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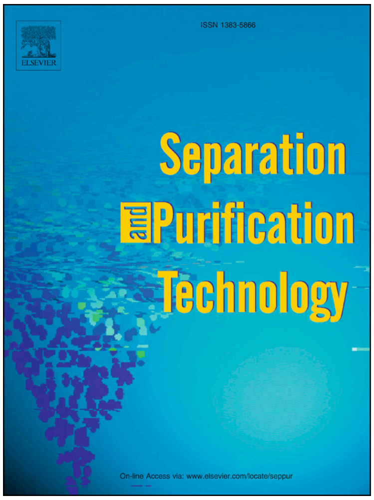

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An environmentally friendly electro-oxidative approach to recover valuable elements from NdFeB magnet waste

Prakash Venkatesan[a*], Z.H.I. Sun[b*], Jilt Sietsma[a], Yongxiang Yang[a]

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

[b] *National Engineering Laboratory for Hydrometallurgical Cleaner Production Technology, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, China*

*Corresponding authors: P. Venkatesan (P.Venkatesan@tudelft.nl), Z. Sun (zhisun@126.com)

Abstract

In this manuscript, we demonstrate a room temperature electrochemical process for efficiently recycling NdFeB magnet waste. First, the magnet waste was completely leached with HCl and then, *in-situ* electrochemical oxidation was performed to selectively oxidize Fe(II) in the leachate to Fe(III). Finally, oxalic acid was added directly to the electro-oxidized leachate which selectively precipitated more than 98% of rare earth elements as rare-earth oxalates. The calcination of rare-earth oxalates produced mixed rare-earth oxides of 99.2% purity and a marketable Fe(III) solution as by-product. The electro-oxidized leachate was also subjected to an alternative neutralization route in which ammonium hydroxide was added to remove iron as ferric hydroxide. The iron free leachate with rare earth elements and cobalt was then subjected to oxalic acid precipitation treatment, which finally produced rare-earth oxides of 99.7% purity. Furthermore, a cobalt-rich solution was obtained in the end and electrowinning studies performed on the solution showed the feasibility of recovering pure metallic cobalt.

1. Introduction

Neodymium iron boron (NdFeB) magnets have a very high energy density and are the strongest permanent magnets currently available [1]. They are widely used in many applications such as hard disk drives, wind turbines, industrial motors, acoustic transducers and electric vehicles. NdFeB magnets contain ~30 wt% of rare earth elements (REEs), about 60-70 wt% iron, 1 wt% boron as well as other additive metals in small quantities. REEs are classified as critical metals because of the high supply risk and increasing demand for them in clean energy applications [2]. Despite their criticality, currently, less than 1% of REEs are being recycled from end of life products [3]. Additionally, around 20-30% of rare earth alloy used as the starting material in magnet manufacturing are lost and are stockpiled as industrial waste [4] [5]. Such industrial waste, combined with end of life products form a potential feedstock for creating a sustainable recycling process [6].

The various approaches investigated hitherto to recycle NdFeB magnets have been summarized in detail by many authors [7-9]. The recycling approaches can be broadly classified into pyrometallurgical and hydrometallurgical routes. Some examples of the pyrometallurgical routes include liquid metal extraction [10], selective chlorination [11, 12] and roasting [13]. However, these pyrometallurgical processes operate at a temperature of around 750-950 ^{o}C and are thus energy intensive. In hydrometallurgical routes, magnets are completely leached with acid followed by direct precipitation of REEs as their double sulfate salts [14, 15]. Rare-earth double sulfates need to undergo an additional conversion step to rare-earth fluorides by reacting with HF. Oxalic acid was also reported as a selective precipitation agent by [16]; however, the role of oxalic acid as precipitation agent is unclear as Fe(II) has been reported to interfere with the selective precipitation [17]. Iron, the major component of NdFeB magnets, is seldom recovered in the hydrometallurgical processes in a useful form. These processes typically consume non-recyclable chemicals such as excess acid, ammonia and sodium hydroxide, involve multiple steps and generate a large amount of waste water. Irrespective of whether the magnet waste is treated at room temperature or high temperature, the speciation of iron plays a major role. Fe(II) tends to be stable in the solution until a pH of 6 and Fe(II) oxalates are highly insoluble, whereas in contrast, Fe(III) precipitates at a pH around 2-3 and Fe(III) oxalates are highly soluble [18, 19].

In this paper, we describe an environmentally friendly electrochemical approach to selectively recover REEs from NdFeB magnet waste. The magnet waste was acid leached with HCl and subsequently *in-situ* electro-oxidation was performed to selectively oxidize Fe(II) to Fe(III). Once the electro-oxidation was complete, rare-earth ions in the solution were selectively precipitated using oxalic acid. More than 98% of REEs present in the magnet was recovered as rare-earth oxides with a product purity higher than 99%. The remaining solution is composed mainly of $FeCl_{3,}$ which can be used in water treatment plants or in mineral ore leaching [20]. The whole process is environmentally friendly as it is carried out in a single reactor, at room temperature and consumes only oxalic acid and current without generating waste.

In addition to this, an alternative route was also explored to recover the valuable additive element, cobalt. Complete iron removal was attained by neutralizing the electro-oxidized leachate with ammonium hydroxide. The pink iron free leachate obtained after neutralization was rich in REEs along with cobalt. Addition of oxalic acid to this leachate selectively precipitated REEs as rare-earth oxalates, which were then calcined to produce mixed rare-earth oxides of remarkable (99.7%) purity. The remaining leachate composed mainly of cobalt and electrowinning studies showed the feasibility of producing metallic cobalt.

The advantages and disadvantages of these two routes are critically evaluated. Importantly, we demonstrate that the speciation of iron in the solution plays a vital role in formulating a hydrometallurgical flowsheet to recycle NdFeB magnets.

