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# An Acid Free Electrified Process for Recycling Rare-Earth Elements from NdFeB Magnet Waste

Prakash Venkatesan,\* Jilt Sietsma, and Yongxiang Yang



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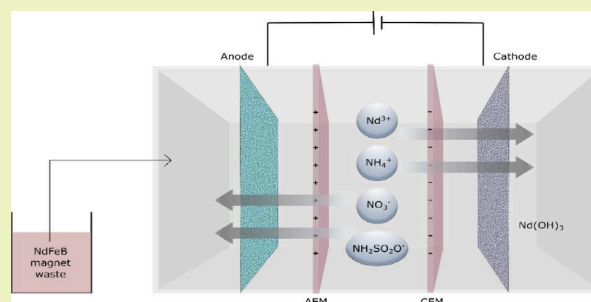
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**ABSTRACT:** Recycling of rare-earth elements (REEs) from NdFeB magnets is an important strategy to mitigate the risks associated with the REE supply chain. In this article, we propose an electrochemical process to recover REEs wherein all the reagents required for both leaching of REEs as well as the precipitation are generated *in situ* electrochemically. A three compartment electrochemical reactor was used in which a rare-earth containing salt along with an additive salt, ammonium sulfamate, was fed into the middle compartment. Upon electrolysis, the salts were split into acid and rare-earth hydroxides. The acid generated in the anolyte compartment was used to leach the NdFeB magnet waste. The rare-earth hydroxides were collected in the catholyte compartment and calcined to obtain rare-earth oxides. More than 95% of REEs and cobalt were extracted into the solution, and more than 85% of iron was removed as  $\text{Fe}(\text{OH})_3$  precipitate in the same step. Subsequently, the leachate was oxidized and neutralized to remove more than 99% of iron. By using electrons as green reagents, this process combines leaching and precipitation in a single reactor enabling process intensification. The leachate produced at the end is rich in REEs and can be fed again into the middle compartment, forming a completely closed-loop process. Overall, the process consumes no acid, only electricity, ammonium hydroxide for neutralization, and an additive salt, ammonium sulfamate.

**KEYWORDS:** electrochemical recycling, acid free process, rare-earth recovery, NdFeB magnets



## INTRODUCTION

Rare-earth elements (REEs) are considered critical metals due to substantial frailties in the supply chain and an increasing demand from the clean-tech sector.<sup>1,2</sup> REEs will play a key role in transitioning to a decarbonized economy as they are essential components in hybrid electric vehicles, wind turbines, batteries, and energy saving lighting. REE production from ores has significant environmental impacts of human toxicity, acidification, and global warming potential.<sup>3,4</sup> Moreover, mining REEs has created the “balancing problem” where naturally abundant elements such as cerium and lanthanum are stockpiled at the cost of elements with more demand such as neodymium and dysprosium. Thus, recycling REEs from manufacturing scrap and end-of-life waste is one of the important strategies to reduce the environmental impact and create an alternative supply chain. Around 22% of REEs produced globally are consumed for production of NdFeB magnets, making them one of the largest applications of REEs in terms of volume and market share.<sup>5,6</sup> Recycling of REEs from NdFeB magnets is under intense investigation in the recent years and the various processes developed thus far have been summarized in multiple reviews.<sup>5,7–11</sup>

Direct recycling of NdFeB magnet waste to new NdFeB magnets using hydrogen gas is effective, but the process is

sensitive to the composition of the magnet waste.<sup>12,13</sup> Alternatively, NdFeB magnets can be indirectly recycled by selectively recovering REEs as rare-earth oxides. NdFeB magnets consist of 20–30% REEs, 60–70% iron, and 1% boron, and thus, selective recovery of REEs over iron is the major objective in NdFeB recycling. Wet-chemical routes are preferred to recover REEs as they operate at room temperature and usually do not require complex set-ups. In wet-chemical processes, NdFeB magnet waste is completely leached into the solution with an inorganic acid. Subsequently, a precipitating agent is added to selectively precipitate REEs as rare-earth double sulfates or rare-earth fluorides.<sup>14–17</sup> However, wet-chemical routes are unselective between REEs and iron, consume excess acid and precipitating agents that cannot be recycled, and require additional steps to discharge metal containing acid waste.

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In contrast to wet-chemical routes, high temperature pyrometallurgical processes offer improved selectivity between REEs and iron.<sup>18–20</sup> In the oxidative roasting process, iron present in the magnet waste is converted into its Fe(III) oxide and REEs into rare-earth oxide. REEs can then be selectively leached into the solution with HCl, leaving behind iron oxide in the residue. Subsequently, the HCl used in this selective leaching step can be recovered through selective precipitation of REEs as rare-earth oxalates, forming a closed-loop process. Recently, an autoclave based process was designed to oxidize iron to ferric oxide to enable selective dissolution of REEs.<sup>21</sup> Nevertheless, these pyrometallurgical processes have high operational temperatures, can release toxic gases that need to be captured with additional set-ups, and are energy intensive.<sup>18,22</sup>

Alternatively, electrochemical processes have been developed by the author in which REEs were selectively extracted over iron at room temperature with no net acid consumed during the leaching step.<sup>23,24</sup> However, precipitation of rare-earth ions from the solution as rare-earth oxalates still requires oxalic acid.<sup>25–27</sup> Oxalic acid is an expensive chemical and the rare-earth oxalates produced from the precipitation step need to be calcined at around 800 °C, which releases CO<sub>2</sub> gas.<sup>28</sup> Thus far, no process has been created wherein NdFeB magnets can be converted into the marketable product of rare-earth oxides without consumption of non-recyclable chemicals.

