ACS Sustainable Chemistry & Engineering

Article

Selective Extraction of REEs from NdFeB Magnets by a Room-Temperature Electrolysis Pretreatment Step

Prakash Venkatesan, Tom Vander Hoogerstraete, Koen Binnemans, Zhi Sun, Jilt Sietsma, and Yongxiang Yang

ACS Sustainable Chem. Eng., **Just Accepted Manuscript** • DOI: 10.1021/acssuschemeng.8b01707 • Publication Date (Web): 25 May 2018

Downloaded from http://pubs.acs.org on May 25, 2018

Just Accepted

"Just Accepted" manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides "Just Accepted" as a service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. "Just Accepted" manuscripts appear in full in PDF format accompanied by an HTML abstract. "Just Accepted" manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are citable by the Digital Object Identifier (DOI®). "Just Accepted" is an optional service offered to authors. Therefore, the "Just Accepted" Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the "Just Accepted" Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these "Just Accepted" manuscripts.

ACS Publications

is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

Published by American Chemical Society. Copyright © American Chemical Society. However, no copyright claim is made to original U.S. Government works, or works produced by employees of any Commonwealth realm Crown government in the course of their duties.

Selective Extraction of REEs from NdFeB Magnets by a Room-Temperature Electrolysis Pretreatment Step

Prakash Venkatesan[a*], Tom Vander Hoogerstraete[b] , Koen Binnemans[b], Zhi Sun[c], Jilt Sietsma[a], Yongxiang Yang[a]

[a]*Department of Materials Science and Engineering, TU Delft, Mekelweg 2, 2628 CD Delft, The Netherlands*

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

[c] *National Engineering Laboratory for Hydrometallurgical Cleaner Production Technology, Institute of Process Engineering, Chinese Academy of Sciences, No. 1, Beier Street, Zhongguancun, Haidian District, Beijing 100190, P.R China*

**Corresponding authors: P.Venkatesan (P.Venkatesan@tudelft.nl)*

ABSTRACT

NdFeB magnets are used in wind turbines, hybrid electric vehicles and are instrumental in progression towards a low-carbon economy. Recycling rare-earth elements (REEs) from NdFeB magnet waste is an important step towards building a sustainable REE supply chain. In this study, we describe an electrochemical process to selectively extract REEs from NdFeB magnet waste at room temperature. First, an electrolysis pretreatment step was performed to convert the elements present in the magnet waste into the respective hydroxides. A dual anode system was used where NdFeB magnet waste was taken as an anode along with an inert anode in an electrochemical reactor. The inert anode was used to ensure that iron in the magnet waste was converted into the Fe(III) form in the mixed hydroxides precipitate. Subsequently, the mixed hydroxides were leached with HCl. More than 97% of REEs and cobalt leached into the solution leaving iron in the residue. REEs were then selectively precipitated as rare-earth oxalates using oxalic acid, which in turn regenerated HCl, resulting in a closed-loop process. Calcination of the rare-earth oxalates yielded rare-earth oxides of high purity (99.2%), which can be used directly for producing rare-earth metals.

Keywords: Nd-Fe-B magnet; Rare earth elements; Electrochemical recycling; Closed-loop process; Metal recovery

INTRODUCTION

The rare earth elements (REEs) are widely used in important technological applications such as permanent magnets, nickel metal hydride batteries, fluid cracking catalysts (FCC) and fluorescent lamps.[1] The European Commission classified REEs as critical raw materials due to supply chain risks and an increasing demand from clean-tech sector.[2] Primary mining of REEs from ores leaves a large environmental footprint and creates a "balance problem" where lesser used cerium and lanthanum are stockpiled at the cost of neodymium and dysprosium.[3-4] Recycling REEs from end-of-life consumer products is one of the important strategies to formulate a sustainable supply chain and to mitigate the balance problem. More than 20% of REEs produced globally are consumed for the production of neodymium iron boron magnets (NdFeB) and thus, they are a valuable secondary resource for recovery of REEs.[5]

NdFeB magnets contain 20-30 wt% of REEs, 60-70 wt% of iron, 1 wt% boron and some admixtures of other metals in minor quantities. Selective extraction of REEs over iron is the major objective in the recycling of NdFeB magnet waste. Comprehensive reviews have summarized the approaches taken thus far to recover REEs from NdFeB magnets.[6-7] Wet chemical processes are preferred as they operate mostly at room temperature. These processes usually consist of complete and unselective dissolution of NdFeB magnets in an acid followed by selective precipitation of the rare earths as double sulfates or fluorides from the solution. Such recycling processes consume a large amount of non-recyclable chemicals such as H_2SO_4, HF, NaOH and generate considerable volumes of waste water.[8] In contrast to selective precipitation of REEs, iron can also be selectively precipitated from the leachate leaving REEs and cobalt in the solution. The speciation of iron in the solution plays an important role as Fe(II) tends to be a stable species in the solution until a pH value of 6 and thus cannot be selectively precipitated over REEs by hydrolysis. On the other hand, Fe(III) undergoes hydrolysis and can be precipitated at a pH of 2 where REEs remain as stable species in solution.[9] However, air oxidation of Fe(II) is kinetically sluggish below pH 7.[10] Recently, an electrochemical route and a chemical route were proposed where complete removal of iron from the leachate was achieved at room temperature by

selective oxidation of Fe(II) in the solution. Nevertheless, both processes required complete dissolution of the magnet waste and thus, generated acid waste.[9, 11]

Pyrometallurgical processes such as selective chlorination, vacuum induction melting, thermal isolation and roasting can selectively and efficiently extract REEs from NdFeB magnet waste.[12-15] However, these pyrometallurgical processes mostly have a high operation temperature of 950 ^{o}C and above and are quite energy intensive. Roasting based combined pyrometallurgical-hydrometallurgical processes are especially interesting as REEs can be extracted from NdFeB magnet waste in a closed loop fashion without consumption of an inorganic acid. Vander Hoogerstraete et al. described such a closed-loop process in which magnet waste was first subjected to an oxidative roasting pretreatment step.[16] During the roasting pretreatment step, REEs and iron were converted into rare-earth oxides and Fe_2O_3 respectively. The roasted magnet was then leached with an amount of acid that was equivalent to the stoichiometric requirement of REEs (nHCl/nREE = 3.5). REEs were selectively extracted into solution leaving iron(III) oxide in the residue. Subsequently, REEs were selectively precipitated from the solution by an oxalic acid precipitation step, which regenerated acid consumed in the leaching step, creating a closed-loop process with no net consumption of HCl.

