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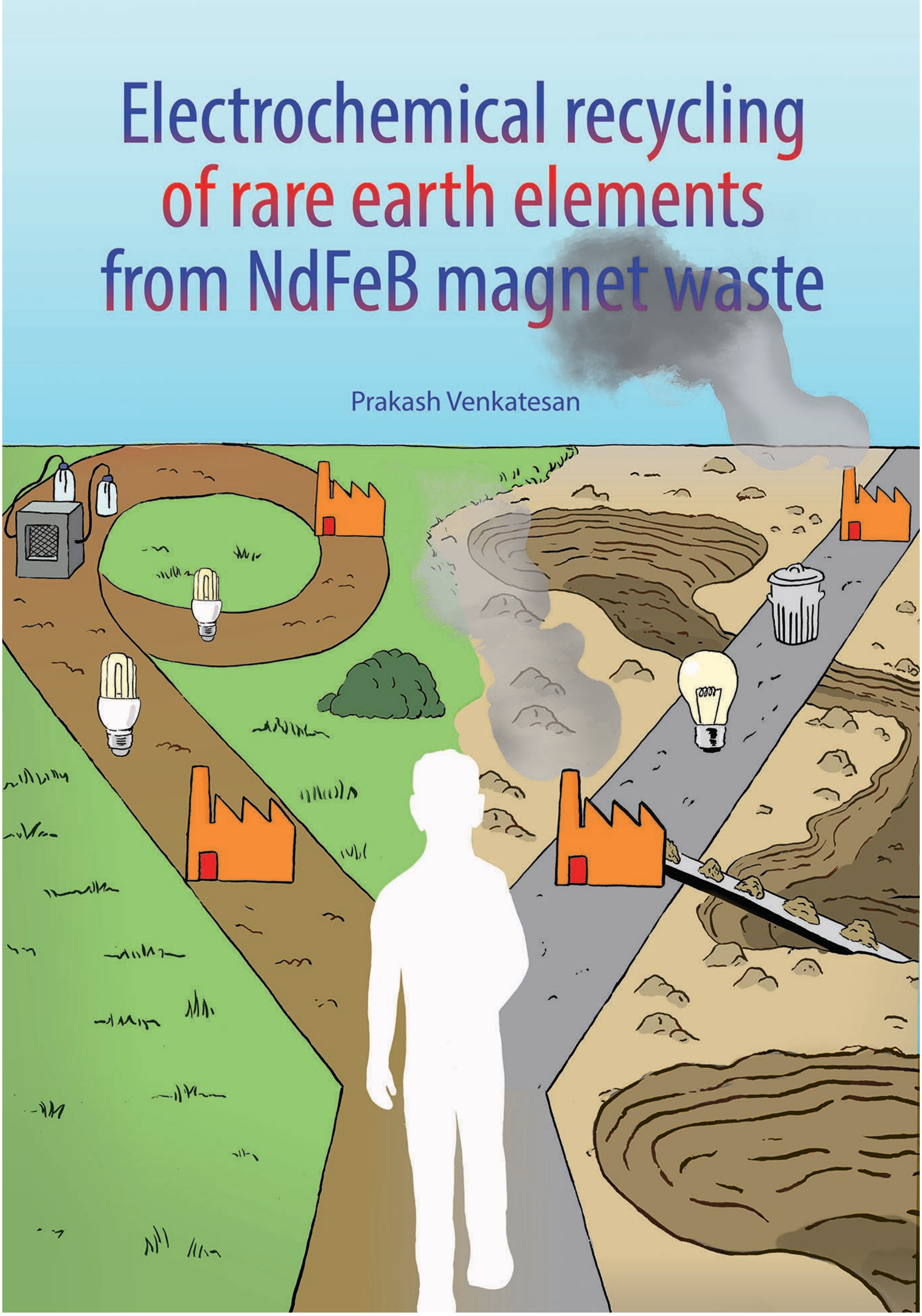