In this paper, for the first time, we propose a completely electrified room-temperature process in which the REEs can be selectively extracted from NdFeB magnet waste and converted into rare-earth oxides without consuming any leachant or a precipitating agent such as oxalic acid. A rare-earth salt solution along with an additive salt ammonium sulfamate is taken in the middle compartment of a three compartment electrochemical reactor separated by an anion and a cation exchange membrane. The salt solutions were electrochemically split to produce an acid in the anolyte. The acid produced leached REEs from the magnet waste present in the anolyte compartment. Concomitantly, rare-earth hydroxides were produced in the catholyte compartment and were calcined to obtain rare-earth oxides. After electrolysis and neutralization, an REE-rich solution is obtained from the leaching of the magnet waste in the anolyte, which can be fed again into the middle compartment in the next run, forming a complete closed-loop process. The effect of type of salt, initial concentration of rare-earth nitrate and ammonium sulfamate, and current density over the metal extraction was systematically studied. The proposed electrolysis process combines leaching and precipitation in a single step, enabling process intensification. The whole flowsheet is acid free and consumes only electricity, water, and a small minimum of salt such as ammonium sulfamate.

## EXPERIMENTAL SECTION

**Materials.** Sodium chloride (NaCl, ≥99%), ammonium sulfamate ((NH<sub>4</sub>)<sub>2</sub>SO<sub>3</sub>, ≥99%), ammonium acetate, hydrochloric acid (HCl, 37%), ammonia solution (25% NH<sub>3</sub> in water), oxalic acid dihydrate (≥99%), and ferrozine (monosodium salt hydrate of 3-(2-pyridyl)-5,6-diphenyl-1,2,4-triazine-*p,p'*-disulfonic acid) were supplied by Sigma-Aldrich, B.V. (Zwijndrecht, The Netherlands). Neodymium nitrate hexahydrate (99.9%) was obtained from Alfa Aesar, 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 scrap used in this study was

supplied by Magneti (Slovenia). These bulk magnets are uncoated and failed the quality control step before getting magnetized, so no demagnetization step was needed. Ball-milling was performed using a Retsch RS100 ball-mill for 2 h to mill the bulk sintered magnets. Immediately after milling, the powder samples were divided into 1 g subsamples and stored in a plastic vial to offset the effect of oxidation on the extraction efficiency calculations.<sup>20</sup>

**Electrochemical Extraction Reactor.** The experiments were performed in a three compartment electrochemical reactor (three chambers each with internal dimension 8 cm × 8 cm × 2 cm with an effective volume of 128 mL). The anolyte and the middle compartment were separated by an anion exchange membrane 1q (FAS-PET-130, anion exchange membranes, Fumatech, Germany), while a cation exchange membrane separated the catholyte from the middle compartment (FKS-PET-130, cation exchange membranes, Fumatech, Germany). A stainless steel wire mesh was used as the cathode (Solana, Belgium) and a mixed metal oxide (35% TaO<sub>2</sub> and 65% IrO<sub>2</sub>) coated titanium electrode was used as the inert anode (Magneto Special Anodes B.V., Schiedam, The Netherlands). The anode and cathode had a projected electrode surface area of 64 cm<sup>2</sup> for each. A spacer material (ElectroCell A/S, Denmark) was placed between the surface of anode and the anion exchange membrane. All experiments were conducted using potentiostat Versastat 4 (Ametek, UK), and the data were obtained using Versastudio software. An Ag/AgCl (3M KCl) reference electrode was placed in the anode compartment. All three compartments were operated at a temperature of 30 ± 2 °C in batch mode at an internal recirculation rate of 50 mL min<sup>-1</sup>. The anolyte and catholyte consisted of 250 mL of 0.05 M ammonium sulfamate solution. The liquids were pumped from three different Scott bottles, which 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 syringe filter of 0.45 μm. The extraction efficiency (%) of any metal M was calculated by

$$E (\%) = \frac{M_L \times V_L}{X_M \times M_T} \times 100 \quad (1)$$

where *E* is the percentage of extraction of metal M (%), *M<sub>L</sub>* is amount of metal M present in the leachate (mg/L), *V<sub>L</sub>* is the volume of the leachate in liters, *X<sub>M</sub>* is the fraction of metal M in the magnet waste, and *M<sub>T</sub>* is the total amount of magnet waste used (mg).

The oxidation state of Fe in the leachate was measured using the ferrozine colorimetric method.<sup>29</sup> The concentration of Fe(II) was measured at wavelength 562 nm using a 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 the 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 completely dissolved in HCl (37%) for analysis. X-ray diffraction was carried out using a Bruker D8 diffractometer with Cu Kα radiation operated at 45 kV. The rare-earth hydroxide powder was deposited over a Pt–Rh strip, and the *in situ* high temperature experiment was carried out from 50–800 °C with steps of 50 °C.