2. Experimental

2.1 Materials

All chemicals are of analytical grade and were used without further purification. Ammonium chloride (99.95%), ammonium acetate, ammonia solution (25% NH_3 in water), hydrochloric acid (37%), oxalic acid dihydrate (≥99%) and ferrozine (monosodium salt hydrate of 3-(2-pyridyl)-5,6-diphenyl- 1,2,4-trazine-p,p'-disulfonic acid), were purchased from Sigma Aldrich, B.V (Zwijndrecht, The Netherlands). A dimensionally stable cylindrical platinum-coated titanium anode of diameter 4 cm and height 5 cm, purchased from Magneto B.V. (Schiedam, The Netherlands) was used as the anode. Nickel wire of diameter 0.8 mm, purchased from Salomons Metalen B.V (Groningen, The Netherlands) was used as the cathode. The pH and temperature were measured by Inolab 7310 pH meter (WTW, The Netherlands) with a Sentix 81 tip. A Universal 320R centrifuge (Hettich, The Netherlands) was used to separate the leachate from the precipitate. The magnet waste (Magneti, Slovenia) used in this study is waste created during production. The ball milling was performed at Umicore (Olen, Belgium) using Retsch RS100 ball mill for two hours to mill the solid sintered magnets. Immediately after milling, the powder samples were directly divided into 10.5 grams and stored in a plastic vial to offset the effect of oxidation on the extraction percentage calculation [21].

2.2 Experimental set-up and procedures

A cylindrical plexiglass electrochemical reactor (Figure 1) of diameter 8 cm and length 10 cm was used for both leaching and electro-oxidation experiments. The electrolyte volume was kept constant at 300 ml throughout the experiments. A heating bath with water was used to maintain the temperature (T) at 25±2 ^{o}C for all experiments. The solution was stirred constantly at 550 rpm with a magnetic stirrer. The electrodes were arranged in the form of concentric cylinders, with the small nickel wire cathode placed exactly in the centre of the Ti/Pt anode. Ag/AgCl (3M KCl) was used as the reference electrode. Both the pH meter and the reference electrode were placed in the reactor for the duration of the experiment. Every hour a sample of 0.5 ml was drawn to determine the concentration of elements in the solution. The cyclic voltammetry for cobalt electrodeposition was performed with a glassy carbon working electrode (0.076 cm^2), an Ag/AgCl (3M KCl) reference electrode and a glassy carbon counter electrode. All experiments were conducted using either the potentiostat Versastat 4 or Parstat 4000 (Ametek, UK) and the data was obtained using Versastudio software.

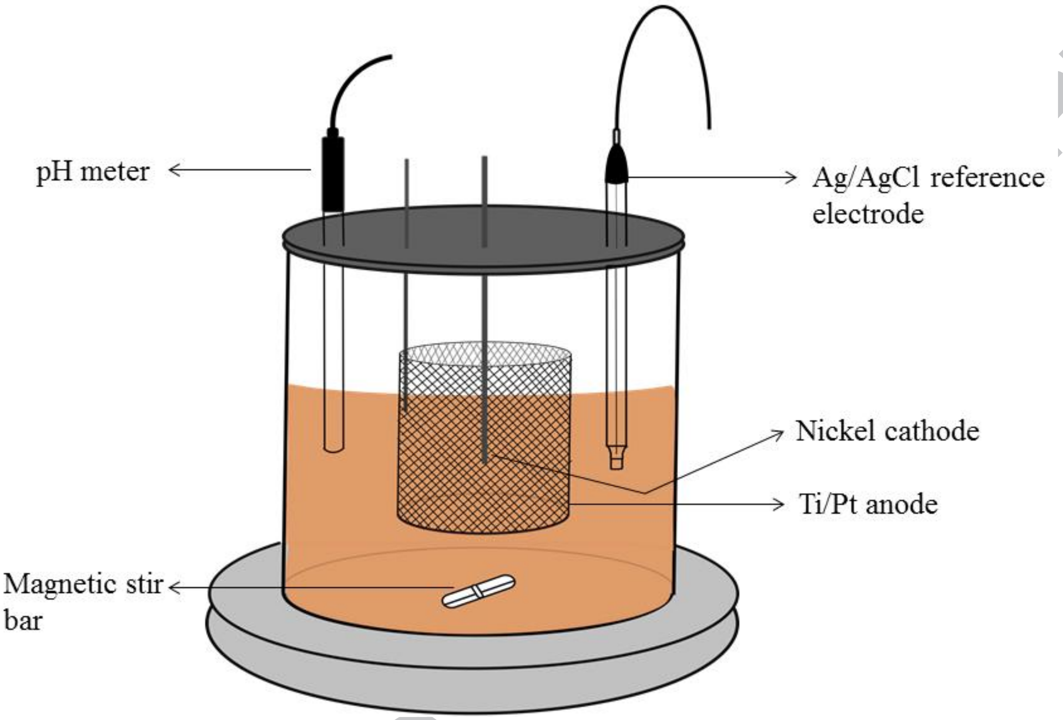


Fig. 1. Schematic illustration of the electrolysis set-up

2.3 Analyses

Elemental concentrations in solution were analysed by inductively coupled plasma – optical emission spectrometry (ICP-OES, Spectro Arcos-OEP). The speciation of iron was determined by the ferrozine calorimetric method [22]. A UV-Vis spectrophotometer (Hitachi, U-2900) was used to quantify Fe(II) at 562 nm. The total iron concentration was measured by ICP-OES. The Fe(III) concentration was calculated as the difference between total Fe concentration and Fe(II) concentration. The sample solutions taken for speciation analysis were filtered using a syringe filter (0.45 µm) and the clear solution was drawn into 2 M HCl and immediately analyzed. The residues were completely dissolved in concentrated HCl (37%) and the leaching yield of any metal is defined as

$$Leaching\ yield\ (\%) = \frac{Amount\ of\ metal\ in\ the\ leachate}{Total\ amount\ of\ metal\ in\ the\ sample} \quad (1)$$

The precipitates obtained after oxalic acid precipitation were washed thoroughly with water and ethanol and calcined at 950 ^{o}C. A Bruker D8 diffractometer with Cu Kα or Co Kα radiation operated at 45 kV and 40 mA was used for X-Ray diffraction analysis. The purity of rare-earth oxides was determined by dissolving the oxides in concentrated HCl (37%) and measuring the composition using ICP-OES.

3. Results and discussion

3.1 Leaching of the magnet waste

The average elemental composition of the magnet waste is given in Table 1. The magnet waste has a relatively high dysprosium content and is typically used in generators, wave guides and hybrid electric cars [23]. The focus of this study is on the extraction and behavior of five major elements: neodymium, dysprosium, praseodymium, iron and cobalt.