Electrochemical recycling of rare earth elements from NdFeB magnet waste

Prakash Venkatesan

Chapter 1 Introduction

1.1 Research Background

Rare earth elements (REEs) are a group of 17 elements (15 lanthanides, scandium and yttrium) that are indispensable in the transition towards a low-carbon economy as they are used in many high-tech and clean energy applications such as wind turbines, hybrid electric vehicles, nickel metal hydride batteries, catalysts and lamp phosphors. REEs are considered to be the most "critical metals" due to their economic importance and risks in supply chain.[1] More than 90% of REEs are produced by China and this monopoly, combined with Chinese restrictions in recent years on international supply quota, has created fragilities in the supply chain. Primary production of REEs from ores leaves a considerable environmental footprint by increased acidification and global warming potential.[2] REE ores such as monazite, xenotime and bastnäsite are complex for extraction and separation. They contain both the naturally abundant cerium and lanthanum as well as the less abundant heavy REEs such as neodymium and dysprosium. However, the market is primarily driven by the demand of neodymium and dysprosium. This uneven demand has caused the stockpiling of huge amounts of cerium and lanthanum leading to a "balancing problem".[3] Thus, the combined factors of increasing demand, supply chain frailties and environmental impact of primary mining has created the necessity to recycle REEs from end of life consumer products. However, less than 1% of REEs are currently being recycled.

NdFeB ($Nd_2Fe_{14}B$) magnets are the strongest magnets available on the market and are a valuable secondary resource from which REEs can be recovered. NdFeB magnet has the highest energy product of all permanent magnets and can provide the same magnetic strength of a ferrite magnet, yet with having ten times smaller size. [4] Typically, NdFeB magnets are composed of 20-30 wt% REEs, 60-70 wt% iron, 1 wt% boron and other minor additives elements such as copper, gallium, zirconium, cobalt, aluminium and niobium. They are used in devices like electric motors and generators, hard disk drives, loudspeakers, sensors and for applications such as hybrid electric vehicles, laptops, wind turbines, air conditioners, transducers, and other electrical appliances. In 2016, more than 20% of REEs produced were consumed for production of NdFeB magnets, making them the largest application among all REEs.[5]

Although a variety of recycling processes have been developed to recycle NdFeB magnets, selective and environmentally friendly extraction of REEs still remains a challenge. Direct recycling of end-of-life (EoL) NdFeB magnets to new NdFeB magnets using hydrogen has been shown to be effective.[6] The magnet waste is first pulverized with hydrogen gas in the hydrogen disproportionation, desorption and recombination process (HDDR). The hydrogenated powder is then realigned in a magnetic field to form directly usable NdFeB magnets. However, the difference in composition among the magnet waste adversely affects the properties of the newly formed magnets after HDDR.[7-8]

As opposed to the magnet-to-magnet direct recycling, indirect recycling involves separation of REEs from the magnet waste to produce rare-earth metals and is especially suited for dealing with low grade and complex EoL magnet waste. Generally, NdFeB indirect recycling processes developed hitherto can be classified into pyrometallurgical and hydrometallurgical processes. Hydrometallurgical processes operate close to room temperatures, usually do not require complicated set-ups and are not energy intensive. Lyman and Palmer developed a hydrometallurgical process in which NdFeB magnets are first completely dissolved in sulfuric acid.[9] Then, oxalic acid or sodium hydroxide is added to selectively precipitate REEs as rare-earth oxalates or rare-earth double sulfates, respectively. In a process by Bandara et al., NdFeB magnet waste is completely dissolved in hydrochloric acid followed by selective precipitation of REEs with oxalic acid.[10] These processes consume an excess of acid (more than what is required just for REEs), generate large amounts of waste water, require multiple steps and consume chemicals that cannot be recycled. Additionally, the role of oxalic acid as a selective precipitating agent is unclear, as iron in Fe(II) form has been reported to co-precipitate with REEs as ferrous oxalates.[11]