NdFeB magnets are heavily prone to corrosion and can thus be anodically dissolved in many electrolytes without passivation.[17-18] However, anodic dissolution of iron results in the formation of Fe(II) in the solution or in the precipitate depending upon the pH.[19] However, as explained earlier, it is important to oxidize iron in the magnet waste to Fe(III) form for selective recovery of REEs. Recently, arsenic removal from groundwater was demonstrated using a dual anode system where an active iron anode was dissolved to produce Fe(II) and an inert anode to simultaneously oxidize Fe(II) to Fe(III) hydroxide. [20]

In this manuscript, we propose a room-temperature electrolysis pretreatment step with a similar dual anode system for recycling NdFeB magnet waste. In this electrolysis pretreatment step with NH_4Cl as the electrolyte, NdFeB magnet waste dissolves as an active metal anode (AMA) and simultaneously, a Ti/Pt inert anode (IA) oxidizes Fe(II) to $Fe(OH)_3$. At the end of this electrolysis step, the REEs and iron in the magnet can be converted into their respective hydroxides, $REE(OH)_3$ and $Fe(OH)_3$ to produce a mixed hydroxides precipitate. This insoluble mixed hydroxides precipitate is similar to the powder obtained after

oxidative roasting and thus, REEs can be selectively leached from this hydroxides mixture with HCl in the ratio of (nHCl/nREE ≤3.5). The effect of different conditions such as the ratio of current density between the two anodes and electrolyte composition were studied and the underlying mechanisms were explored. The process produced iron-free REE-rich leachates and iron hydroxide by-product that can be used in pigment and gas sensors industries. The whole process consumes only electricity, water and oxalic acid.

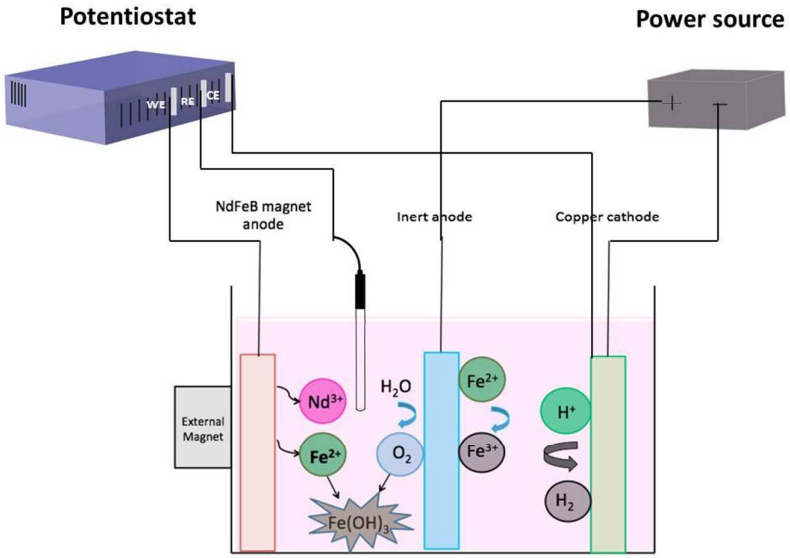


Figure 1. Schematic representation of dual anode electrolysis reactor to recycle NdFeB magnet waste. (WE- Working electrode; RE- Reference electrode; CE- Counter electrode)

EXPERIMENTAL SECTION

Materials and Methods. Solid sintered magnets used as electrodes were supplied by Magneti Ljublijana (Slovenia) and their composition as measured with ICP-OES is listed in Table 1. HCl (37%), oxalic acid dihydrate (≥99%)and NH_4Cl (99.95%) were purchased from Sigma-Aldrich (Zwijndrecht, The Netherlands). External hold magnets (EHM) were purchased from Supermagnete (Okeo, Germany). A dimensionally stable cylindrical platinum coated titanium anode (Ti/Pt DSA, fully platinum coated, Magneto B.V. Schiedam) of 3 cm diameter and 3 cm height was used as inert electrode. Copper plates used as cathodes were purchased from Salomon Metalen B.V. The pH and temperature were measured by Inolab 7310 pH meter (WTW, The Netherlands) with a Sentix 81 tip. A universal 320R centrifuge was used to separate the leachate from the precipitate. The solutions were analyzed with

inductively coupled plasma- optical emission spectrometry (ICP-OES, PerkinElmer Optima 3000DV). The chloride concentration was measured using ion chromatography (Dionex DX-120 Ion Chromotograph). The leach residue and the rare-earth oxides were characterized with XRD using Bruker D8 diffractometer with Cu Kα radiation operating at 45 kV.

Table 1. Chemical composition of the magnet (wt%)

Element	Wt (%)	Element	Wt (%)
Fe	64.38	Cu	0.17
Nd	23.14	Al	0.06
Dy	6.05	Gd	0.02
Co	2.86	Ni	0.02
B	1.1	Nb	0.01
Pr	0.84	Total	98.86
Ga	0.22		

Experimental set up and procedure. A PMMA reactor (10 × 10 × 7 cm) was used as an electrochemical cell and the electrolyte volume was kept constant at 200 mL during the experiment. Solid sintered magnet (2.5 × 1.5 × 0.55 cm) was soldered to a wire and the soldered portion was carefully covered with a polymer resin to prevent solder material from contaminating the leachates. A copper plate with an area of 23 cm^2 (10 × 2.3 cm) was dipped into the electrolyte as cathode and the back of the plate was masked with an insulating tape. Ag/AgCl (3M KCl) was used as a reference electrode and both the reference electrode and pH meter were immersed in the electrolytic cell throughout the experiment. A PTFE overhead stirrer was used to agitate the electrolyte at a constant rotating speed of 500 rpm. A separate power source was used to connect inert platinized titanium (Ti/Pt) anode and copper cathode (Figure 1). A water bath was used to maintain the temperature of electrochemical cell and the accuracy of it was found to be ±2 ^oC as measured by a pH meter equipped with a temperature sensor. An external hold magnet (EHM) was placed outside the PMMA reactor to attract the active magnet anode to the side of the wall thereby preventing the falling down of loose magnet particles. For the polarization measurements, the solid magnet was embedded in a resin with 1 cm^2 exposed area. Samples were mechanically polished up to 1200 silicon carbide paper and 1 μm with diamond paste, then ultrasonically cleaned in ethanol. All the

experiments were conducted using potentiostat Versastat 4 (Ametek, UK) and the data was obtained using Versastudio software

Iron removal using dual anode system. The dependency of Fe(II) oxidation on the ratio of current passed between active magnet anode (AMA) and inert anode (IA) was studied by drawing a 1 mL sample out during the duration of experiment. The current in AMA was kept constant at 0.5 A while the current at IA was changed to see the effect of iron oxidation. The samples were centrifuged at 5500 rpm for 10 minutes and the aqueous phase was filtered using a syringe filter (0.45 μm) leaving out the residue.

Solution measurement and calculations. The solution obtained immediately after electrolysis was measured by filtering the aqueous phase through syringe filter (0.45 μm). The electrolysis experiments were done in triplicates. The leach residue obtained after electrolysis was completely dissolved in concentrated HCl (37%, 12 M) and diluted with distilled water to determine the total amount of metals present in the residue. The percentage of extraction of any metal into the leachate is defined as

$$\%E = \frac{\text{Amount of metal in the leachate}}{\text{Amount of metal in the leachate and precipitate}} \times 100 \quad (1)$$

The anodic dissolution efficiency (ŋ) for the dissolution of NdFeB alloy was calculated as follows.

$$\eta = \frac{M_0}{M_t} \text{ x } 100\ (\%) \quad (2)$$

where M_0 and M_t are the observed and theoretical mass loss respectively. The observed mass loss was calculated as the sum of the amount of metal present in the leachate and the precipitate. The theoretical mass loss for the NdFeB alloy was calculated as

$$M_t = \frac{It}{FN_{EQ}} \quad (3)$$

where I is the current supplied (A), F is Faraday's constant (96500 Coulomb/equivalent), t is the time of electrolysis in seconds and N_{EQ} is the total number of equivalents obtained from dissolving an unit mass of the alloy. [21]

$$N_{EQ} = \sum \frac{f_i n_i}{a_i} \quad (4)$$

where f_i, n_i, a_i are mass fraction, number of electrons exchanged and atomic weight respectively of the ith alloying element. Power consumption, P (kWh/kg) is calculated as

$$P = \frac{(V_{MA} + V_{IA})\,(I_{MA} + I_{IA})\,t}{3600 \times m} \quad (5)$$

where V_{MA} and V_{IA}, are the voltage (V) measured between the magnet anode and the copper cathode and the voltage measured between inert anode and copper cathode respectively. I_{MA} and I_{IA} are the current supplied on the magnet anode and inert anode viz in ampere. t is the duration of the electrolysis and m is the amount of magnet dissolved. Thus the reported values are kWh per kilogram of magnet waste.