Table 1 Chemical composition of the magnet (wt%)

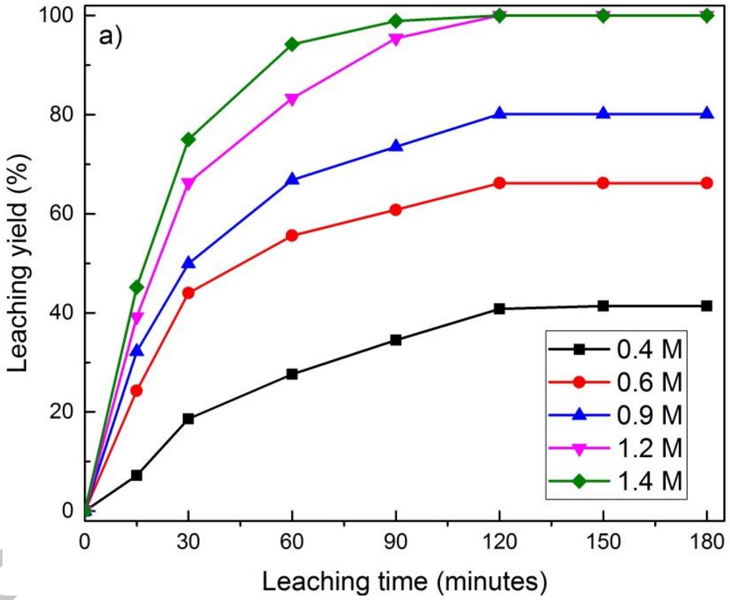
Element	Fe	Nd	Dy	Co	B	Pr	Cu	Ga	Al	Gd	Ni	Si	Total
Wt %	66.34	22.10	5.78	2.89	1.11	0.91	0.19	0.17	0.17	0.09	0.06	0.02	99.8

Hydrochloric acid was chosen as the leaching agent in this study as chloride is the preferred anion in the subsequent solvent extraction step to separate individual REEs [24]. For the leaching and subsequent electro-oxidation experiments, the solid to liquid ratio was kept constant with a magnet weight of 10.5 grams and liquid volume of 300 ml. Ammonium chloride (Concentration, $\mathrm{C_{NH_4Cl}} = 3\mathrm{M}$) was used as the additive in all experiments to increase the conductivity of the solution. Moreover, high concentration of chlorides is deemed to be crucial for novel ionic liquid based solvent extraction processes as they act as salting agents [13, 25]. To determine the amount of acid required to leach the magnet completely, a leaching study was performed. NdFeB magnets are highly reactive due to very negative standard reduction potential of REEs and can be easily leached using common inorganic acids such as hydrochloric acid [16], sulfuric acid and even with mild acids like acetic acid within few hours [26]. The redox half reactions and the corresponding standard reduction potentials of various metals present in the magnets are given elsewhere [27]. The acid dissolution reactions of the major elements are

$$2\mathrm{RE} + 6\,\mathrm{HCl} \leftrightarrow 2\mathrm{RECl_3} + 3\mathrm{H_2} \uparrow \qquad (2)$$

$$\mathrm{Fe} + 2\ \mathrm{HCl} \leftrightarrow \mathrm{FeCl_2} + \mathrm{H_2} \uparrow \qquad (3)$$

The leaching yield of both REEs and iron increase with increase in concentration of HCl (Fig.2). REEs leach slightly faster than iron. Nevertheless, for concentrations of HCl 1.2 M and above, complete leaching of magnet was achieved within two hours. This is consistent with Vander Hoogerstraete et al's leaching investigation [13], where for molar ratios of REEs to HCl above 15 (nREE nHCl ≥ 15), magnet powders dissolved completely. Leachate obtained after dissolving the magnet waste with 1.2 M HCl had an end pH of 0.5±0.1. This fully leached solution was used subsequently in all electro-oxidation experiments.



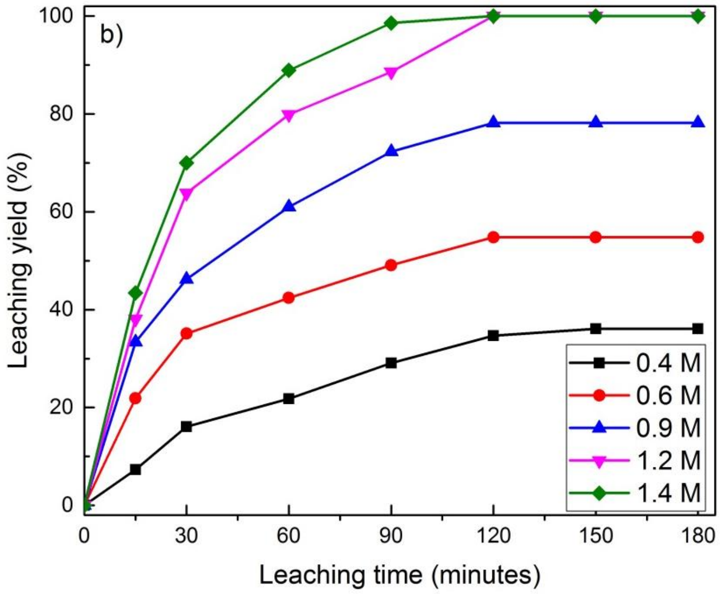


Fig. 2. Effect of acid concentration on the leaching yield (%) of (a) REEs and (b) iron from NdFeB magnet waste powder (Stirring rate 550 rpm, T = 25 °C, $C_{NH_4Cl} = 3M$)

3.2 *In-situ* electrochemical oxidation of Fe(II)

Electrolytic oxidation of Fe(II) is considered to be an effective method for treating pickling effluents, acid mine drainage [28] and industrial waste water [29]. Although the process can be done at high efficiency in divided reactors, un-divided reactors are simple to construct and consume less energy. The possible anodic reactions in such an un-divided reactor are

$$\mathrm{Fe^{2+}} \rightarrow \mathrm{Fe^{3+}} + \mathrm{e^-} \;(E^o = 0.77\,V) \tag{4}$$

$$\mathrm{2H_2O} \rightarrow \mathrm{O_2} + \mathrm{4H^+} + \mathrm{4e^-} \;(E^o = 1.23\ V) \tag{5}$$

$$\mathrm{2Cl^-} \rightarrow \mathrm{Cl_2} + \mathrm{2e^-} \;(E^o = 1.36\ V) \tag{6}$$

where E^0 is the standard reduction potential. The desired anodic process is reaction (4). Reactions (5) and (6) are considered parasitic as they reduce the current efficiency. However, oxygen evolution reaction also improves localized convection near the electrode surface and can thus contribute positively to Fe(II) oxidation [30]. The possible cathodic reactions are

$$\mathrm{Fe^{3+}} + \mathrm{e^-} \rightarrow \mathrm{Fe^{2+}} \;(E^o = 0.77\,V) \tag{7}$$

$$\mathrm{2H^+} + \mathrm{2e^-} \rightarrow \mathrm{H_2} \;(E^o = 0\,V) \tag{8}$$

$$\mathrm{Fe^{2+}} + \mathrm{2e^-} \rightarrow \mathrm{Fe} \;(E^o = -0.44\ V) \tag{9}$$

$$\mathrm{Co^{2+}} + \mathrm{2e^-} \rightarrow \mathrm{Co} \;(E^o = -0.28\,V) \tag{10}$$

The most undesirable cathodic reaction in this system is reaction (7); the back reduction of Fe(III) to Fe(II) is also thermodynamically favorable as it occurs at a relatively positive potential. However, it was demonstrably subverted [30] in a cylindrical reactor system having an anode of substantially higher area than the cathode, thus promoting the hydrogen gas evolution reaction (8) to be the major cathodic reaction.