In contrast, pyrometallurgical processes such as selective chlorination, liquid metal extraction, vacuum induction melting, thermal isolation and roasting can efficiently recycle NdFeB magnets.[12-15] Roasting process are particularly interesting as they can selectively extract REEs from the waste in a closed-loop manner without net inorganic acid consumption. Recai et al., developed a sulfation roasting processes in which all REEs in magnet waste are converted into rare-earth sulfates and iron is converted into Fe_2O_3 in the first step. [16] Subsequently, rare-earth sulfates are extracted selectively into the solution by water leaching, leaving the water-insoluble Fe_2O_3 as residue. Similarly, Vander Hoogerstraete et al., oxidatively roasted NdFeB magnets converting both REEs and iron into their respective oxides.[17] The roasted magnet was then leached with hydrochloric acid that is equivalent to the stoichiometric requirement of REEs (nHCl/nREE = 3.5). REEs were selectively extracted into the solution, leaving out ferric oxide/hydroxide in the precipitate. The acid used in the leaching step was recovered in the further solvent extraction step, making the whole process acid free. However, these pyrometallurgical processes operate at a very high temperature of 750-900 ^{o}C and are thus highly energy intensive.

Irrespective of the operational temperature of recycling processes, a key parameter to take into account for designing an environmentally friendly recycling route for recycling NdFeB magnets is the speciation of iron. For hydrometallurgical processes, it is important to determine the speciation of iron in the leachate because of two main reasons. (a) Fe(II) remains in the leachate as soluble species below a pH of 6. Selective extraction of REEs by increasing the pH of the leachate is not possible since both REEs and Fe(II) can undergo hydrolysis and co-precipitate. (b) Addition of precipitating agents like oxalic acid is also problematic since Fe(II) oxalates are highly insoluble and can be precipitated together with REEs. As opposed to Fe(II), Fe(III) can undergo hydrolysis at a pH around 3. Also, Fe(III) oxalates are highly soluble which allows for selective precipitation of the insoluble rare-earth oxalates with oxalic acid. Thus, a key step in formulating a process for NdFeB magnet waste treatment would be oxidation of Fe(II) to Fe(III).

Electrochemistry is an integral part of recycling metals and is often used to recover metals while simultaneously regenerating acid.[18] Electrochemical processes are environmentally friendly as they can electrons as reagents, and can enhance the kinetics of processes by controlling vital parameters such as potential and current. This thesis explores four different electrochemical processes to recycle NdFeB magnets with the key reaction being electro-oxidation of Fe(II). The differences in mechanisms between direct anodic oxidation of Fe(II), oxidation of Fe(II) by water electrolysis, oxidation of Fe(II) by *in-situ* electrochlorination are investigated and presented in different chapters. This thesis, for the first time, demonstrates electrochemistry based flowsheets in which REEs are selectively and efficiently extracted at room temperature.

1.2 Outline of the thesis

The objective of this thesis is to develop processes to recycle NdFeB magnets based on green chemistry principles. Therefore, the processes conceived should not release dangerous chemicals, produce minimal waste, be selective in extracting REEs, operate at room temperature and be cost effective.

Chapters 2-5 describe the four different electrochemical routes that were conceived and investigated to recycle NdFeB magnet waste.

Chapter 2 presents a method in which NdFeB magnet waste is at first completely leached with HCl. Subsequently, Fe(II) in the leachate is selectively electro-oxidized in an undivided electrochemical reactor to Fe(III). More than 99% of Fe(II) was electro-oxidized within four hours from the acidic leachate ($pH \leq 2$) whereas only less than 2% of Fe(II) could be oxidized if only air was used. Two different routes are then investigated to selectively extract REEs from the electro-oxidized leachate. This chapter provides evidence for a) the anodic oxidation mechanism of Fe(II) and b) the role of iron speciation in selective precipitation of REEs with oxalic acid.

A closed-loop process where NdFeB magnet waste is directly used as an anode together with an inert anode in an is described in **Chapter 3**.The dual anode strategy is shown to produce mixed REE and Fe(III) hydroxides which is identical to mixed oxide powder obtained after oxidative roasting process. Subsequently REEs and cobalt are leached selectively with HCl at room temperature.

Chapter 4 is dedicated to the development of an electrochemical membrane reactor with two chambers separated by an anion exchange membrane for selective REE extraction from NdFeB magnet waste. The influence of various critical parameters such as the current density, concentration of NaCl in catholyte and anolyte on simultaneous selective extraction of REEs and iron removal is systematically studied. This work demonstrates selective and inorganic acid free extraction of REEs from pulverized magnet waste at room temperature.