## RESULTS AND DISCUSSION

**Electrochemical Leaching.** The elemental composition of the NdFeB magnet waste is given in Table 1. The magnet scrap investigated here has a high dysprosium content and is generally used in electric vehicles. Various leaching studies have been carried out on NdFeB magnets using HCl, H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub>, organic acids such as acetic acid, and ionic liquids.<sup>15,16,30,31</sup>

The solubility of rare-earth sulfates is low and the formation of highly insoluble rare-earth double sulfates is problematic as

**Table 1. Elemental Composition of NdFeB Magnets in wt %**

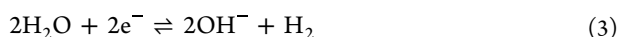
element	wt (%)	element	wt (%)
Fe	66.75	Gd	0.16
Nd	21.14	Si	0.08
Dy	5.9	Cu	0.08
Co	3.0	Ni	0.02
B	1.1	Al	0.1
Pr	0.62	total	99.09

they require further conversion steps. Nitrates are chosen over chlorides in this study to eliminate the possibility of anodic chlorine evolution in the electrochemical reactor.<sup>32</sup> Electrochemical salt splitting in membrane reactors has been investigated for several applications such as electrodialysis, brine water treatment, capacitive deionization and even for treating metal ores.<sup>33–35</sup> The three compartment electrochemical reactor used in this study is illustrated in Figure 1. The anolyte and middle compartment are separated by an anion exchange membrane (AEM). The catholyte and the middle compartment are separated by a cation exchange membrane (CEM).

In the first step, rare-earth nitrate salt that is only slightly in excess to the stoichiometric amount of REEs and cobalt present in the magnet waste is fed into the middle compartment. It is important to note that this ratio is maintained to ultimately enable selective recovery of REEs and cobalt in the solution, leaving out the major impurity of iron as ferric hydroxide in the residue. During electrolysis, water is oxidized at the anolyte compartment by the reaction



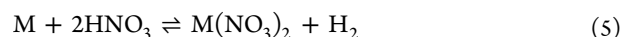
Anions such as nitrates migrate through the AEM from the middle compartment to the anolyte and combine with the protons to form nitric acid. Simultaneously, the rare-earth cations migrate through the CEM to the catholyte compartment where water is reduced to hydroxide ions by



The REEs combine with the hydroxide ions and can be precipitated as rare-earth hydroxides which, upon calcination, produce rare-earth oxides. This obviates the use of an external precipitating agent.

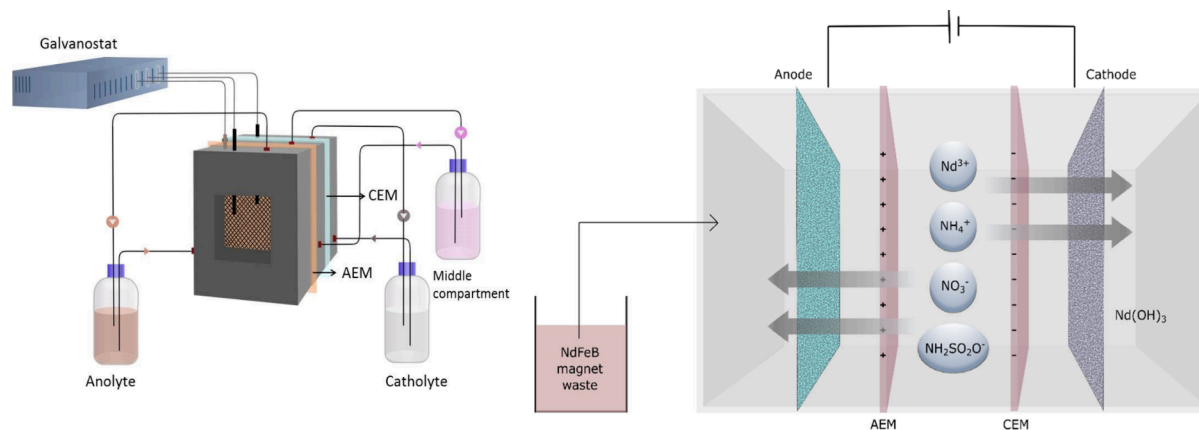
**Effect of  $\text{Nd}(\text{NO}_3)_3$  Concentration.** A 1 g portion of NdFeB magnet waste was taken in the Scott bottle that is in circulation with the anolyte compartment (Figure 1). Neodymium nitrate salt solution was used in the middle compartment since that is the desired end product from the anolyte after the electrolysis step. Three different concentrations of neodymium in the middle compartment were investigated:  $1.2n$ ,  $4n$ , and  $6n$ , where  $n$  is the mass of REEs and cobalt together in the magnet waste in grams. All experiments were performed at  $30 \text{ Am}^{-2}$  except a control experiment where no electrolysis was performed. Figure 2A shows the effect of the neodymium nitrate concentration on the extraction of REEs and iron from the magnet waste. Firstly, the control experiment with no current showed no dissolution of metals on the anolyte or the catholyte side of the compartment.