A control experiment was carried out with just air bubbling over a period of 64 hours. Even after 64 hours, less than 2% of Fe(II) was found to be oxidized by air . Recai et al. also observed that more than 98% of iron remained as Fe(II) in the solution after NdFeB magnets were completely leached with sulfuric acid [31]. This sluggish oxidation kinetics of Fe(II) in the leachate can be attributed to the end pH of the leachate (0.5±0.1). The rate of Fe(II) oxidation is well known to be dependent on pH [32] and in acidic solutions of pH less than 2, the kinetics of oxidation by air or dissolved oxygen is extremely sluggish. Hence, electrochemical oxidation was investigated in this flowsheet to oxidize Fe(II).

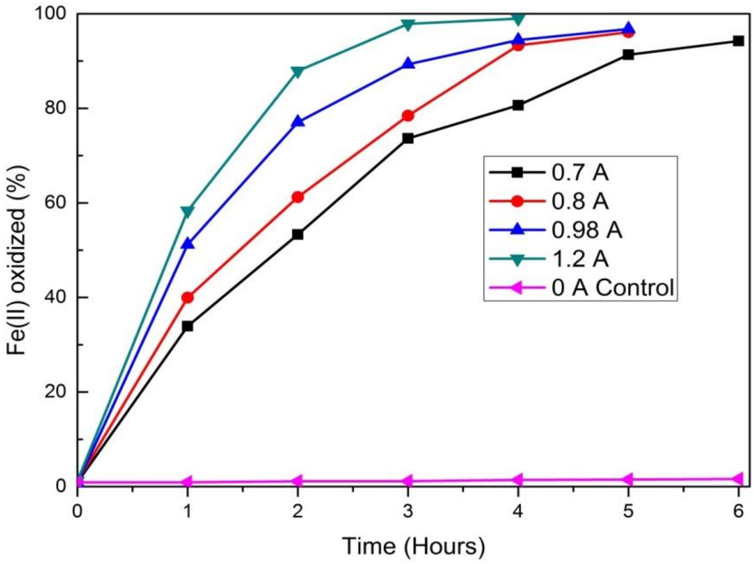


Fig. 3. Rate of Fe(II) oxidation as a function of current density (Stirring rate 550 rpm, T = 25 ^{o}C, $C_{NH_4Cl} = 3M$)

Galvanostatic electrolysis was performed on the leachates and Fig. 3 shows the effect of different currents on the rate of Fe(II) oxidation. The solution color changed from slightly pink to intense brown over the period of electrolysis. The pH increased slightly until two hours to 1.6 due to the competing reactions (4) and (8), but gradually decreased and settled around 0.9±0.2. Approximately at 2 hours, the solution turned sludgy indicating the occurrence of $Fe(OH)_3$ precipitation. This could be explained from the presence of relatively high concentration of iron in solution (0.13 M) and the very low solubility product of ferric hydroxide (K_{sp} ($Fe(OH)_3$) = 2.79 x 10^{-39}) [33]. With these values, the pH at which the precipitation will occur was calculated to be 1.4 and the precipitation during the experiment occurred at pH 1.4±0.2. The amount of Fe(II) oxidized increased with increase in current. At a current of 1.2 A, 98.9% of Fe(II) was oxidized within four hours.

The electrochemical response to galvanostatic electrolysis is plotted in Fig. 4 as change in anode potential over time.

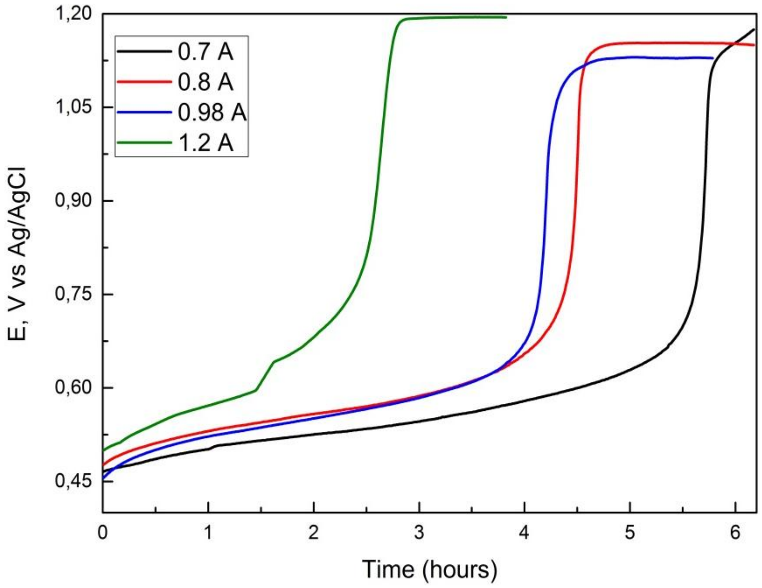


Fig. 4. Evolution of anode potential (V, vs Ag/AgCl) for different current intensities (Stirring rate 550 rpm, T = 25 °C, $C_{NH_4Cl} = 3M$)