Chapter 5 delves into the possibility of going from NdFeB magnet waste directly into final product rare-earth oxide in one step. A three chamber electrochemical reactor with an anion and cation exchange membrane is constructed. Direct conversion of rare-earth nitrates into nitric acid and rare-earth hydroxides by electro-separation is examined. The kinetics of the process is determined by systematically varying the current density. The produced rare-earth hydroxides were calcined to obtain pure rare-earth oxides. The crucial step of electrochemical salt-splitting offers the important advantage of avoiding using expensive oxalic acid as precipitating agent and thus eliminates the emission of carbon dioxide. This chapter for the first time demonstrates completely acid-free and selective extraction of REEs from NdFeB magnet waste at room temperature.

Chapter 6 compares various processes developed in this thesis in terms of their cost effectiveness, environmental impact, process kinetics and potential of scaling up. At the end of the thesis, summary, conclusions and recommendations for future are presented.

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Chapter 2 An electro-oxidative approach to recover valuable elements from NdFeB magnet waste

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 produces 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.

This chapter is based on the published scientific paper - Prakash Venkatesan, Zhi Sun, Jilt Sietsma, Yongxiang Yang, Separation and Purification Technology, Volume 191, January 2018, 384-391.

2.1 Introduction

Neodymium iron boron (NdFeB) magnets have a very high magnetic 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 °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 chapter, 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 is 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 is rich in REEs along with cobalt. Addition of oxalic acid to this leachate selectively precipitates 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 shows 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.

2.2 Experimental

2.2.1 Materials

All chemicals are of analytical grade and were used without further purification. Ammonium chloride (NH_4Cl 99.95%), ammonium acetate, ammonia solution (25% NH_3 in water), hydrochloric acid (HCl 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]

2.2.2 Experimental set-up and procedures

A cylindrical plexiglass electrochemical reactor (Figure 2.1) 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.

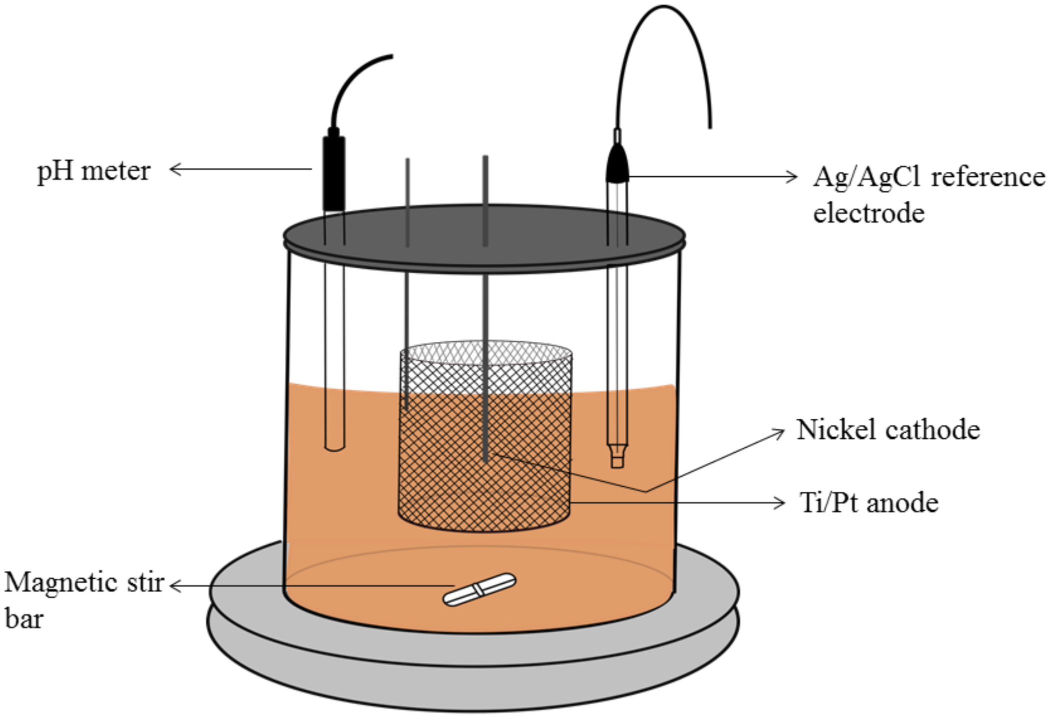

Figure 2.1 Schematic illustration of the electrolysis set-up.