It can be seen that at all different concentrations of  $\text{Nd}(\text{NO}_3)_3$  in the middle compartment, REEs and Fe were dissolved from the magnet waste into the leachate due to nitric acid formation in the anolyte (Figure 2A). Nitric acid leached REEs, Fe, and cobalt from the magnet waste into the solution by the reactions



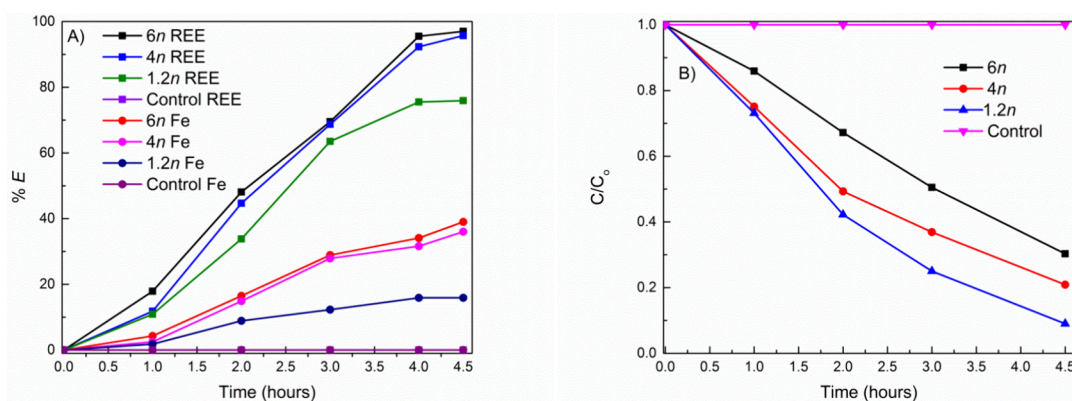
where M is either Fe or Co.

Dissolution of metals in concentrated nitric acid can produce  $\text{NO}_x$  gases. However, under dilute concentrations, eqs 4 and 5 are valid.<sup>36</sup> When the concentration of neodymium in the middle compartment was  $1.2n$ , around 75% of REEs dissolved from the magnet waste and only 15% of iron was co-extracted into the solution. The incomplete extraction of REEs was due to two reasons. Firstly, with a decrease in concentration of Nd in the middle compartment, the conductivity of the solution dropped, which was accompanied by a sharp increase in voltage toward the end of the experiment. Secondly, there was back diffusion of  $\text{OH}^-$  ions from the catholyte compartment into the middle compartment, which increased the pH and caused partial precipitation of REEs in the middle compartment.<sup>37</sup> With increase in Nd concentration in the middle compartment to  $4n$  and  $6n$ , more than 95% of REEs from the waste were extracted into the leachate. In contrast, more than  $65 \pm 2\%$  of iron present in the waste was removed from the leachate in the same step as



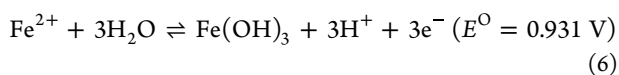
**Figure 1.** (A) Schematic illustration of the three-compartment membrane electrochemical reactor. (B) Overview of the flow of anions and cations in the reactor. AEM, anion exchange membrane; CEM, cation exchange membrane.





**Figure 2.** (A) Influence of Nd concentration in the middle compartment over the extraction of metals from the magnet waste in the anolyte. (B) Removal of Nd from the middle compartment where  $C_0$  is the initial concentration of Nd and  $C$  is the concentration of Nd at time  $t$ .  $n$  is the mass of REEs and cobalt together in the magnet waste in grams.

$\text{Fe}(\text{OH})_3$  precipitate. This oxidative precipitation is primarily due to anodic oxidation of  $\text{Fe}(\text{II})$  in the anolyte compartment as



It has to be noted that this oxidative-precipitation reaction also releases acid back, which can be used *in situ* to further leach the magnet waste. The pH of the anolyte was around 2 during the electrolysis due to the competing reactions of iron leaching from the waste (eq 5) and  $\text{Fe}(\text{II})$  oxidation (eq 6).<sup>23</sup> The pH decreased to  $1.6 \pm 0.2$  at the end of the electrolysis. The end pH of the catholyte was marked by a sharp increase to  $12.5 \pm 0.5$ , indicating the production of  $\text{OH}^-$  ions. Neodymium from the middle compartment is transported through the CEM and is mainly precipitated as  $\text{Nd}(\text{OH})_3$  in the catholyte. Similar to the observations of Maes et al., no hydroxide precipitates were found on the surface of the cathode and most of the precipitates were deposited at the bottom of the cell.<sup>38</sup>

Decrease of the concentration of Nd from the middle compartment is presented in Figure 2B. At 1.2n, more than 92% of Nd was removed from the central compartment into the catholyte. With increase in Nd concentration, the removal of Nd from the middle compartment decreased, mainly due to completion of the leaching of the magnet waste in the anolyte. The voltage during the whole of electrolysis remained constant for both 4n and 6n runs. However, at 1.2n, at the end of the electrolysis, the voltage abruptly increased due to near complete removal of Nd ions from the central compartment, which decreases the conductivity. The average voltage and energy consumption are listed in Table 2.

