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Selective Extraction of Rare-Earth Elements from NdFeB Magnets by a Room-Temperature Electrolysis Pretreatment Step

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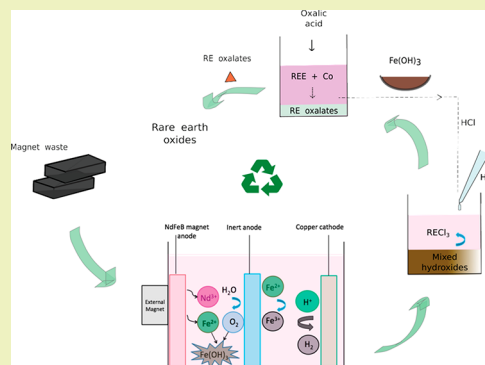
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ABSTRACT: NdFeB magnets are used in wind turbines and hybrid electric vehicles and are instrumental in progression toward a low-carbon economy. Recycling rare-earth elements (REEs) from NdFeB magnet waste is an important step toward building a sustainable 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 (FCCs), and fluorescent lamps.¹ The European Commission classified REEs as critical raw materials due to supply chain risks and an increasing demand from the 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 nonrecyclable chemicals such as H₂SO₄, HF, NaOH and generate considerable volumes of wastewater.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

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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 °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 Fe₂O₃ 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 NH₄Cl 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 byproduct that can be used in pigment and gas sensors industries. The whole process consumes only electricity, water, and oxalic acid.

EXPERIMENTAL SECTION

Materials and Methods. Solid sintered magnets used as electrodes were supplied by Magneti Ljubljana (Slovenia) and their composition as measured with ICP-OES is listed in Table 1. HCl (37%), oxalic acid dihydrate (≥99%), and NH₄Cl (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

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		

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 Chromatograph). The leach residue and the rare-earth oxides were characterized with XRD using Bruker D8 diffractometer with Cu K α radiation operating at 45 kV.

Experimental Setup and Procedure. A PMMA reactor (10 cm × 10 cm × 7 cm) was used as an electrochemical cell and the electrolyte volume was kept constant at 200 mL during the experiment. A solid sintered magnet (2.5 cm × 1.5 cm × 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 cm² (10 cm × 2.3 cm) was dipped into the electrolyte as cathode and the back of the plate was masked with an insulating tape. Ag/AgCl (3 M 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 °C 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 cm² 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 the 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 min 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 triplicate. 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

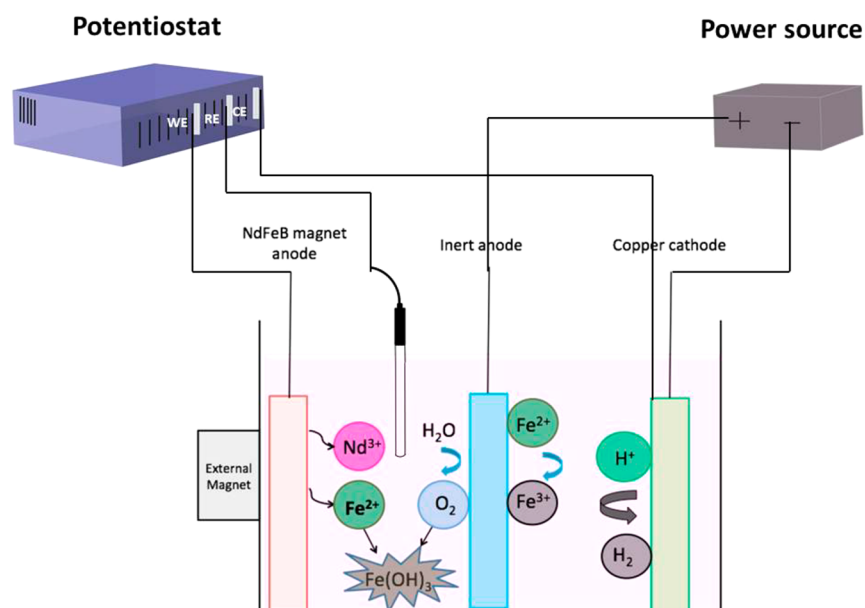


Figure 1. Schematic representation of dual anode electrolysis reactor to recycle NdFeB magnet waste. (WE working electrode; RE reference electrode; CE counter electrode).