RESULTS AND DISCUSSION

Anodic dissolution behavior of magnet scrap. The electrochemical dissolution behavior of NdFeB magnets was characterized by anodic polarization measurements (Figure 2) at different concentrations of NH_4Cl over a constant pH of 4±0.3. The electrochemical dissolution reactions of major elements from the magnet anode are

$$Nd \rightleftharpoons Nd^{3+} + 3e^- \ (E^0 = -2.323\ V) \quad (6)$$

$$Dy \rightleftharpoons Dy^{3+} + 3e^- \ (E^0 = -2.295\ V) \quad (7)$$

$$Fe \rightleftharpoons Fe^{2+} + 2e^- \ (E^0 = -0.477\ V) \quad (8)$$

$$Co \rightleftharpoons Co^{2+} + 2e^- \ (E^0 = -0.28\ V) \quad (9)$$

Over the scanned potential range, the polarization curves show an increase in current with increasing potential. This indicates an active dissolution behavior of NdFeB magnets without any passivation. Increase in the NH_4Cl concentration resulted in higher dissolution current densities and is consistent with the fact that chloride ions act as pitting agents promoting dissolution.[22]

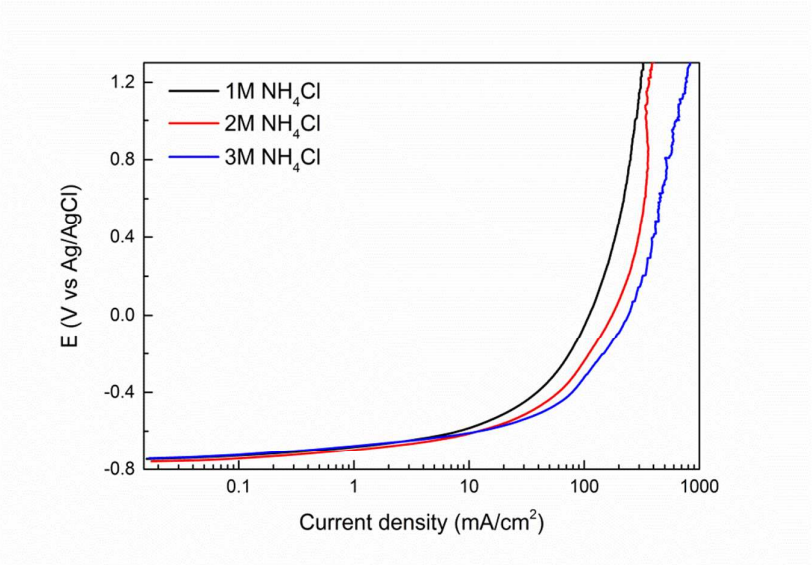


Figure 2. Potentiodynamic polarization curves of NdFeB magnets in 1 M, 2 M and 3 M NH_4Cl, at scan rate 2 mVs^{-1} and temperature 25±2 ^oC.

NdFeB magnets have a matrix phase ($Nd_2Fe_{14}B$) as well as Nd-rich and B-rich phases in the grain boundaries. Due to galvanic coupling, the Nd-rich and B-rich phases preferentially dissolve creating voids in the microstructure which facilitates the mechanical degradation of matrix phase. El moniem et al., anodically dissolved NdFeB magnets at different current densities and found that the actual mass loss was higher than the theoretically calculated faradaic mass loss.[23] This is due to the mechanical degradation phenomenon of the magnets and this was also observed in our anodic polarization tests. Pulverization of the matrix phase leads to falling down of loose magnetic particles that are no longer in electrical contact. This poses a challenge to effective anodic dissolution. To solve this issue, a permanent NdFeB magnet was placed outside the reactor wall as an external hold magnet (EHM) which was magnetically attached to the NdFeB active magnet anode (AMA) inside the reactor. During the course of all the electrolysis experiments, it was observed that the loose particles held on to the AMA due to the influence of the magnetic field. A constant current of 0.5 A (initial current density, 420 A/m^2) was applied on the AMA for all the rest of the experiments to investigate the effect of other parameters such as electrolyte concentration and current density at inert anode. However, an industrial reactor can accelerate the dissolution kinetics of the magnet waste by operating at mass transfer limited current densities for anodic dissolution.

Oxidation of iron at inert anode. Anodic dissolution of NdFeB magnets produces Fe(II) ions which need to be oxidized to Fe(III) to achieve effective separation between REEs and iron. To study the effect of current on the oxidation of Fe(II), a constant current (I_{NdFeB}) of 0.5 A was maintained at the AMA and four different currents (0 A, 0.06 A, 0.12 A, 0.2 A) were applied to the inert anode. The experiments were conducted between a pH of 2 and 6 with periodic addition of HCl to keep the un-oxidized Fe(II) as soluble species. Platinized titanium (Ti/Pt) was chosen for this study as the inert anode as it was found to have high exchange current density for oxidation of Fe(II) and has been applied for treatment of pickling effluents.[24,25] The control experiment (0 A) showed the highest dissolution of iron into the leachates (Figure 3).

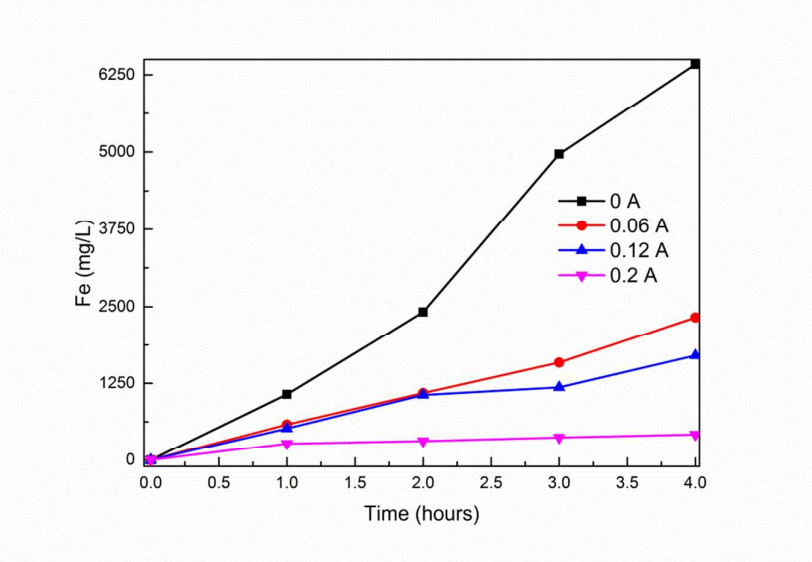


Figure 3. Influence of the current density over Fe(II) dissolution into the leachate (Stirring rate 500 rpm, I_{NdFeB} = 0.5 A, T = 25±2 ^{o}C, C_{NH4Cl} = 3 M NH_4Cl)