Even though around  $35 \pm 3\%$  of iron was present in the leachate at 4n and 6n runs, more than 83% of  $\text{Fe}(\text{II})$  is oxidized and was present in the  $\text{Fe}(\text{III})$  form. While  $\text{Fe}(\text{II})$  species can

be stable in species until pH of 7,  $\text{Fe}(\text{III})$  can be hydrolyzed and removed as  $\text{Fe}(\text{OH})_3$  precipitate around pH 3.<sup>24,30</sup> Thus, by increasing the pH above 3, more than 80% of iron from the magnet scrap could be removed as an  $\text{Fe}(\text{OH})_3$  residue.

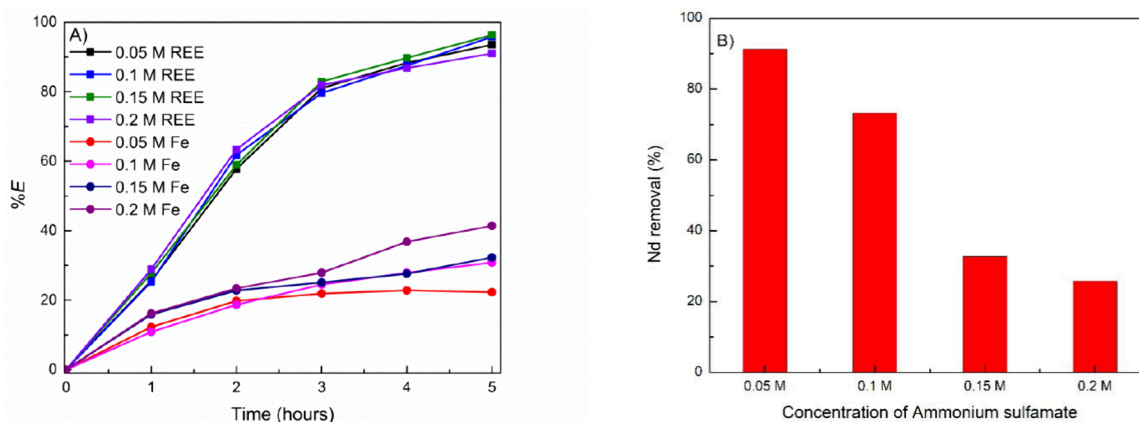
Nevertheless, in order to effectuate a complete closed loop process, the amount of neodymium fed into the middle compartment in the form of  $\text{Nd}(\text{NO}_3)_3$  should be stoichiometrically equivalent to that of the REEs present in the magnet waste. Thus, the excess requirement of  $\text{Nd}(\text{NO}_3)_3$  salt to leach the magnet waste here is problematic and at exact stoichiometric concentration of 1.2n the extraction is incomplete. To overcome these issues, the excess requirement of  $\text{Nd}(\text{NO}_3)_3$  was compensated by adding an inexpensive additive, ammonium sulfamate.

**Influence of Ammonium Sulfamate.** Ammonium sulfamate was chosen in this study, as other salts such as sulfates or chlorides can cause double sulfate precipitation or chlorine evolution. In addition to imparting conductivity to the middle compartment, electrochemical splitting of ammoniacal salts can produce ammonia gas, which can be captured by the conventional stripping process.<sup>39</sup> The effect of ammonium sulfamate concentration on metal extraction was investigated by keeping the concentration of Nd constant at 1.2n and at a constant current density of  $30 \text{ Am}^{-2}$ . It can be seen from Figure 3A that the addition of 0.05 M ammonium sulfamate is enough for extraction of more than 93% of REEs from the magnet waste. Increase in concentration of ammonium sulfamate only slightly increased the REE extraction, whereas Fe was also co-extracted into the solution. Importantly, more than 90% of Nd was removed from the middle compartment (Figure 3B) when the concentration of ammonium sulfamate was at 0.05 M. The removal of Nd was significantly reduced with increase in the additive salt due to the fact that ammonium cations can also competitively cross the CEM to form ammonia at the catholyte. Also, in contrast to the previous run with pure neodymium nitrate solutions, an increase in ammonium sulfamate concentration lowered the oxidation of  $\text{Fe}(\text{II})$ . This can be explained by the oxidizing capacity of nitrate ions to convert  $\text{Fe}(\text{II})$  to  $\text{Fe}(\text{III})$ .<sup>40</sup> Nevertheless, under the optimum condition of 0.05 M, more than 95% of REEs could be extracted, along with a removal of 85% of iron. The average cell voltage was slightly higher when compared to pure neodymium salt experiments (Table 3).