2.2.3 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

$$\text{Leaching yield (\%)} = \frac{M_L \text{ x } V_L}{X_M \text{ x } M_T} \text{ X } 100 \tag{2.1}$$

where M_L is amount of metal M present in the leachate (mg/l), $V_L$is the volume of the leachate in liters, X_M is the fraction of metal M in the magnet waste and $M_T$is the total amount of magnet waste used (mg). 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.

2.3 Results and Discussion

2.3.1 Leaching of the magnet waste

The average elemental composition of the magnet waste is given in Table 2.1. 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 2.1 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, $C_{\mathrm{NH_4Cl}} = 3\mathrm{M}$) 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

$$\mathrm{2REE} + 6\,\mathrm{HCl} \leftrightarrow \mathrm{2REECl_3} + \mathrm{3H_2} \uparrow \tag{2.2}$$

$$\mathrm{Fe} + 2\,\mathrm{HCl} \leftrightarrow \mathrm{FeCl_2} + \mathrm{H_2} \uparrow \tag{2.3}$$

The leaching yield of both REEs and iron increase with increase in concentration of HCl (Figure.2.2). REEs leach slightly faster than iron. Nevertheless, for HCl concentrations of 1.2 M and more, 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.

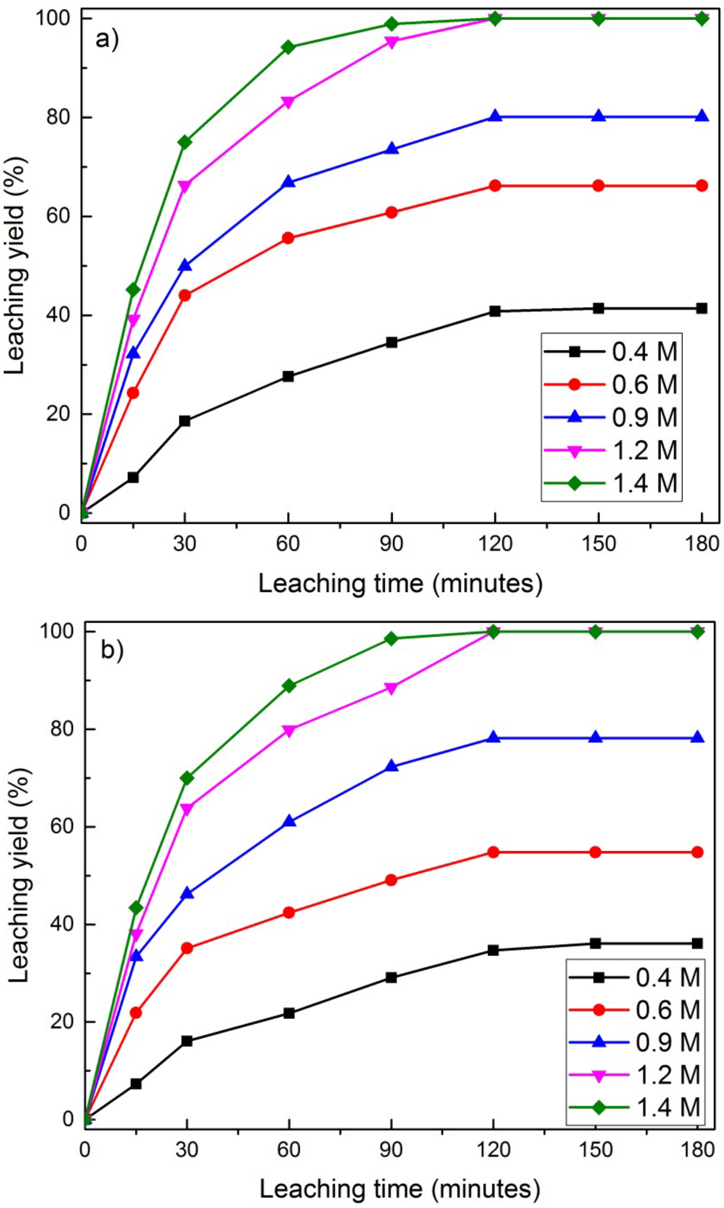

Figure 2.2 Effect of acid concentration on the leaching yield (%) of (a) REEs and (b) iron from NdFeB magnet waste powder (Stirring rate 550 rpm, $T = 25\,^{o}\mathrm{C}, C_{\mathrm{NH_4Cl}} = 3\mathrm{M}$). Relative standard deviation < 3.6%.