The anodic potential curves show two distinctive behaviors: first, it follows a gradual profile until a critical time after which it steeply rises to a plateau at 1.1-1.2 V. Once the plateau is reached, the anode potential remains constant for the rest of the experiment. The time taken to reach the plateau decreases with increase in current indicating that charge transfer over the electrode electrolyte interface as the rate determining mechanism for Fe(II) oxidation. The sloping increase of potential until critical time indicates constant decrease of Fe(II) concentration as per the Nernst equation (11)

$$E = E^0 + \frac{RT}{nF} \ln \frac{[Fe^{3+}]}{[Fe^{2+}]} \tag{11}$$

where R, T, n and F are ideal gas constant, temperature, number of electrons and Faraday's constant respectively. The sharp increase of the anode potential to the constant plateau is attributed to oxygen gas evolution by oxidation of water. From combining Fig. 3 & 4, it can be seen that more than 90% of Fe(II) is oxidized before the critical time where water electrolysis becomes the dominant mechanism. Hence, it can be concluded that most of the Fe(II) is oxidized by direct anodic oxidation over the surface of the anode. It has also been proven elsewhere [28] that oxidation of Fe(II) by electrolysis of water is sluggish in solutions of pH less than 2 and anodic Fe(II) oxidation remains the major mode of oxidation. Additionally, the Ti/Pt anode system chosen for this study showed highest exchange current density for Fe(II) oxidation [34]. The cathodic reaction was mainly hydrogen gas evolution, however, a small amount of metallic iron (0.2±0.2 g) was also observed as a deposit. In a reactor with large amount of Fe(III), the following reaction

$$\mathrm{Fe} + \mathrm{Fe}^{3+} \rightarrow 2\,\mathrm{Fe}^{2+} \tag{12}$$

where metallic iron deposit is re-dissolved into the solution as Fe(II) is also likely to occur [30]. Nevertheless, the metallic iron deposit observed during the experiments is negligible. The ICP-OES analysis of the cathodic deposit showed that more than 99% of the deposit is iron with little co-deposition of cobalt. The electro-oxidative process was quite selective as RE^{3+} are stable species in the solution and thus were not deposited cathodically.

The average cell voltage and energy consumption is given in Table 2. The current densities are for an anodic area of 87.9 cm^2 and the energy consumption is calculated based on the amount of iron oxidized.

$$P = V\,I\,t\,/\,(X_{Fe} * ŋ) \tag{13}$$

where P is the energy consumed (kWh/kg), V is the average cell voltage in volts, I is the current supplied (A) , t is the duration of electrolysis (hours) , X_{Fe} is the amount of iron in solution in grams and ŋ is the % of Fe(II) oxidized at the end of electrolysis. Overall, almost all of Fe(II) was oxidized with reasonable energy consumption of around 1.4 kWh/kg of iron.

Table 2 Average cell voltage and energy consumption at different current densities

Current density (Am^{-2})	Average cell voltage (V)	Energy consumption (kWh/kg)

80	2.18	1.40
91	2.26	1.35
112	2.31	1.67
136	2.37	1.38

3.3 Direct oxalic acid precipitation of REEs

The electro-oxidized leachate was subjected to two different routes to recover the REEs, the first of which was directly adding oxalic acid to the leachate. Fe(III) is found to be extremely stable in oxalic acid solution, in contrast with Fe(II) oxalate which has a very low solubility product ($K_{sp(\text{ferrous oxalate})} = 3.2 \times 10^{-7}$). This difference in solubility has also been utilized in leaching iron from red mud with oxalic acid when it is in Fe(III) form and precipitating iron from the solution with oxalic acid when it is in Fe(II) form [19, 35]. Oxalic acid forms strong water-insoluble complexes with REEs and are used for precipitating REEs as oxalates with the following reaction

$$2\ \text{RECl}_3 + 3\text{H}_2\text{C}_2\text{O}_4 \rightarrow \text{RE}_2(\text{C}_2\text{O}_4)_3 + 6\text{HCl} \tag{14}$$

The stoichiometric equivalent of oxalic acid is 1.5 moles per mole of rare earth elements ($\text{nC}_2\text{O}_4^{2-} / \text{nREE}^{3+} = 1.5$). This difference between solubility of Fe(III) and REE oxalates was exploited and selective precipitation experiments were performed on electro-oxidized leachates. A set of control experiments on un-oxidized leachates was also carried out to determine the influence of Fe speciation in selective rare earth precipitation. The electro-oxidized leachates were slightly sludgy and were centrifuged and filtered before precipitation experiments. Filtering removed only 3±1 % of total iron present in the solution and the rest remained as soluble Fe(III) ions.

The results for precipitation are given in Table 3, where UO-L stands for un-oxidized leachate and EO-L stands for electro-oxidized leachate. The precipitation % corresponds to the amount of metals precipitated from the leachate as oxalates.

Table 3 Metal precipitation % from leachates by precipitation with oxalic acid

Leachate type	($nC_2O_4^{2-}$ / $nREE^{3+}$)	REE, %	Fe, %
UO-L	1.5	86±2	<0.01
UO-L	3	95±2	0.8±0.2
EO-L	1.5	No precipitation	No precipitation
EO-L	3	No precipitation	No precipitation
EO-L	4.5	89±2	<0.01
EO-L	5	96±2	<0.01
EO-L	6	98.9±0.3	<0.01

The as-obtained oxalates were calcined at 950 °C. The resultant oxides were redissolved in acid and analyzed using ICP-OES and XRD. The composition of the oxides obtained from un-oxidized and oxidized leachates are presented as weight percentages in Table 4. Our results reaffirm the findings of Lyman et al [17], that large presence of Fe(II) interferes with selective precipitation of REEs using oxalic acid. At $nC_2O_4^{2-}$ / $nREE^{3+}$ = 1.5, the REE precipitation from the un-oxidized leachate was incomplete, albeit without any interference from Fe(II). However, contrary to the observations of Bandara et al [16], increasing the amount of oxalic acid resulted in co-precipitation of Fe(II) from the un-oxidized leachate. In fact, the compositional analysis of the oxides obtained at $nC_2O_4^{2-}$ / $nREE^{3+}$ = 3 from un-oxidized leachate revealed not only substantial (~15%) interference from iron but also the presence of other impurities such as cobalt and boron (10%). On the other hand, REEs could be completely and selectively precipitated from the electro-oxidized leachate without any interference from Fe(III). However, at least 3-4 times stoichiometric excess was found to be necessary to complete the precipitation.

Table 4 Purity of rare-earth oxides obtained after calcination at 950 °C, in weight percentage.

Leachate type	($nC_2O_4^{2-}$ / $nREE^{3+}$)	REE [%]	Fe [%]	Other impurities [%]
UO-L	1.5	99.2	0.6	-
UO-L	3	75±2	14.5±1	10±1
EO-L	5	99.88	0.12	-
EO-L	6	99.94	0.05	-

Fig. 5 compares the XRD patterns of oxides obtained from un-oxidized and electro-oxidized leachates. At $nC_2O_4^{2-}$ / $nREE^{3+} > 1.5$, for un-oxidized leachates, $NdFeO_3$ was found to be the main phase indicating the presence of iron impurity. In contrast, electro-oxidized leachates produced oxides, which have Nd_2O_3 as the major phase, and can be directly used in magnet manufacturing.