**Effect of Current Density.** One of the important advantages of electrochemical leaching over other hydro-

**Table 2.** Average Cell Voltage, Energy Consumption, and Percentage of Fe Oxidized under Different Concentrations of Nd ( $C_{\text{Nd}}$ ) in the Middle Compartment

$C_{\text{Nd}}$	Fe extracted (%)	Fe oxidized (%)	cell voltage (V)	energy consumption (kWh/kg)	content (wt %)
1.2n	$15.9 \pm 0.4$	$88 \pm 2$	5.44	4.65	0.16
4n	$36.0 \pm 1.2$	$83 \pm 3$	4.53	3.88	0.08
6n	$39.3 \pm 0.6$	$81 \pm 2$	4.48	3.83	0.08



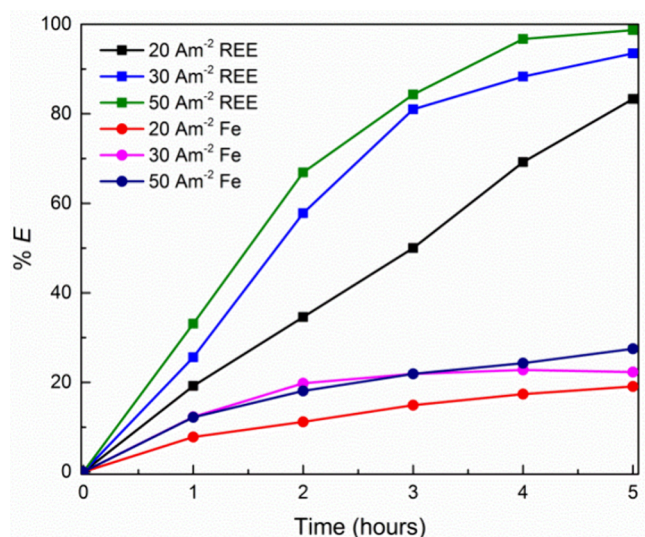
**Figure 3.** (A) Percentage of extraction of REEs and Fe at different concentrations of ammonium sulfamate. (B) Percentage removal of Nd from the middle compartment at  $30 \text{ Am}^{-2}$  and at  $1.2n$ .

**Table 3.** Average Cell Voltage, Energy Consumption, and Percentage of Fe Oxidized under Different Concentrations of Ammonium Sulfamate ( $C_{\text{ams}}$ ) in the Middle Compartment along with  $1.2n \text{ Nd}(\text{NO}_3)_3$

current density ( $\text{Am}^{-2}$ )	$C_{\text{ams}}$ (M)	Fe extracted (%)	Fe oxidized (%)	average cell voltage (V)	energy consumption (kWh/kg of magnet waste)
30	0.05	$22.3 \pm 0.2$	$83 \pm 2$	6.9	6.6
30	0.1	$30.8 \pm 1.1$	$75 \pm 2$	6.5	6.2
30	0.15	$32.3 \pm 0.5$	$70 \pm 1$	6.4	6.0
30	0.2	$41.4 \pm 1.2$	$66 \pm 2$	5.7	5.4
20	0.05	$19.1 \pm 1.5$	$85 \pm 1$	4.8	4.6
50	0.05	$27.5 \pm 1.6$	$81 \pm 1$	8.1	7.7

metallurgical processes is the ability to extract metals with enhanced kinetics at high current densities. Figure 4 shows the effect of different current densities over extraction of REEs and Fe at  $1.2n$  and  $0.05 \text{ M}$  ammonium sulfamate in the middle compartment.

At  $20 \text{ Am}^{-2}$ , the extraction of REEs was incomplete at  $5 \text{ h}$  whereas with an increase in current density, the rate of metal



**Figure 4.** Effect of current density over extraction of REEs and Fe at  $1.2n$  and  $0.05 \text{ M}$  ammonium sulfamate in the middle compartment.

extraction increased. At  $50 \text{ Am}^{-2}$ , more than 97% of REEs are extracted into the solution with the simultaneous removal of 80% of iron from the waste as  $\text{Fe}(\text{OH})_3$ . However, with an increase in current density, the net cell voltage as well as the energy consumption increased (Table 3). At  $30$  and  $50 \text{ Am}^{-2}$ , around  $91 \pm 2\%$  of Nd was removed from the middle compartment and was recovered as  $\text{Nd}(\text{OH})_3$ , indicating an effective one step process. The process was complete within  $5 \text{ h}$  and is significantly faster when compared to the aqueous corrosion process, which took a week.<sup>41</sup>

**Neutralization and Iron Removal.** The electrolysis step oxidized more than 80% of iron. However, complete removal of iron is necessary for creating the closed-loop process and to obtain REE-rich leachates. Air oxidation of  $\text{Fe}(\text{II})$  is highly dependent on pH, and the kinetics can be enhanced by increasing the pH above 6.<sup>42</sup> Thus, the residual  $15 \pm 3\%$  of iron was removed by increasing the pH of the leachate to  $6.3 \pm 0.2$  with the neutralizing agent, ammonium hydroxide. The pH was increased every hour for the first  $6 \text{ h}$ , and the leachate was then stirred in air for  $36 \text{ h}$ . After centrifugation and filtering, the leachate was completely free of iron. Though an additional stripping column was not employed in our experiments, ammonia gas evolved from the cathode in the electrolysis process can be stripped, dissolved, and used as the neutralizing agent as well.<sup>43</sup> The final leachate was rich in REEs and cobalt with  $\geq 95\%$  recovery for REEs and cobalt from the magnet waste after the electrolysis and neutralization steps (Table 4). Cobalt can be subsequently recovered from the leachate using electrowinning or solvent extraction processes.<sup>44,45</sup>