With increase in current densities at the inert anode ($I_{Ti/Pt}$), dissolution of Fe(II) into the leachate decreased. This can be attributed to either direct anodic oxidation of Fe(II), which has been found to be the predominant Fe(II) oxidation method, or by indirect electrochemical oxidation through dissolved oxygen.[26-27]

$$Fe^{2+} + 3\,H_2O \rightleftharpoons FeOH_3 + 3H^+ + e^- \ (E^0 = 0.931\ V) \quad (10)$$

$$2\,H_2O \rightleftharpoons 4H^+ + 4e^- + O_2 \ (E^0 = 1.23\ V) \quad (11)$$

The drop in Fe(II) dissolution was accompanied by the presence of sludgy $Fe(OH)_3$ precipitate. Around 0.2 A in the IA, ≥94% of Fe(II) was removed as $Fe(OH)_3$ in comparison

with the control experiment. Further increase in current density did not result in substantial removal of Fe(II) and hence, 0.2 A was chosen as current density at the inert anode.

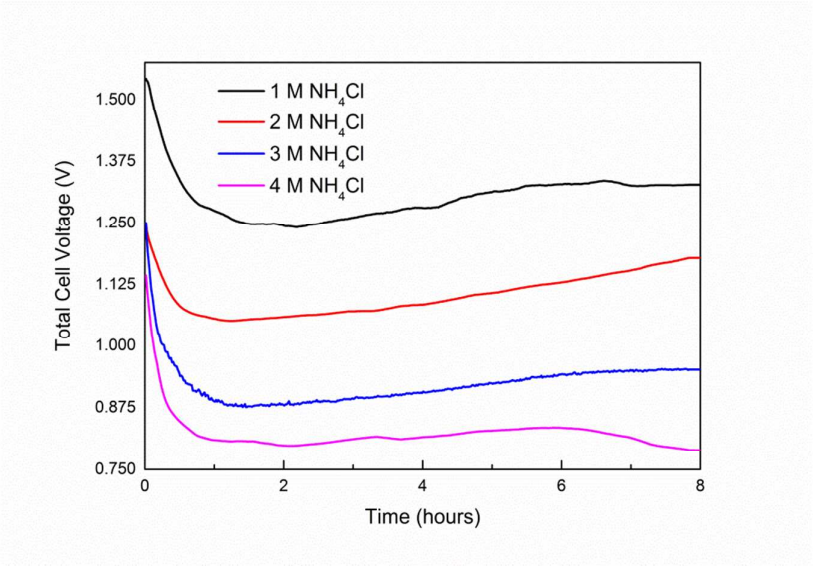


Figure 4. Effect of NH_4Cl concentration on the total cell voltage supplied between active magnet anode and the copper cathode (Stirring rate 500 rpm, duration of electrolysis = 8 hours, T = 25±2 ^oC, I_{NdFeB} = 0.5 A, $I_{Ti/Pt}$ = 0.2 A)

Effect of NH_4Cl concentration. The effect of NH_4Cl concentration on the galvanostatic electrolytic process was investigated by keeping the currents I_{NdFeB} and $I_{Ti/Pt}$ constant at 0.5 A and 0.2 A respectively. The electrolysis experiments were carried out for 8 hours at room temperature, 25±2 ^oC. No acid was added during the electrolysis pretreatment step. The anodic potential for all NH_4Cl concentrations remained well below 0 V (vs Ag/AgCl), hinting a highly efficient dissolution process without any parasitic reactions consuming the supplied charge (Table 2). The anodic dissolution efficiency was ≥98% irrespective of the concentration of the electrolyte. Enhanced kinetics and efficient anodic dissolution are important improvements over other room-temperature pretreatment processes such as aqueous corrosion which takes a week.[28]

Table 2. Effect of NH_4Cl concentration on magnet anode potential, magnet dissolution, anodic dissolution efficiency and energy consumption of the electrolysis step.

NH_4Cl molarity (M)	Anode potential (V vs Ag/AgCl)	Mass of magnet dissolved (g)	Anodic dissolution efficiency (%)	Mass gain at cathode (g)	Energy consumption (kWh/kg)
1	-0.34 to -0.23	4.7±0.1	97.2±0.4	0.12	3.6
2	-0.29 to -0.20	4.85±0.15	98.1±0.2	0.20	3.3
3	-0.30 to -0.22	4.9±0.1	99.3±0.4	0.13	3.0
4	-0.28 to -0.21	5±0.1	99.8±0.1	0.22	2.9

The total cell voltage and the energy consumption decreased with the increase in NH_4Cl concentration (Figure 4). High chloride concentrations (1M and above) enhances the metal dissolution via chloride adsorption mechanism and can therefore be the reason behind the voltage drop.[29] An initial drop in cell voltage was also observed which can be attributed to an increase in the conductivity of the electrolyte due to introduction of ions from dissolution of the magnet waste. The cell voltage between the inert anode and the copper cathode remained around 1.8-2.1 V for the whole duration of the experiment. Hydrogen gas evolution was the predominant cathodic reaction combined with deposition of a small amount of metallic iron.

$$2H^+ + 2e^- \rightleftharpoons H_2 \ (E^0 = 0\ V) \quad (12)$$

$$Fe^{2+} + 2e^- \rightleftharpoons Fe \ (E^0 = -0.44\ V) \quad (13)$$

At the end of electrolysis, a sludgy precipitate was obtained. The end pH of the leachate after electrolysis was around 6.6±0.3. In spite of adding no acid during the electrolysis step, both cobalt and REEs were extracted into the leachate, at varying amounts with iron as minor impurity as shown in Table 3.

Table 3. Percentage extraction of cobalt and REEs after electrolysis step

NH_4Cl Molarity	Co (%)	REEs (%)	Fe (%)
1 M	99.1±0.5	14.5±0.2	0
2 M	98.8±0.9	13.6±0.6	0.1
3 M	99.3±0.2	12.9±0.4	0.4±0.1
4 M	99.5±0.2	12.5±0.5	0.8±0.2

The near complete extraction of cobalt at the end of electrolysis can be explained by cobalt's tendency to form stable ammoniacal complexes.[30-31] However, REEs are not known to form ammine complexes and it was surprising that around 12-15 % of REEs were extracted into the solution at the end of the electrolysis step. A possible explanation could be that in addition to oxidation of Fe(II) and water at the inert anode, chloride ions were oxidized to produce chlorine gas which could then oxidatively dissolve metals.[32]

$$2\,Cl^- \rightleftharpoons Cl_2 + 2e^- \quad (14)$$

No significant loss of chloride ions was measured after the end of the electrolysis step by ion chromatography. Thus, the electro-generated chlorine gas could have contributed *in-situ* to the dissolution of REEs. This could also explain the minor dissolution of iron into the leachates at high concentrations of NH_4Cl. To remove the minor iron impurity, the leachate obtained at the end of electrolysis step was further stirred in air to oxidize the remnant Fe(II). It was observed that almost all iron could be removed from the leachate within 12 hours.