The direct oxalic acid precipitation from electro-oxidized leachates not only produced pure rare-earth oxides but also a very potent $FeCl_3$ solution with minor impurity of dissolved oxalate anions as by-product. $FeCl_3$ is used as leachant in precious metal recycling from PCBs, mineral ore leaching etc. [20] and also in water treatment industries [36]. Despite excess consumption of oxalic acid, this route is environmentally benign as it produced no solid waste or waste water. Furthermore, the leaching followed by electro-oxidation can be carried out in the same reactor, thereby reducing the number of steps needed for recycling.

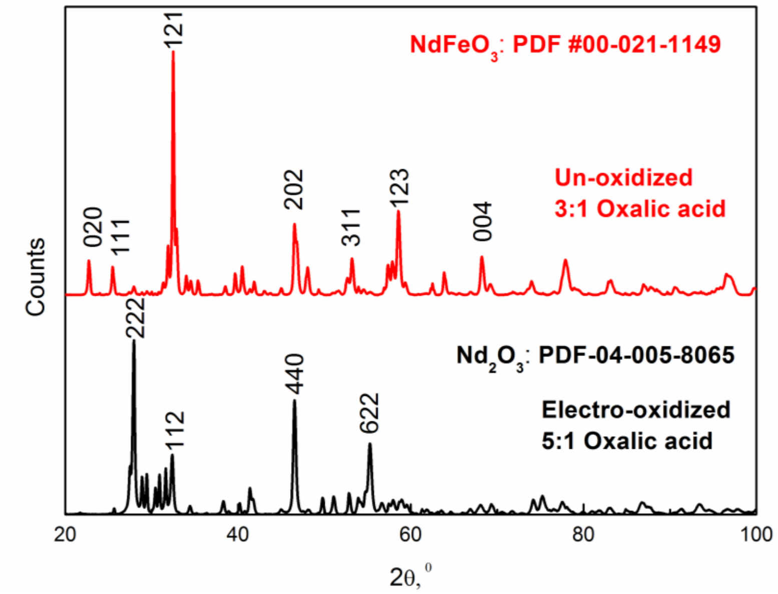


Fig. 5. XRD pattern of oxides after calcining the oxalates of un-oxidized and electro-oxidized leachates

3.4 Neutralization route

The alternative route to direct oxalic precipitation is a neutralization route which was explored with the goal of producing rare-earth oxides of very high purity and recovering cobalt. Due to its reasonable price ammonia was used as a neutralization agent [37]. The rare-earth elements are stable in the solution until a pH of 7.5 [38] (K_{sp} $Nd(OH)_3 = 1.9 \times 10^{-21}$) in comparison with Fe(III), which will completely hydrolyze and precipitate at a pH of around 3.5. Thus, the *in-situ* electro-oxidation process (section 3.2) of Fe(II) to Fe(III) also allows selective removal of iron. Subsequently, ammonia was added dropwise to the electro-oxidized leachate until the pH was raised to 4.3±0.2, approximately at which point the solution turns extremely sludgy and viscous. 12-15 ml of ammonia was enough to cause the precipitation of Fe(III). The solution was then stirred further for 2 hours, centrifuged and then filtered.

Table 5 Composition of leachates and retention percentage of major elements

Elements	Nd (mg/L)	Dy (mg/L)	Pr (mg/L)	Co (mg/L)	Fe (mg/L)
Electro-oxidized leachate	7735	2023	319	1011	23219
After neutralization	7318	1921	314	1002	<0.1
Retention [%]	95±2	96.5±1	98±0.5	98.5±0.5	-

The filtered leach liquor was a pure pink solution and the retention of various elements into the solution are given in Table 5. More than 95% of major REEs were retained in the leachate and a complete removal of iron was observed. The leach residue was found by XRD to be β- FeO(OH) akagenite (Fig.6).

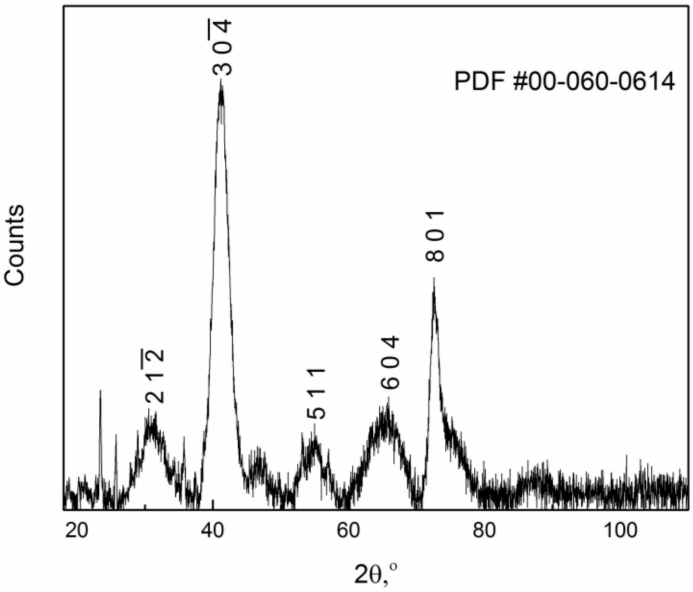


Fig. 6. XRD pattern of be β-Akagenite FeO(OH) obtained after neutralization & precipitation of electro-oxidized leachate

Four different polymorphs are possible for the Fe(III) oxide hydroxides: α-FeO(OH) goethite, β- FeO(OH) akaganeite, γ-FeO(OH) lepidocrocite and δ-FeO(OH) feroxyhite [39]. Similar to our results, either goethite [25] or akaganeite [31] were obtained by other researchers after precipitating Fe(III) from the magnet leachate by neutralization. The oxide hydroxides can be transformed into hematite by heating at 250-300 °C.

$$2\ \mathrm{FeOOH} \rightarrow \mathrm{Fe_2O_3} + \mathrm{H_2O} \tag{15}$$

Akaganeite itself can potentially be used in pigment industries, in gas sensors and ion exchangers [40]. The resultant leach liquor rich in REEs and cobalt can be directly used for REE extraction and separation in the current rare earth extraction plants [7].