**Obtention of Rare-Earth Oxides.** The product obtained from the catholyte was heated stepwise until  $800^\circ \text{C}$  in order

**Table 4.** Composition of the Leachates after Electrolysis and Neutralization at  $30 \text{ Am}^{-2a}$

type of leachate	Nd (mg/L)	Dy (mg/L)	Pr (mg/L)	Co (mg/L)	Fe (mg/L)
completely leached magnet waste	845.6	236	24.8	124	2670
leachate after electrolysis	820.2	223	24.04	120.9	560.7
after neutralization	793.5	219.8	23.8	120.3	<0.1
retention (%)	$94 \pm 1$	$93 \pm 1$	$96 \pm 0.5$	$97 \pm 0.5$	—

<sup>a</sup>Metal concentration is given in mg/L.



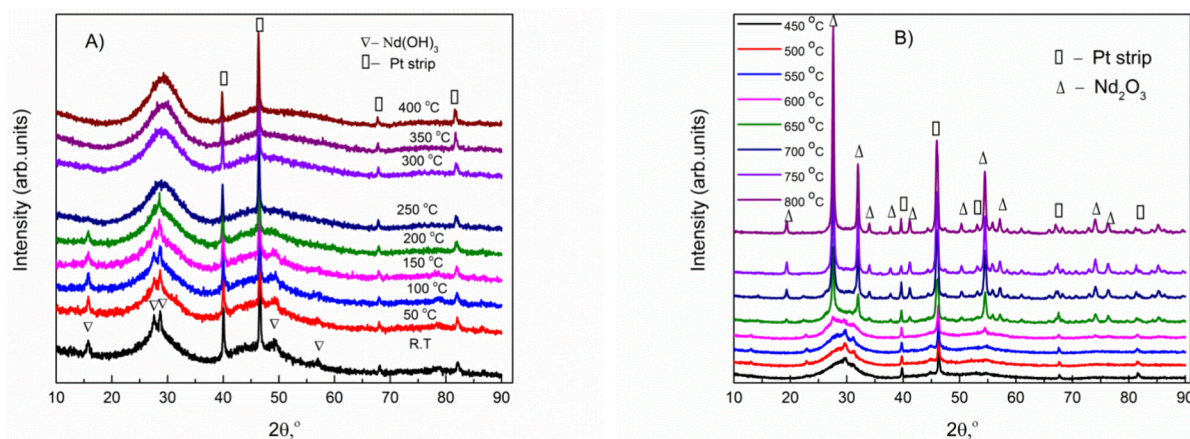


Figure 5. XRD of the obtained rare-earth hydroxides at different temperatures from (A) R.T. to 400 °C and (B) 450 to 800 °C with steps of 50 °C.

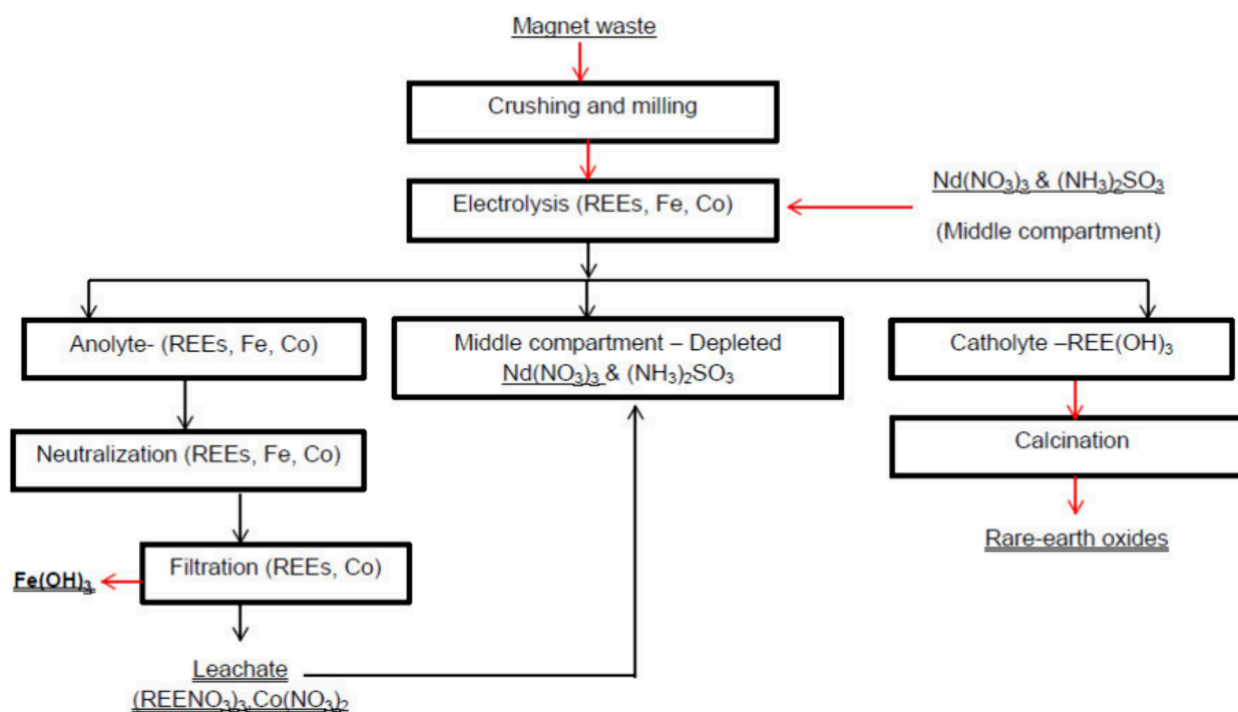


Figure 6. Flowsheet of the proposed recycling scheme. Black arrow, liquid streams; red arrow, solid streams.