Overall, the electrolysis pretreatment step can be performed with an energy consumption of 3 kWh/kg of magnet waste at room temperature. The energy consumption is twice as high as the electrochemical oxidative approach we investigated before to recycle NdFeB magnet waste.[11] However, the electro-oxidative approach required complete and unselective dissolution of magnet waste in acid. Recently, we investigated a membrane based electrochemical reactor to selectively dissolve REEs from NdFeB magnet waste.[33] In comparison with the membrane process which consumed 5.5 kWh/kg of magnet waste, the dual anode reactor developed in this manuscript consumed lesser energy.

Selective acid leaching. Following the electrolysis step, the mixed hydroxides precipitate was leached with different concentrations of HCl to selectively extract the REEs.

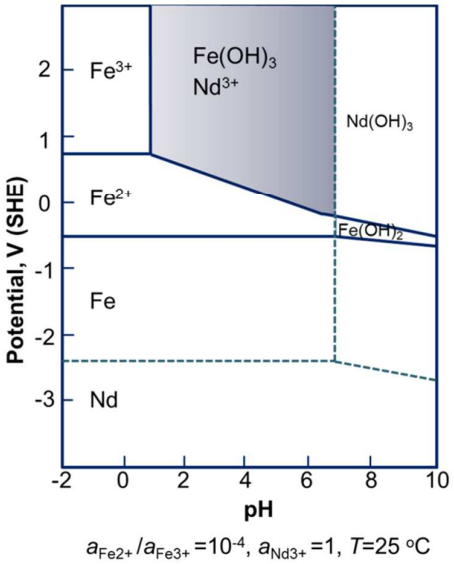


Figure 5. Potential–pH diagram of the Fe–H_2O and Nd–H_2O systems (regenerated according to data from [34] and HSC chemistry 6)

The potential-pH diagram for Nd-H_2O system and the Fe-H_2O system is shown in Figure 5. REEs are stable in the solution until a pH of 7 (K_{sp} $Nd(OH)_3$ = 1.9 x 10^{-21}) while iron remains as $Fe(OH)_3$ precipitate at a pH of around 3 and above.[35] Thus, REEs can be selectively leached from the mixed hydroxides precipitate to the solution leaving iron in the residue. The end pH of the leachate was adjusted to 4 to ensure no Fe(III) was extracted into the solution.

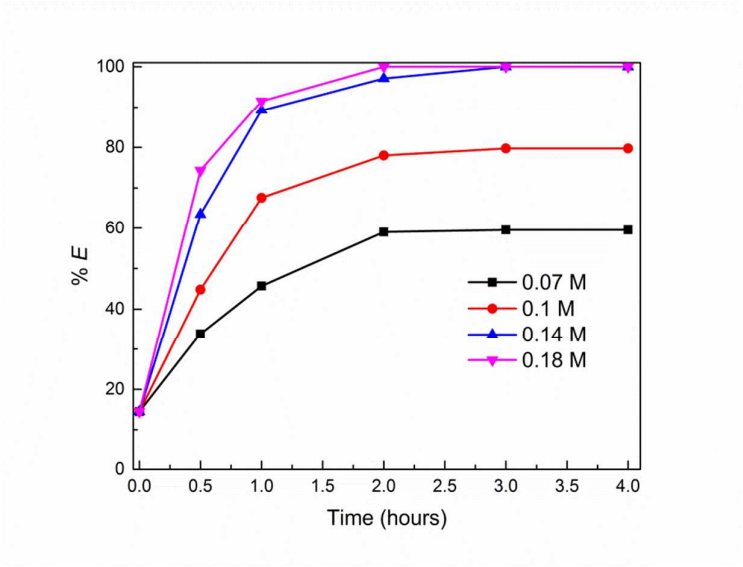


Figure 6. Percentage extraction of REEs as a function of the HCl concentration (T = 25±2 ^{o}C and stirring rate 500 rpm).

A pink leachate was obtained where REEs were completely and selectively extracted at a concentration of 0.14 M HCl and above (Figure 6). This process took less than 3 hours and it is considerably faster than the selective leaching step following oxidative roasting pretreatment which took five days.[16] The number of moles of acid required per mole of REEs present in the mixed hydroxide precipitate (nHCl/nREEs) was only 2.5, lower than the stoichiometric requirement of 3. This lower than stoichiometric consumption of HCl is due to the partial extraction of REEs at the end of electrolysis step.

The composition of the leachate obtained after the acid leaching step is given in Table 4. The concentration of cobalt decreased with increase in NH_4Cl concentration whereas the concentration of REEs were more or less the same. This could be explained by higher dissolution of iron during electrolysis with increase in NH_4Cl concentration due to pitting corrosion. Despite the decrease of cobalt concentration in the leachate, the percentage of extraction of cobalt remained above 98% irrespective of NH_4Cl concentration. Nevertheless, it can be seen that Fe(II) oxidation by inert anode was effective and no iron was present in the solution. The concentration of REEs can be further increased with prolonged time of electrolysis or by increasing the amount of magnet waste handled per batch of the experiment.

XRD pattern of the leach residue after the acid leaching process consisted mainly of Akaganeite (Figure 7). Akaganeite is the β phase of the Fe(III) oxyhydroxides FeOOH and is

usually formed in the presence of chloride ions. Akaganeite can be used in gas sensors, in water treatment industry or as pigments. [36]

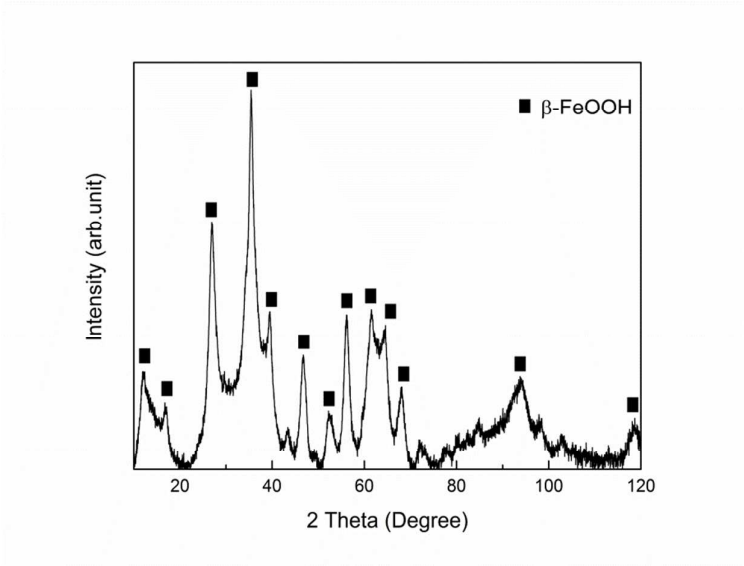


Figure 7: XRD pattern of Akaganeite FeOOH, leach residue obtained after acid leaching step.