2.3.2 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

$$\mathrm{Fe^{2+}} \rightarrow \mathrm{Fe^{3+}} + \mathrm{e^-} \; (E^o = 0.77 \mathrm{~V}) \tag{2.4}$$

$$\mathrm{2H_2O} \rightarrow \mathrm{O_2} + \mathrm{4H^+} + \mathrm{4e^-} \; (E^o = 1.23 \mathrm{~V}) \tag{2.5}$$

$$\mathrm{2Cl^-} \rightarrow \mathrm{Cl_2} + \mathrm{2e^-} (E^o = 1.36 \mathrm{~V}) \tag{2.6}$$

where E^0 is the standard reduction potential. The desired anodic process is reaction (2.4). Reactions (2.5) and (2.6) 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

$$\mathrm{Fe^{3+} + e^- \rightarrow Fe^{2+}} \quad (E^o = 0.77\ \mathrm{V}) \tag{2.7}$$

$$\mathrm{2H^+ + 2e^- \rightarrow H_2} \quad (E^o = 0\ \mathrm{V}) \tag{2.8}$$

$$\mathrm{Fe^{2+} + 2e^- \rightarrow Fe} \quad (E^o = -0.44\ \mathrm{V}) \tag{2.9}$$

$$\mathrm{Co^{2+} + 2e^- \rightarrow Co} \quad (E^o = -0.28\ \mathrm{V}) \tag{2.10}$$

The most undesirable cathodic reaction in this system is reaction (2.7); 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 (2.8) 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).

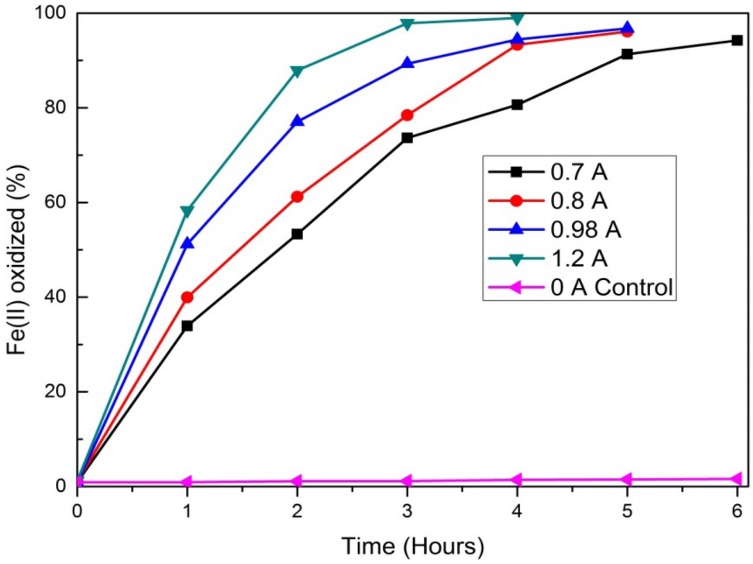

Figure 2.3 Rate of Fe(II) oxidation as a function of current density (Stirring rate 550 rpm, $T = 25\ ^{o}\mathrm{C}$, $C_{\mathrm{NH_4Cl}} = 3\mathrm{M}$). Relative standard deviation < 3.2%

Galvanostatic electrolysis was performed on the leachates and Figure 2.3 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} $(Fe(OH)_3 = 2.79 \times 10^{-39})$).[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 Figure. 2.4 as change in anode potential over time.