to study the transformation of rare-earth hydroxides to oxides. XRD measurements were made for every 50 °C. The unchanging peaks at  $2\theta$  values of 40° and 46° were from the Pt–Rh strip on which the powder was heated (Figures 5A and 5B). It can be seen that the catholyte product is crystalline  $\text{Nd}(\text{OH})_3$  at room temperature. The  $\text{Nd}(\text{OH})_3$  peaks disappeared at around 300 °C, which can be attributed to the formation of  $\text{NdOOH}$  intermediate.<sup>46</sup> Upon further heat treatment, the hydroxide completely transformed into cubic neodymium oxide at 650 °C and remained the same until 800 °C. Though not quantified in this study, in addition to rare-earth hydroxides, hydrogen gas (eq 3) is also produced as a byproduct in the catholyte.

**Overall Process.** The overall recycling process is simple and consists of three distinct steps. Firstly, the powdered magnet waste was taken in the anolyte compartment of a three compartment electrochemical reactor. In the middle compartment, a neodymium salt solution that is almost the

stoichiometric equivalent of the REEs and cobalt present in the waste was fed along with an additive ammonium sulfamate salt. Upon electrolysis, the salt was split into acid and rare-earth hydroxides in the anolyte and catholyte, respectively. The acid was used to leach the magnet waste from the solution. Around  $95 \pm 1\%$  of REEs were dissolved into the solution with over 80% of removal of iron as  $\text{Fe}(\text{OH})_3$  precipitate. The iron removal during the electrolysis step was caused by the anodic oxidation of  $\text{Fe}(\text{II})$ .

The residual iron was removed by neutralization with ammonia and air oxidation. Finally, a rare-earth rich solution is obtained from the anolyte part of the reactor, and rare-earth hydroxides are obtained from the catholyte part of the reactor. The rare-earth rich solution can be fed again into the middle compartment to continue the electrolysis process again, forming a complete closed loop process. The overall process flowsheet is illustrated in Figure 6. The average cell voltage decreases with an increase in concentration of the salts



neodymium nitrate and ammonium sulfamate. Increase in current density also increases the cell voltage; nevertheless, metals are extracted at faster kinetics. The total energy consumption for 1.2*n* and 0.05 M ammonium sulfamate is 6.6 kWh/kg of NdFeB magnet waste. The magnet scrap can be processed at an operational cost of €0.8 kg<sup>-1</sup> assuming an average energy cost of €0.12 per kilowatt hour. It is important to note that avoiding usage of oxalic acid is not only cost saving but also avoids carbon emissions and lowers the global warming potential of the process.<sup>47</sup> Rare-earth oxides can be produced from this process at an operational cost less than 3 euros per kilogram, and currently, the price of neodymium oxide is €50 per kilogram. A life cycle assessment done on a hydrometallurgical recycling process to recycle NdFeB magnets quantitatively indicated that the major environmental hotspots were (a) high acid consumption and (b) hazardous wastewater treatment.<sup>48</sup> The closed-loop approach presented in this article markedly reduces the acid consumption by utilizing the principle of electrochemical salt splitting in a membrane electrolysis reactor. Furthermore, the removal of the major impurity iron as ferric hydroxide at an early stage simplifies the handling of wastewater as opposed to the jarosite process. Importantly, the REE solution free of iron impurities obtained from the anolyte can be utilized as the feed in the middle compartment in the subsequent batches, ensuring an entirely closed-loop and electrified process.

## CONCLUSION

An acid free electrified process was developed to recover REEs from NdFeB magnet waste at room temperature. We demonstrate that REEs can be recovered as rare-earth hydroxides in a three chamber electrochemical reactor by obtaining acid from its own salt. Around 95% of REEs were recovered from the magnet waste with partial removal of iron during the electrolysis step in the anolyte compartment. Complete iron removal was achieved by neutralizing the leachate and air oxidation. Concomitantly, more than 90% of the rare-earth cations were recovered as rare-earth hydroxides in the catholyte compartment. Subsequently, the rare-earth hydroxides were calcined to obtain pure rare-earth oxide, which can be used for rare-earth metal production. This process obviates the use of acid for the leaching reaction and oxalic acid as the precipitating agent. The combination of the extraction and precipitation steps into a single reactor was developed for the first time, resulting in process intensification. The overall process can be performed at a reasonable energy consumption of 6 kWh/kg of magnet waste. The whole flowsheet is environmentally friendly, as it consumes no acid.

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## Notes

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