Similar to Recai et al.,[15] around 10±4% of boron was extracted into the leachate and most of the boron was present in the residue. Iron hydroxides have the capacity to act as metal scavengers and boron is often removed from the leachate by coagulation or electrocoagulation with ferric hydroxide.[37-38] Nevertheless, further analysis is necessary to completely understand the boron chemistry in this recycling process. Though a relatively pure magnet waste is used in this manuscript, this pretreatment process can also be used for complex end-of-life magnet waste. The other minor elements such as nickel, copper can be co-extracted into the leachate while aluminium can be precipitated along with iron. [39]

Table 4. Composition of leachates after acid leaching step

NH_4Cl molarity (M)	Nd mg/L	Dy mg/L	Pr mg/L	Co mg/L	Fe mg/L
1M	6827	1411	365	198	<0.1
2M	6789	1378	368	129	<0.1
3M	6684	1576	351	60	<0.1
4M	7110	1481	387	60	<0.1

Oxalic acid precipitation of REEs. Oxalic acid is traditionally used for precipitating REEs from the solution. [40]

$$2\,RECl_3 + 3H_2C_2O_4 \rightarrow RE_2(C_2O_4)_3 + 6HCl \quad (15)$$

In comparison with cobalt oxalates ($Ksp_{(cobalt\ oxalate)} = 6 \times 10^{-8}$), rare-earth oxalates are highly insoluble ($Ksp_{(neodymium\ oxalate)} = 1.3 \times 10^{-31}$) and this difference can be used to selectively precipitate REEs over cobalt. [41-42, 9, 11] Around 98.5±0.5 % of REEs and 99.2±0.2 % of cobalt were recovered from the selective leaching step. Iron was removed almost completely from the leachate. A small excess of oxalic acid ($nC_2O_4^{2-}$ / $nREE^{3+} = 2$) was sufficient to precipitate 99% of REEs from the solution as rare-earth oxalates while less than 0.5% of cobalt co-precipitated. Overall, around 97.5±0.5 % of REEs can be recovered from the magnet waste. Then, the rare-earth oxalates were calcined at 950 ^{o}C to obtain rare-earth oxides (Figure 8). ICP-OES analysis of the obtained oxides exhibited a high purity (99.2±0.2%) with minor impurities of cobalt and copper. Importantly, the acid used in the selective acid leaching step is regenerated resulting in a closed-loop process.

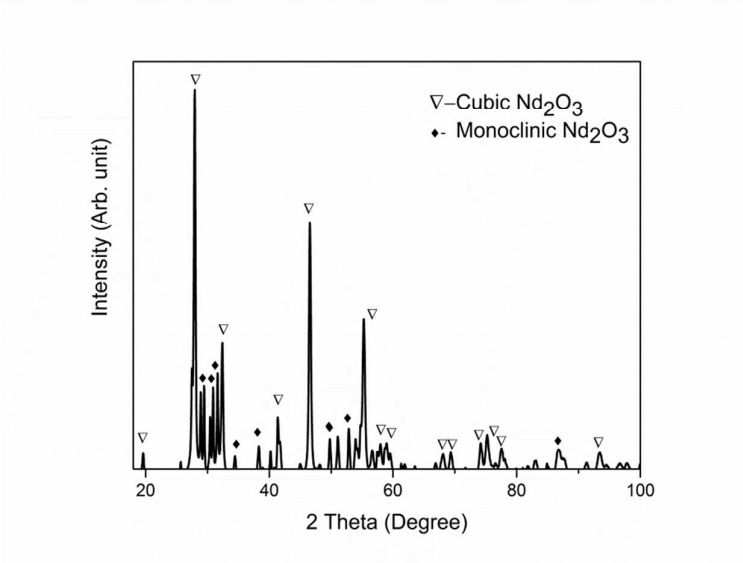


Figure 8: XRD pattern of the rare-earth oxides obtained after the calcination step.

CONCLUSIONS

We developed an environmentally friendly recycling process to selectively extract REEs from NdFeB magnet at room temperature. The overall process consists of five distinctive steps

(Figure 9). The magnet waste was first subjected to an electrolysis pretreatment step where the solid sintered magnet was made as an anode along with a Ti/Pt inert anode. The components in the magnet waste were converted into a mixed hydroxides precipitate. The ratio of current supplied between magnet anode and inert anode was optimized to ensure efficient oxidation of Fe(II) to $Fe(OH)_3$. NH_4Cl was used as the electrolyte and an increase in NH_4Cl concentration increased the anodic dissolution efficiency and lowered the energy consumption. REEs and cobalt were then selectively leached with HCl from the mixed hydroxides precipitate leaving iron hydroxide in the residue. Subsequently, oxalic acid was added to selectively precipitate rare-earth oxalates and to regenerate the acid used in the leaching step forming a closed-loop process with no net consumption of HCl. Calcination of rare-earth oxalates produced rare-earth oxides of high purity (99.2%). The whole process consumes only electricity, water and oxalic acid. The electrolysis pretreatment process is an effective room temperature alternative to high temperature roasting pretreatment process. The process can be scaled-up with an acceptable energy consumption of 3 kWh/kg of NdFeB magnet waste.

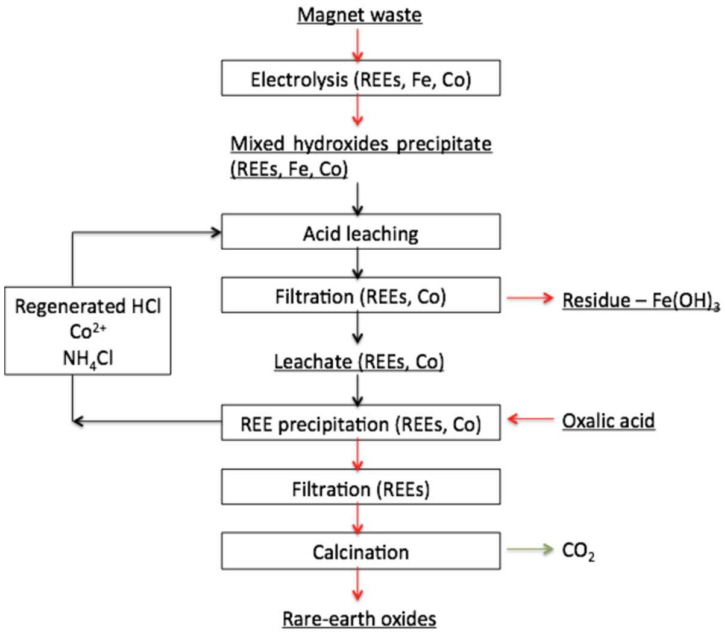


Figure 9. Process flowsheet for the proposed recycling scheme. Red arrows: solid stream, black arrows: liquid stream, green arrow: gaseous stream.

ACKNOWLEDGEMENTS

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 authors' view, exempting the Community from any liability. Project website: www.erean.eu. The authors also acknowledge Michel Van den brink and Ruud Hendrikx of TU Delft for their contribution in ICP-OES and XRD analyses respectively.