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

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

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

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

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

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

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

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

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

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 kilowatt hours 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)

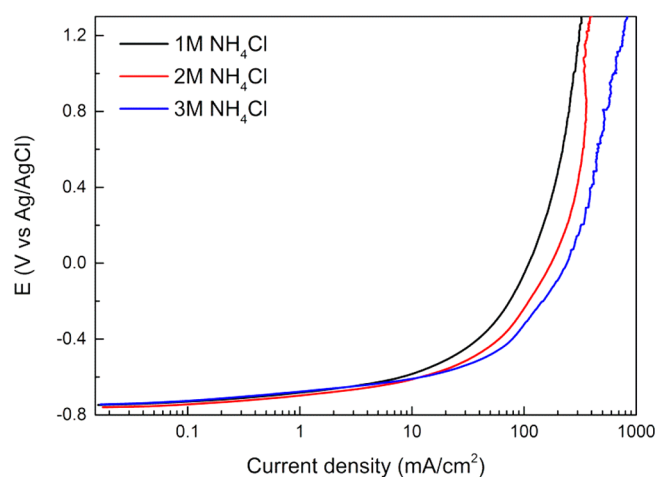
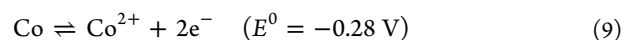
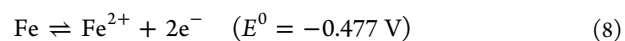
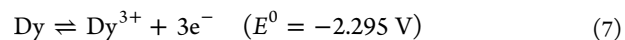
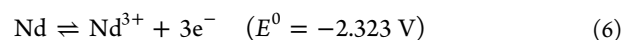


Figure 2. Potentiodynamic polarization curves of NdFeB magnets in 1, 2, and 3 M NH_4Cl , at a scan rate 2 mV/s and temperature 25 ± 2 °C.

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



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

NdFeB magnets have a matrix phase ($\text{Nd}_2\text{Fe}_{14}\text{B}$) 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-Moneim 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 needs 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, 0.06, 0.12, 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 unoxidized 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).

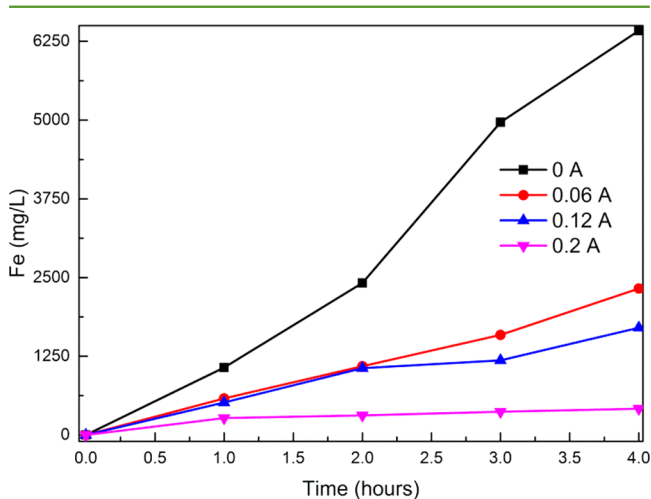
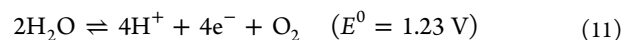
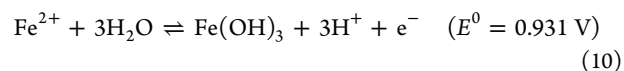


Figure 3. Influence of the current density over Fe(II) dissolution into the leachate (stirring rate 500 rpm, $I_{\text{NdFeB}} = 0.5 \text{ A}$, $T = 25 \pm 2 \text{ }^\circ\text{C}$, $C_{\text{NH}_4\text{Cl}} = 3 \text{ M NH}_4\text{Cl}$).

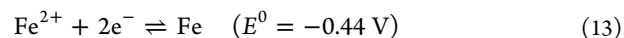
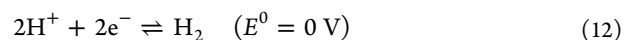
With increase in current densities at the inert anode ($I_{\text{Ti/Pt}}$), dissolution of Fe(II) into the leachate decreased. This can be attributed to either direct anodic oxidation of Fe(II), which has been found to be the predominant Fe(II) oxidation method, or by indirect electrochemical oxidation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



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

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 $I_{\text{Ti/Pt}}$ constant at 0.5 and 0.2 A, respectively. The electrolysis experiments were carried out for 8 h at room temperature, $25 \pm 2 \text{ }^\circ\text{C}$. 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 at a highly efficient dissolution process without any parasitic reactions consuming the supplied charge (Table 2). The anodic dissolution efficiency was $\geq 98\%$ 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

The total cell voltage and the energy consumption decreased with the increase in NH_4Cl concentration (Figure 4). High chloride concentrations (1 M and above) enhance the metal dissolution via the 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.

