.pdf, 2016.
11. K. Binnemans, P. T. Jones, B. Blanpain, T. Van Gerven, Y. Yang, A. Walton and M. Buchert, *Journal of Cleaner Production*, 2013, **51**, 1-22.
 12. Y. Yang, A. Walton, R. Sheridan, K. Güth, R. Gauß, O. Gutfleisch, M. Buchert, B.-M. Steenari, T. Van Gerven, P. T. Jones and K. Binnemans, *Journal of Sustainable Metallurgy*, 2017, **3**, 122-149.
 13. C. Tunsu, M. Petranikova, M. Gergorić, C. Ekberg and T. Retegan, *Hydrometallurgy*, 2015, **156**, 239-258.
 14. S. S. Behera and P. K. Parhi, *Separation and Purification Technology*, 2016, **160**, 59-66.
 15. M. A. R. Önal, C. R. Borra, M. Guo, B. Blanpain and T. Van Gerven, *Journal of Rare Earths*, 2017, **35**, 574-584.
 16. J. W. Lyman and G. R. Palmer, *High Temperature Materials and Processes*, 1993, **11**, 175-187.
 17. H. M. D. Bandara, K. D. Field and M. H. Emmert, *Green Chem.*, 2016, **18**, 753-759.
 18. P. Venkatesan, Z. H. I. Sun, J. Sietsma and Y. Yang, *Separation and Purification Technology*, 2018, **191**, 384-391.
 19. M. A. R. Önal, E. Aktan, C. R. Borra, B. Blanpain, T. Van Gerven and M. Guo, *Hydrometallurgy*, 2017, **167**, 115-123.
 20. M. A. R. Önal, C. R. Borra, M. Guo, B. Blanpain and T. Van Gerven, *Journal of Sustainable Metallurgy*, 2015, **1**, 199-215.
 21. T. Vander Hoogerstraete, B. Blanpain, T. Van Gerven and K. Binnemans, *RSC Adv.*, 2014, **4**, 64099-64111.
 22. E. Viollier, P. W. Inglett, K. Hunter, A. N. Roychoudhury and P. Van Cappellen, *Applied Geochemistry*, 2000, **15**, 785-790.
 23. J. P. Rabatho, W. Tongamp, Y. Takasaki, K. Haga and A. Shibayama, *Journal of Material Cycles and Waste Management*, 2013, **15**, 171-178.
 24. Y. Yang, X. Wang, M. Wang, H. Wang and P. Xian, *Hydrometallurgy*, 2015, **157**, 239-245.
 25. B. Morgan and O. Lahav, *Chemosphere*, 2007, **68**, 2080-2084.
 26. C. Lupi, M. Pasquali and A. Dell'era, *Waste Manag*, 2005, **25**, 215-220.
 27. M. Paidar, V. Fateev and K. Bouzek, *Electrochimica Acta*, 2016, **209**, 737-756.
 28. S. Maes, W.-Q. Zhuang, K. Rabaey, L. Alvarez-Cohen and T. Hennebel, *Environmental Science & Technology*, 2017, **51**, 1654-1661.
 29. D. Bejan and N. J. Bunce, *Journal of Applied Electrochemistry*, 2015, **45**, 1239-1254.
 30. V. Baramashenko and J. Jörissen, *Journal of Applied Electrochemistry*, 2005, **35**, 1311-1319.
 31. J. Choi, S. Shim and J. Yoon, *Journal of Industrial and Engineering Chemistry*, 2013, **19**, 215-219.
 32. D. Ghernaout, M. W. Naceur and A. Aouabed, *Desalination*, 2011, **270**, 9-22.
 33. H. Hikita, S. Asai, H. Ishikawa and Y. Saito, *Chemical Engineering Science*, 1975, **30**, 607-616.
 34. E.-y. Kim, M.-s. Kim, J.-c. Lee, M. K. Jha, K. Yoo and J. Jeong, *Minerals Engineering*, 2008, **21**, 121-128.
 35. D. Pilone and G. H. Kelsall, *Electrochimica Acta*, 2006, **51**, 3802-3808.
 36. Y. Kataoka, T. Ono, M. Tsubota and J. Kitagawa, *AIP Advances*, 2015, **5**, 117212.
 37. D. Dupont and K. Binnemans, *Green Chemistry*, 2015, **17**, 856-868.
 38. D. Y. Chung, E. H. Kim, E. H. Lee and J. H. Yoo, *Journal of Industrial and Engineering Chemistry*, 1998, **4**, 277-284.
 39. J. Shibata, N. Murayama, M. Niinae and T. Furuyama, *Materials transactions* 2012, **53**, 2181-2186.
 40. T. Vander Hoogerstraete, S. Wellens, K. Verachtert and K. Binnemans, *Green Chemistry*, 2013, **15**, 919-927.
 41. I. G. Sharma, P. Alex, A. C. Bidaye and A. K. Suri, *Hydrometallurgy*, 2005, **80**, 132-138.
 42. J. C. Villalba, S. Berezoski, K. d. A. Cavicchiolli, V. Galvani and F. J. Anaissi, *Materials Letters*, 2013, **104**, 17-20.
 43. T. E. Lister, P. Wang and A. Anderko, *Hydrometallurgy*, 2014, **149**, 228-237.
 44. K. Habib, K. Parajuly and H. Wenzel, *Environmental Science & Technology*, 2015, **49**, 12441-12449.
 45. A. Lixandru, P. Venkatesan, C. Jönsson, I. Poenaru, B. Hall, Y. Yang, A. Walton, K. Güth, R. Gauß and O. Gutfleisch, *Waste Management*, 2017, **68**, 482-489.



A closed loop room temperature electrochemical process for selective recovery of REEs from NdFeB magnet waste.