REFERENCES

1. Charalampides, G.; Vatalis, K. I.; Apostoplos, B.; Ploutarch-Nikolas, B., Rare Earth Elements: Industrial Applications and Economic Dependency of Europe. *Procedia Economics and Finance* **2015,** *24*, 126-135. DOI: 10.1016/S2212-5671(15)00630-9.
2. European Commision, E. C. *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: **2017**.
3. Binnemans, K.; Jones, P. T., Rare Earths and the Balance Problem. *J. Sustain. Metallurgy* **2015,** *1* (1), 29-38. DOI: 10.1007/s40831-014-0005-1.
4. Weng, Z.; Haque, N.; Mudd, G. M.; Jowitt, S. M., Assessing the energy requirements and global warming potential of the production of rare earth elements. *J. Clean. Prod.* **2016,** *139*, 1282-1297. DOI: 10.1016/j.jclepro.2016.08.132.
5. Gambogi, J. *2014 Minerals Yearbook: Rare earths*; U.S Geological Service: Reston https://minerals.usgs.gov/minerals/pubs/commodity/rare_earths/myb1-2014-raree.pdf, **2016**.
6. Binnemans, K.; Jones, P. T.; Blanpain, B.; Van Gerven, T.; Yang, Y.; Walton, A.; Buchert, M., Recycling of rare earths: a critical review. *J. Clean. Prod.* **2013,** *51*, 1-22. DOI: 10.1016/j.jclepro.2012.12.037.
7. Yang, Y.; Walton, A.; Sheridan, R.; Güth, K.; Gauß, R.; Gutfleisch, O.; Buchert, M.; Steenari, B.-M.; Van Gerven, T.; Jones, P. T.; Binnemans, K., REE Recovery from End-of-Life NdFeB Permanent Magnet Scrap: A Critical Review. *J. Sustain. Metallurgy* **2016**, 1-28. DOI: 10.1007/s40831-016-0090-4.
8. Lyman, J. W.; Palmer, G. R., Recycling of Rare Earths and Iron from NdFeB Magnet Scrap. *High Temp. Mater. Processes* **1993,** *11* (1-4), 175-187. DOI: 10.1515/HTMP.1993.11.1-4.175.
9. Önal, M. A. R.; Borra, C. R.; Guo, M.; Blanpain, B.; Van Gerven, T., Hydrometallurgical recycling of NdFeB magnets: Complete leaching, iron removal and electrolysis. *Journal of Rare Earths* **2017,** *35* (6), 574-584. DOI: 10.1016/S1002-0721(17)60950-5.
10. Morgan, B.; Lahav, O., The effect of pH on the kinetics of spontaneous Fe(II) oxidation by O_2 in aqueous solution--basic principles and a simple heuristic description. *Chemosphere* **2007,** *68* (11), 2080-4. DOI: 10.1016/j.chemosphere.2007.02.015.
11. Venkatesan, P.; Sun, Z. H. I.; Sietsma, J.; Yang, Y., An environmentally friendly electro-oxidative approach to recover valuable elements from NdFeB magnet waste. *Sep. Purif. Technol.* **2018,** *191* (Supplement C), 384-391. DOI: 10.1016/j.seppur.2017.09.053.
12. Itoh, M.; Miura, K.; Machida, K.-i., Novel rare earth recovery process on Nd–Fe–B magnet scrap by selective chlorination using NH_4Cl. *J. Alloys Compd.* **2009,** *477* (1-2), 484-487. DOI: 10.1016/j.jallcom.2008.10.036.
13. Maroufi, S.; Khayyam Nekouei, R.; Sahajwalla, V., Thermal Isolation of Rare Earth Oxides from Nd–Fe–B Magnets Using Carbon from Waste Tyres. *ACS Sustainable Chem. Eng.* **2017,** *5* (7), 6201-6208. DOI: 10.1021/acssuschemeng.7b01133.

14. Bian, Y.; Guo, S.; Jiang, L.; Liu, J.; Tang, K.; Ding, W., Recovery of Rare Earth Elements from NdFeB Magnet by VIM-HMS Method. *ACS Sustainable Chem. Eng.* **2016,** *4* (3), 810-818. DOI: 10.1021/acssuschemeng.5b00852.
15. Önal, M. A. R.; Borra, C. R.; Guo, M.; Blanpain, B.; Van Gerven, T., Recycling of NdFeB Magnets Using Sulfation, Selective Roasting, and Water Leaching. *J. Sustain. Metallurgy* **2015,** *1* (3), 199-215. DOI: 10.1007/s40831-015-0021-9.
16. Vander Hoogerstraete, T.; Blanpain, B.; Van Gerven, T.; Binnemans, K., From NdFeB magnets towards the rare-earth oxides: a recycling process consuming only oxalic acid. *RSC Adv.* **2014,** *4* (109), 64099-64111. DOI: 10.1039/c4ra13787f.
17. Sueptitz, R.; Tschulik, K.; Uhlemann, M.; Schultz, L.; Gebert, A., Effect of high gradient magnetic fields on the anodic behaviour and localized corrosion of iron in sulphuric acid solutions. *Corros. Sci.* **2011,** *53* (10), 3222-3230. DOI: 10.1016/j.corsci.2011.05.070.
18. Zheng, J.; Jiang, L.; Chen, Q., Electrochemical Corrosion Behavior of Nd-Fe-B Sintered Magnets in Different Acid Solutions. *Journal of Rare Earths* **2006,** *24* (2), 218-222. DOI: 10.1016/s1002-0721(06)60097-5.
19. Lakshmanan, D.; Clifford, D. A.; Samanta, G., Ferrous and Ferric Ion Generation During Iron Electrocoagulation. *Environ. Sci. Technol.* **2009,** *43* (10), 3853-3859. DOI: 10.1021/es8036669.
20. Tong, M.; Yuan, S.; Zhang, P.; Liao, P.; Alshawabkeh, A. N.; Xie, X.; Wang, Y., Electrochemically induced oxidative precipitation of Fe(II) for As(III) oxidation and removal in synthetic groundwater. *Environ. Sci. Technol.* **2014,** *48* (9), 5145-53. DOI: 10.1021/es500409m.
21. Jones, D., *Principles and prevention of corrosion*. Prentice Hall: New Jersey, 1996.
22. Sato, N., The stability of localized corrosion. *Corros. Sci.* **1995,** *37* (12), 1947-1967. DOI: 10.1016/0010-938X(95)00076-V.
23. El-Moneim, A. A.; Gebert, A.; Schneider, F.; Gutfleisch, O.; Schultz, L., Grain growth effects on the corrosion behavior of nanocrystalline NdFeB magnets. *Corros. Sci.* **2002,** *44* (5), 1097-1112. DOI: 10.1016/S0010-938X(01)00123-8.
24. L. Cifuentes; Glasner, R., Kinetics of Fe^{2+}/Fe^{3+} oxidation on various anode materials. *Rev.Metal.Madrid* **2003,** *39*, 260-267.
25. Bisang, J. M., Electrochemical treatment of waste solutions containing ferrous sulfate by anodic oxidation using an undivided reactor. *Journal of Applied Electrochemistry* **2000,** *30* (4), 399-404. DOI: 10.1023/A:1003934209915.
26. Park, S.-M.; Shin, S.-Y.; Yang, J.-S.; Ji, S.-W.; Baek, K., Selective Recovery of Dissolved Metals from Mine Drainage Using Electrochemical Reactions. *Electrochim. Acta* **2015,** *181*, 248-254. DOI: 10.1016/j.electacta.2015.03.085.
27. Lee, J.; Darus, H. B.; Langer, S. H., Electrogenerative oxidation of ferrous ions with graphite electrodes. *J. Appl. Electrochem.* **1993,** *23* (7), 745-752. DOI: 10.1007/bf00243345.
28. Kataoka, Y.; Ono, T.; Tsubota, M.; Kitagawa, J., Improved room-temperature-selectivity between Nd and Fe in Nd recovery from Nd-Fe-B magnet. *AIP Advances* **2015,** *5* (11), 117212. DOI: 10.1063/1.4935570.
29. Sato, N., 1989 Whitney Award Lecture: Toward a More Fundamental Understanding of Corrosion Processes. *Corrosion* **1989,** *45* (5), 354-368. DOI: doi:10.5006/1.3582030.
30. Dupont, D.; Binnemans, K., Rare-earth recycling using a functionalized ionic liquid for the selective dissolution and revalorization of Y_2O_3:Eu^{3+} from lamp phosphor waste. *Green Chem.* **2015,** *17* (2), 856-868. DOI: 10.1039/C4GC02107J.
31. Katsiapi, A.; Tsakiridis, P. E.; Oustadakis, P.; Agatzini-Leonardou, S., Cobalt recovery from mixed Co–Mn hydroxide precipitates by ammonia–ammonium carbonate leaching. *Miner. Eng.* **2010,** *23* (8), 643-651. DOI: 10.1016/j.mineng.2010.03.006.
32. Pilone, D.; Kelsall, G. H., Metal Recovery from Electronic Scrap by Leaching and Electrowinning IV. In *Electrometallurgy and Environmental Hydrometallurgy*, John Wiley & Sons, Inc.: 2013; pp 1565-1575. DOI: 10.1002/9781118804407.ch37.