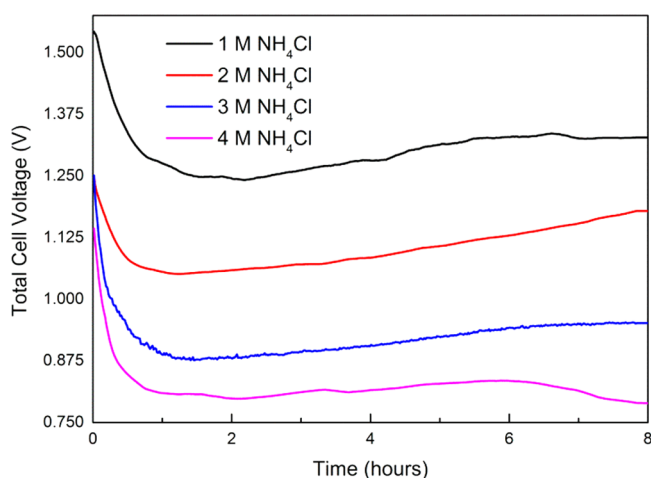


At the end of electrolysis, a sludgy precipitate was obtained. The end pH of the leachate after electrolysis was around 6.6 ± 0.3 . In spite of adding no acid during the electrolysis step, both cobalt and REEs were extracted into the leachate, at varying amounts with iron as minor impurity as shown in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

The near complete extraction of cobalt at the end of electrolysis can be explained by tendency of cobalt 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

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

**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 h, $T = 25 \pm 2^\circ\text{C}$, $I_{\text{NdFeB}} = 0.5\text{ A}$, $I_{\text{Ti/Pt}} = 0.2\text{ A}$).**Table 3.** Percentage Extraction of Cobalt and REEs after the 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

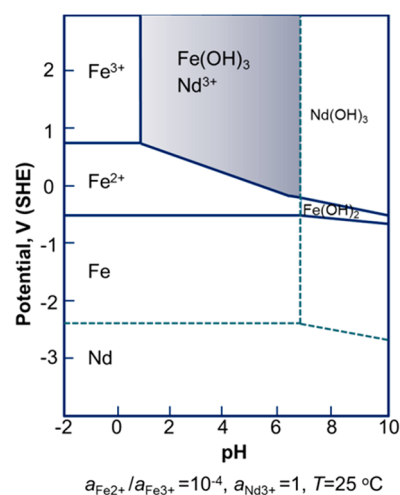


No significant loss of chloride ions was measured after the end of the electrolysis step by ion chromatography. Thus, the electro-generated chlorine gas could have contributed *in situ* to the dissolution of REEs. This could also explain the minor dissolution of iron into the leachates at high concentrations 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 h.

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.

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

**Figure 5.** Potential–pH diagram of the Fe– H_2O and Nd– H_2O systems (regenerated according to data from ref 34 with HSC Chemistry 6 software).

solution until a pH of 7 ($K_{\text{sp}} \text{Nd}(\text{OH})_3 = 1.9 \times 10^{-21}$) while iron remains as $\text{Fe}(\text{OH})_3$ 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.

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 h, and it is considerably faster than the selective leaching step following oxidative roasting pretreatment which took 5 days.¹⁶ The number of moles of acid required per mole of REEs present in the mixed hydroxide precipitate ($n\text{HCl}/n\text{REEs}$) 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

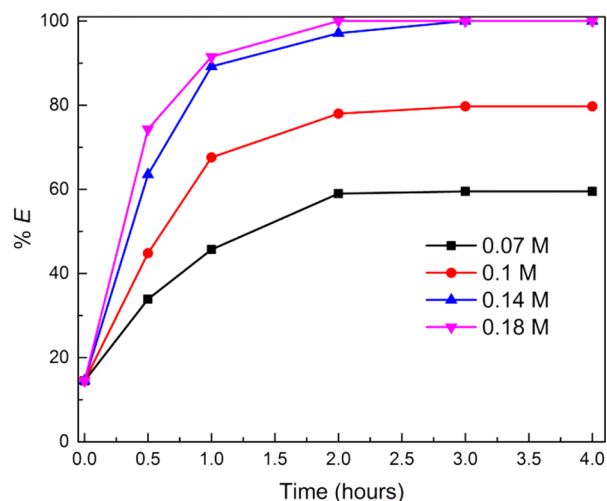


Figure 6. Percentage extraction of REEs as a function of the HCl concentration ($T = 25 \pm 2 \text{ }^\circ\text{C}$ and stirring rate 500 rpm).