3.4.1 Selective rare-earth oxalate precipitation

The pink leachate after neutralization was once again treated with oxalic acid to find if selective precipitation of REEs as oxalates is possible. Rare earth oxalates are highly insoluble ($Ksp_{(\mathrm{neodymium\ oxalate})} = 1.3 \times 10^{-31}$) [41] in comparison to cobalt oxalate ($Ksp_{(\mathrm{cobalt\ oxalate})} = 6 \times 10^{-8}$)[42] and thus oxalic acid was added to the leachate to selectively precipitate REEs. A slight excess ($nC_2O_4^{2-} / nREE^{3+} = 2$) of oxalic acid to rare-earths was found to be sufficient to precipitate 99% of REEs from the leachate. Similar to Recai et al.'s results[31], oxalic acid precipitation was selective for REEs and the cobalt loss from the leachate was found to be less than 0.2 ±0.2 %. Upon calcination, the rare earth oxalates gave a mixed rare-earth oxide of purity 99.7 ±0.2%. The average compositional analysis of rare-earth oxides obtained had, 76.73 wt% of Nd, 20.1 wt% of Dy, 3.16 wt% of Pr and 0.05% of cobalt.

3.4.2 Cobalt electrowinning

Although cobalt is a minor additive to the NdFeB magnets, it is considered to be one of the most critical metals due to its widespread use in important applications such as Li-ion batteries. After selective precipitation of REEs from the pink leachate, a pure cobalt chloride solution of concentration ~1 g/L was obtained. Cyclic voltammetry studies with different scan rates performed on the pure cobalt leachate is shown in Fig. 7(a). When scanned in negative direction, the reductive current starts around -1050 mV due to simultaneous occurrences of competing reactions (8) and (10).

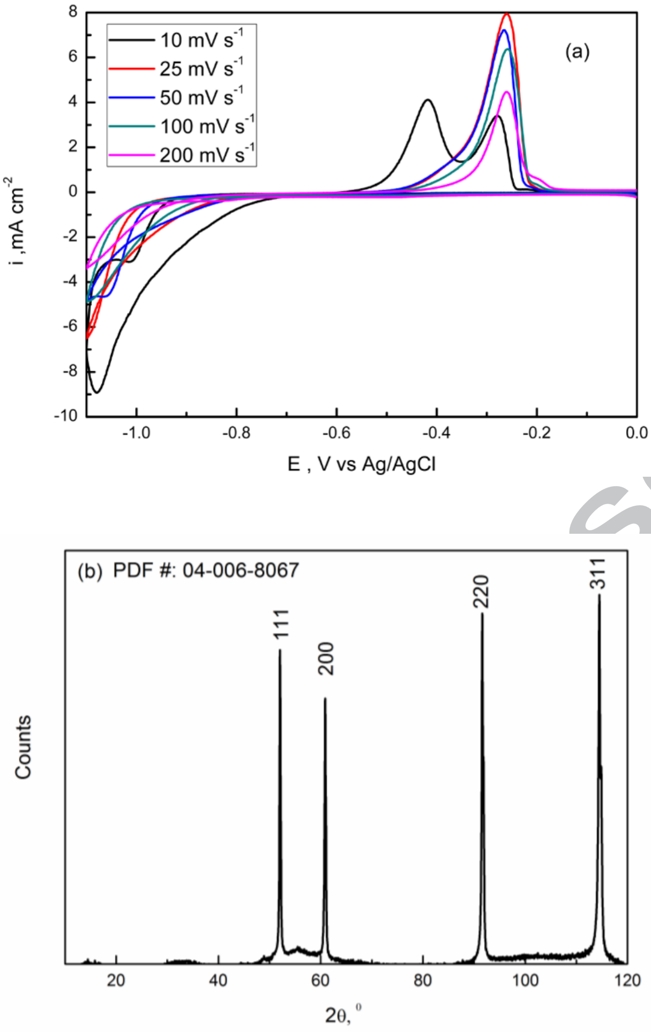


Fig. 7. (a) Cyclic voltammetry of cobalt solution at different scan rates (b) XRD pattern of the electrodeposited cobalt at 250 Am^{-2}

The current density continues to increase in negative direction with no apparent limiting current density or cathodic peak. This together with decrease of peak current with increasing scan rates indicates that the electrodeposition process is activation controlled. The deposited cobalt is anodically stripped back at peak potential -0.26 V with a broad anodic peak at high scanning rates. However at a slow scanning rate of 10 mVs^{-1}, interestingly, two anodic peaks are observed. This can be attributed to cobalt stripping from two different phases formed on the glassy carbon electrode surface [43]. An electrodeposition test was carried out over a nickel working electrode of area 1 cm^2 at a current density of 250 Am^{-2} for three hours. XRD of the deposit showed phases of pure cobalt (Fig. 7(b)).

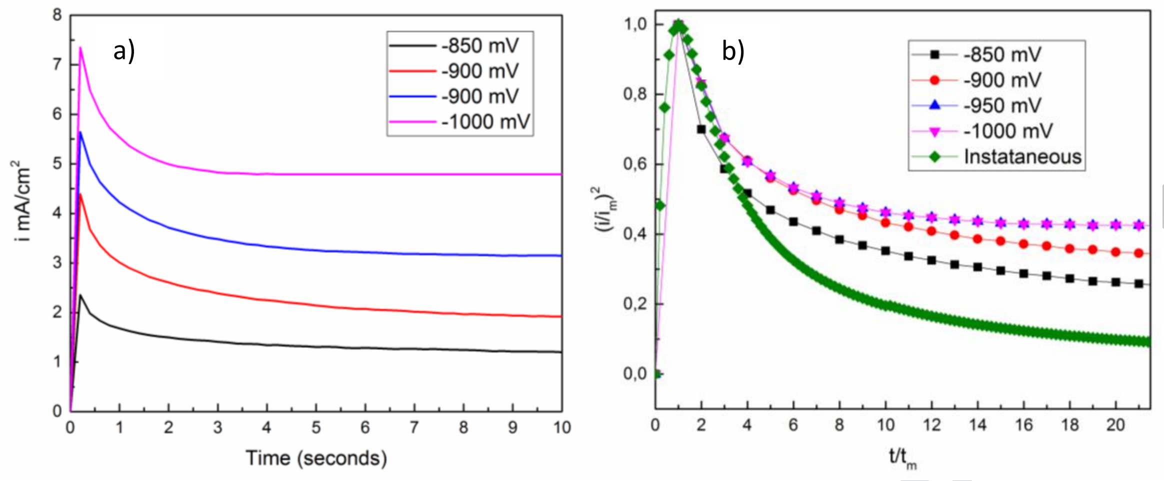


Fig.8. a) Chronoamperometry of cobalt during electrodeposition on glassy carbon electrode and b) corresponding Scharifker-Hills' model

Chronoamperometry was used as a tool to diagnose the nucleation mechanism of cobalt from the remnant leachate. The obtained chronoamperograms (Fig.8) were well defined until -1000 mV and shows sharp decrease in current densities at lower potentials. However, the transient currents do not decay completely to zero. One possible explanation for this phenomenon could be the co-occurrence of hydrogen evolution reaction together with cobalt electrodeposition[44]. Instantaneous nucleation mechanism was obtained in the corresponding Scharifker-Hills' model until $t/t_m = 2$. The deviation from the model at higher t/t_m can also be attributed majorly to the occurrence of the parasitic reaction of hydrogen evolution[45].