33. Venkatesan, P.; Vander Hoogerstraete, T.; Hennebel, T.; Binnemans, K.; Sietsma, J.; Yang, Y., Selective electrochemical extraction of REEs from NdFeB magnet waste at room temperature. *Green Chem.* **2018,** *20* (5), 1065-1073. DOI: 10.1039/C7GC03296J.

34. Tanaka, M.; Oki, T.; Koyama, K.; Narita, H.; Oishi, T., Chapter 255 - Recycling of Rare Earths from Scrap. In *Handbook on the Physics and Chemistry of Rare Earths*, Jean-Claude, G. B.; Vitalij, K. P., Eds. Elsevier: 2013; Vol. Volume 43, pp 159-211. DOI: 10.1016/B978-0-444-59536-2.00002-7.

35. Tobias, R. S.; Garrett, A. B., The Thermodynamic Properties of Neodymium Hydroxide $Nd(OH)_3$, in Acid, Neutral and Alkaline Solutions at 25°; the Hydrolysis of the Neodymium and Praseodymium Ions, Nd^{3+}, Pr^{3+}. *J. Am. Chem. Soc.* **1958,** *80* (14), 3532-3537. DOI: 10.1021/ja01547a011.

36. Villalba, J. C.; Berezoski, S.; Cavicchiolli, K. d. A.; Galvani, V.; Anaissi, F. J., Structural refinement and morphology of synthetic akaganèite crystals, [β-FeO(OH)]. *Mater. Lett.* **2013,** *104*, 17-20. DOI: 10.1016/j.matlet.2013.04.004.

37. Riano, S.; Binnemans, K., Extraction and separation of neodymium and dysprosium from used NdFeB magnets: an application of ionic liquids in solvent extraction towards the recycling of magnets. *Green Chem.* **2015,** *17* (5), 2931-2942. DOI: 10.1039/C5GC00230C.

38. Xu, Y.; Jiang, J.-Q., Technologies for Boron Removal. *Ind. Eng. Chem. Res.* **2008,** *47* (1), 16-24. DOI: 10.1021/ie0708982.

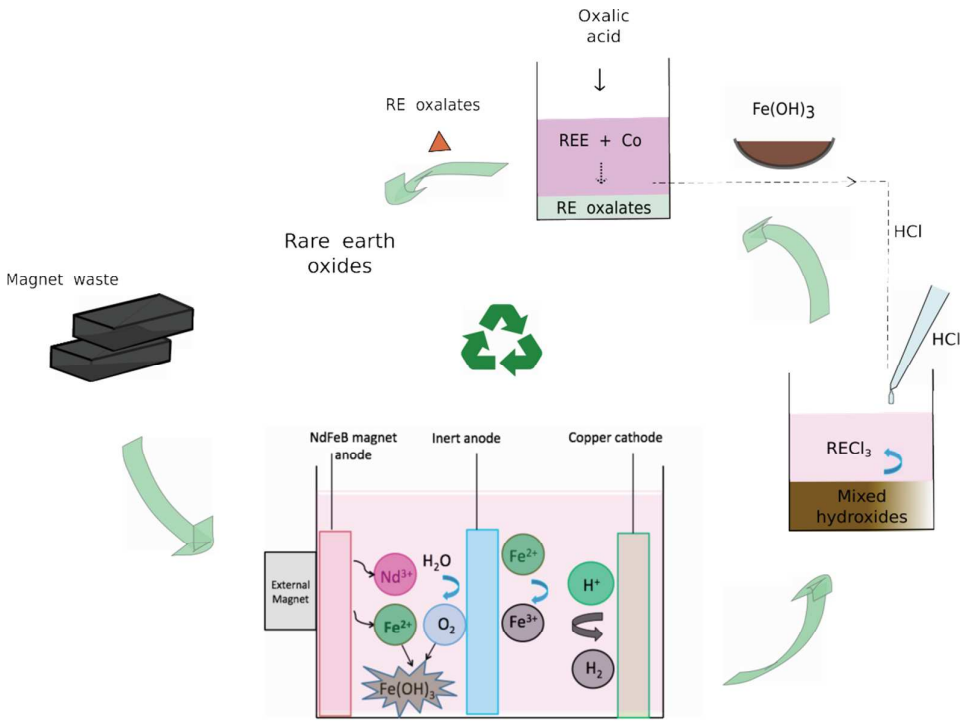
39. Borra, C. R.; Mermans, J.; Blanpain, B.; Pontikes, Y.; Binnemans, K.; Van Gerven, T., Selective recovery of rare earths from bauxite residue by combination of sulfation, roasting and leaching. *Miner. Eng.* **2016,** *92*, 151-159. DOI: 10.1016/j.mineng.2016.03.002.

40. Huang, X.; Dong, J.; Wang, L.; Feng, Z.; Xue, Q.; Meng, X., Selective recovery of rare earth elements from ion-adsorption rare earth element ores by stepwise extraction with HEH(EHP) and HDEHP. *Green Chem.* **2017,** *19* (5), 1345-1352. DOI: 10.1039/C6GC03388A.

41. Shibata, J.; Murayama, N.; Niinae, M.; Furuyama, T., Development of Adavanced Separation Technology of Rare Metals Using Extraction and Crystallization Stripping. *Mater. Trans.* **2012,** *53* (12), 2181-2186. DOI: 10.2320/matertrans.M2012234.

42. Chung, D. Y.; Kim, E. H.; Lee, E. H.; Yoo, J. H., Solubility of Rare Earth Oxalate in Oxalic and Nitric Acid Media. *J. Ind. Eng. Chem.* **1998,** *4* (4), 277-284.

TOC Abstract



Synopsis: A closed-loop room temperature electrolysis pretreatment step to selectively recover REEs from NdFeB magnet waste with no HCl consumption.