Table 4. Composition of Leachates after the Acid Leaching Step

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

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

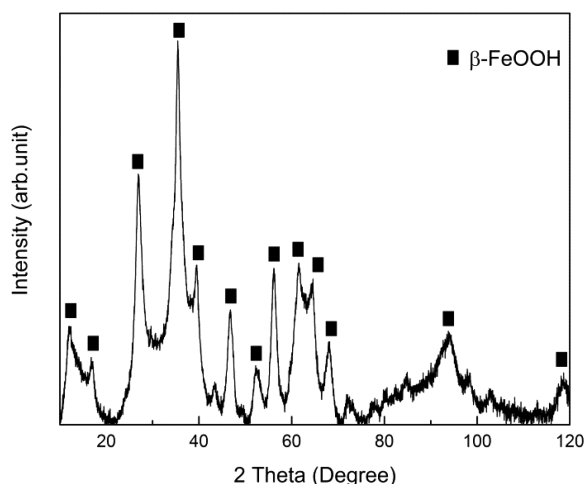


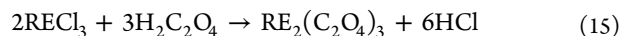
Figure 7. XRD pattern of Akaganeite FeOOH , leach residue obtained after acid leaching step.

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

Similar to the work of Önal et al.,¹⁵ around $10 \pm 4\%$ 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 coextracted into the leachate while aluminum can be precipitated along with iron.³⁹

Oxalic Acid Precipitation of REEs. Oxalic acid is traditionally used for precipitating REEs from the solution.⁴⁰



In comparison with cobalt oxalates ($K_{\text{sp}}(\text{cobalt oxalate}) = 6 \times 10^{-8}$), rare-earth oxalates are highly insoluble ($K_{\text{sp}}(\text{neodymium oxalate}) = 1.3 \times 10^{-31}$), and this difference can be used to selectively precipitate REEs over cobalt.^{41,42,9,11} Around $98.5 \pm 0.5\%$ of REEs and $99.2 \pm 0.2\%$ of cobalt were recovered from the selective leaching step. Iron was removed almost completely from the leachate. A small excess of oxalic acid ($n\text{C}_2\text{O}_4^{2-}/n\text{REE}^{3+} = 2$) was sufficient to precipitate 99% of REEs from the solution as rare-earth oxalates while less than 0.5% of cobalt coprecipitated. Overall, around $97.5 \pm 0.5\%$ of REEs can be recovered from the magnet waste. Then, the rare-earth oxalates were calcined at $950 \text{ }^\circ\text{C}$ to obtain rare-earth oxides (Figure 8).

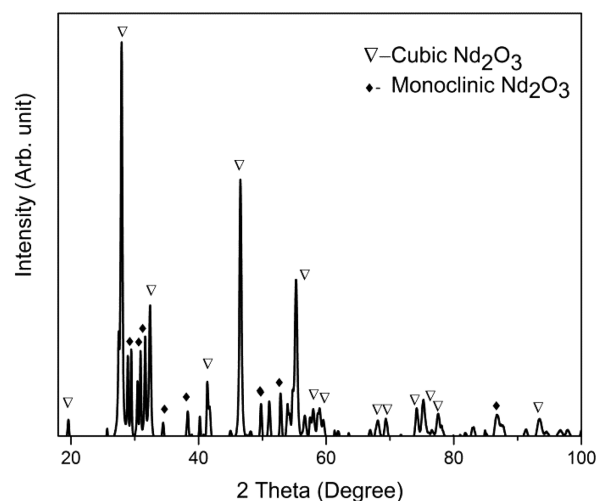


Figure 8. XRD pattern of the rare-earth oxides obtained after the calcination step.

ICP-OES analysis of the obtained oxides exhibited a high purity ($99.2 \pm 0.2\%$) 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.

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

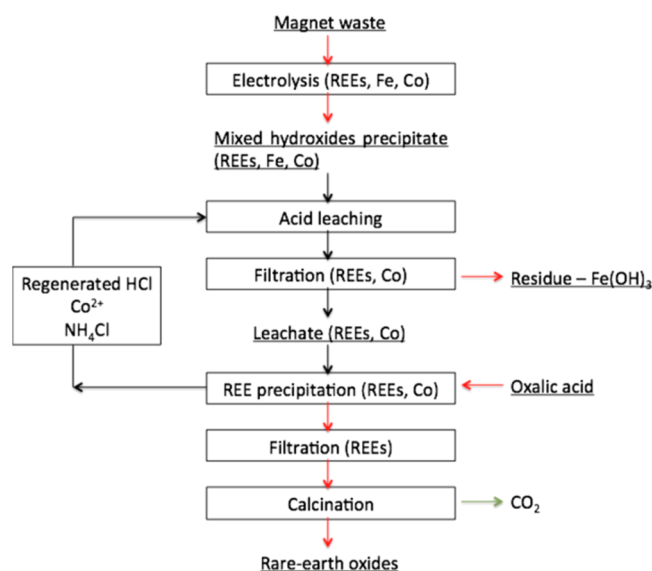


Figure 9. Process flowsheet for the proposed recycling scheme (red arrows solid stream, black arrows liquid stream, green arrow gaseous stream).

efficient oxidation of Fe(II) to Fe(OH)₃. NH₄Cl was used as the electrolyte and an increase in NH₄Cl 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.

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Notes

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