3.5 Comparison of two routes

Fig.9 summarizes the complete flowsheet with the two different routes. After complete dissolution of magnet waste with HCl, *in-situ* electro-oxidation was performed to oxidize 99% of Fe(II) into Fe(III). This electro-oxidized leachate was subjected to two different routes. The material balance for both the direct oxalic acid precipitation and neutralization route (Table S1-S3) indicates that the direct oxalic acid precipitation route consumes 5 times more oxalic acid that the neutralization route. However, a rich Fe(III) solution was obtained as a marketable by-product which also valorizes the acid used in the leaching step. Thus, the direct oxalic acid precipitation route produces no liquid waste. Unlike the direct precipitation route, the neutralization route involves multiple steps and consumes ammonia, which cannot be recycled. However, the neutralization route also provides the possibility to obtain the vital minor additive in the form of pure cobalt solution or metallic cobalt. Both the routes emit carbon-dioxide during the calcination process..

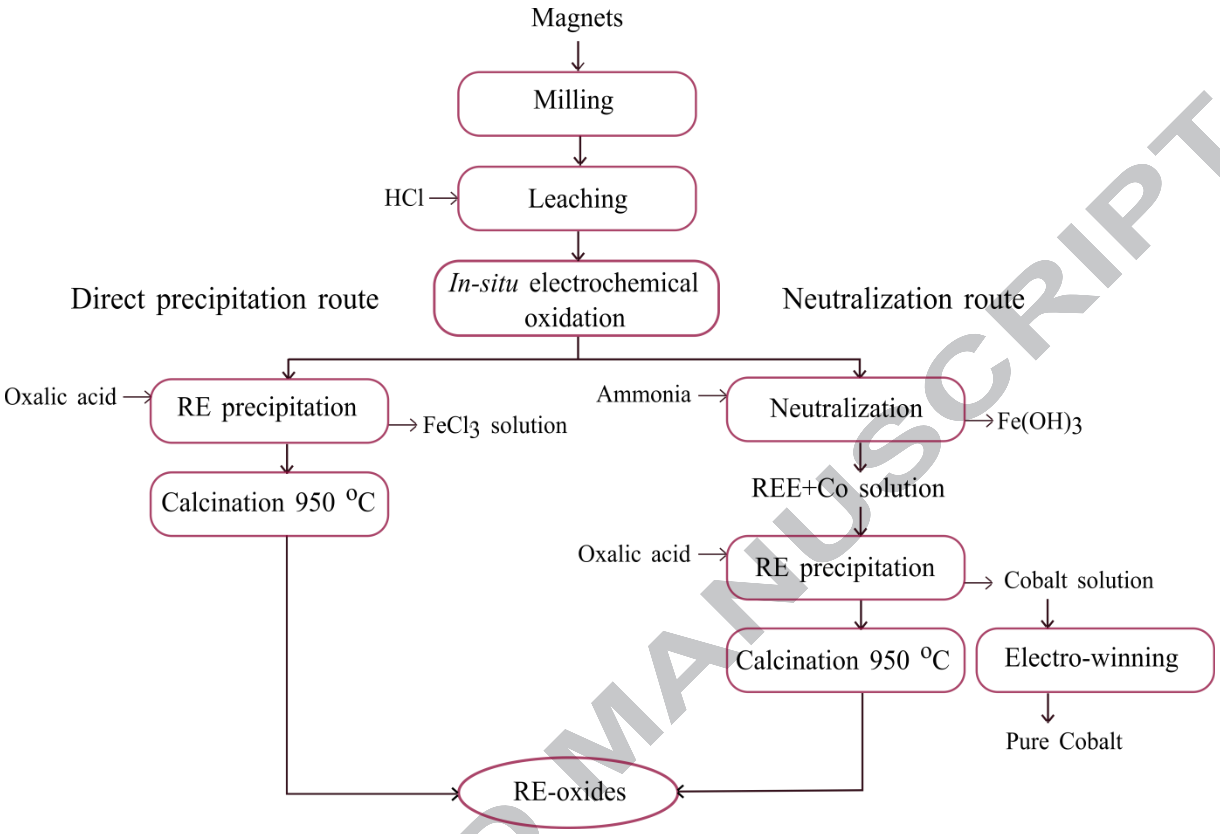


Fig. 9. Process flowsheet of electrochemical recycling of NdFeB illustrating the two different routes

4. Conclusions

A proof of principle for electrochemical approach was developed to effectively recover valuable elements from NdFeB magnet waste. The speciation of iron in solution is shown to be one of the most critical parameters in developing a flow sheet for NdFeB recycling. In the first route of direct oxalic precipitation more than 97% of REEs could be precipitated as rare-earth oxides with purity of 99.2%. This route is environmentally friendly, produces no waste and the remaining $FeCl_3$ solution can be directly sold to different industries. Alternatively, in the second route, neutralization with ammonia completely removed iron from the electro-oxidized leachate. The produced pink leachate was composed only of REEs and cobalt. Oxalic acid precipitation of the pink leachate produced rare-earth oxides of very high purity (99.9%) leaving a cobalt rich solution. Though the process consumes ammonia and has multiple steps, it also gives a possibility of recovering cobalt as valuable metallic deposit. On the whole, the successful *in-situ* electro-oxidation described in this manuscript provides two distinctive choices for recycling valuable metals from NdFeB waste.

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Highlights

- An electro-oxidative process to recover REEs from NdFeB magnet waste is proposed
- > 95% REEs are recovered as mixed rare-earth oxides with ≥99 % purity
- Valuable $FeCl_3$ by product was obtained that can be used in water treatment industry
- Speciation of iron is shown to be a critical parameter to recycle NdFeB magnets