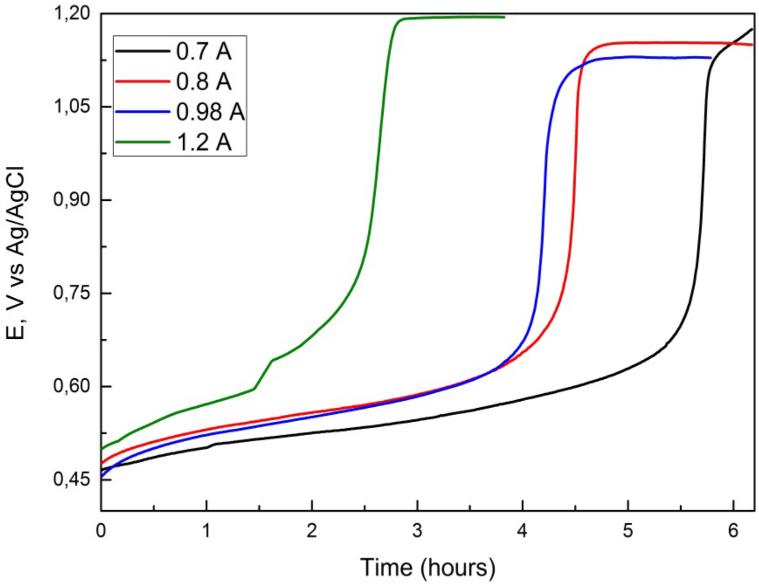

Figure 2.4 Evolution of anode potential (V, vs Ag/AgCl) for different current intensities (Stirring rate 550 rpm, T = 25 °C, $C_{NH_4Cl} = 3M$)

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 according to the Nernst equation

$$E = E^0 + \frac{RT}{nF} \ln \frac{[Fe^{3+}]}{[Fe^{2+}]} \tag{2.11}$$

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. 2.3 & 2.4, 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

$$\mathrm{Fe} + \mathrm{Fe}^{3+} \rightarrow 2\,\mathrm{Fe}^{2+} \tag{2.12}$$

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 REE^{3+} are stable species in the solution and thus were not deposited cathodically.

The average cell voltage and energy consumption is given in Table 2.2. 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 according to

$$P\ = VIt\ /\ (X_{Fe} * \eta) \tag{2.13}$$

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 η is the fraction 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 2.2 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

2.3.3 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 ($K_{sp}= 3.2 \times 10^{-7}$). 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

$$2\ \text{REECl}_3 + 3\text{H}_2\text{C}_2\text{O}_4 \rightarrow \text{REE}_2(\text{C}_2\text{O}_4)_3 + 6\text{HCl} \qquad (2.14)$$

The stoichiometric equivalent of oxalic acid is 1.5 moles per mole of rare earth elements ($n\text{C}_2\text{O}_4^{2-} / n\text{REE}^{3+} = 1.5$). 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 2.3, where UO-L stands for un-oxidized leachate and EO-L stands for electro-oxidized leachate. The amount of precipitation corresponds to the amount of metals precipitated from the leachate as oxalates.

Table 2.3 Metal precipitation % from leachates by precipitation with oxalic acid.

Leachate type	($n\text{C}_2\text{O}_4^{2-} / n\text{REE}^{3+}$)	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 2.4. Our results confirm the findings of Lyman et al.,[17] that significant presence of Fe(II) interferes with selective precipitation of REEs using oxalic acid. At $n\text{C}_2\text{O}_4^{2-} / n\text{REE}^{3+} = 1.5$, 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 $n\mathrm{C_2O_4}^{2-}$ / $n\mathrm{REE}^{3+}$= 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 2.4 Purity of Purity of rare-earth oxides obtained after calcination at 950 °C, in weight percentage.

Leachate type	($n\mathrm{C_2O_4}^{2-}$ / $n\mathrm{REE}^{3+}$)	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. 2.5 compares the XRD patterns of oxides obtained from un-oxidized and electro-oxidized leachates. At $n\mathrm{C_2O_4}^{2-}$ / $n\mathrm{REE}^{3+}$ > 1.5, for un-oxidized leachates, $\mathrm{NdFeO_3}$ was found to be the main phase indicating the presence of iron impurity. In contrast, electro-oxidized leachates produced oxides, which have $\mathrm{Nd_2O_3}$ 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 $\mathrm{FeCl_3}$ solution with minor impurity of dissolved oxalate anions as by-product. $\mathrm{FeCl_3}$ 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.

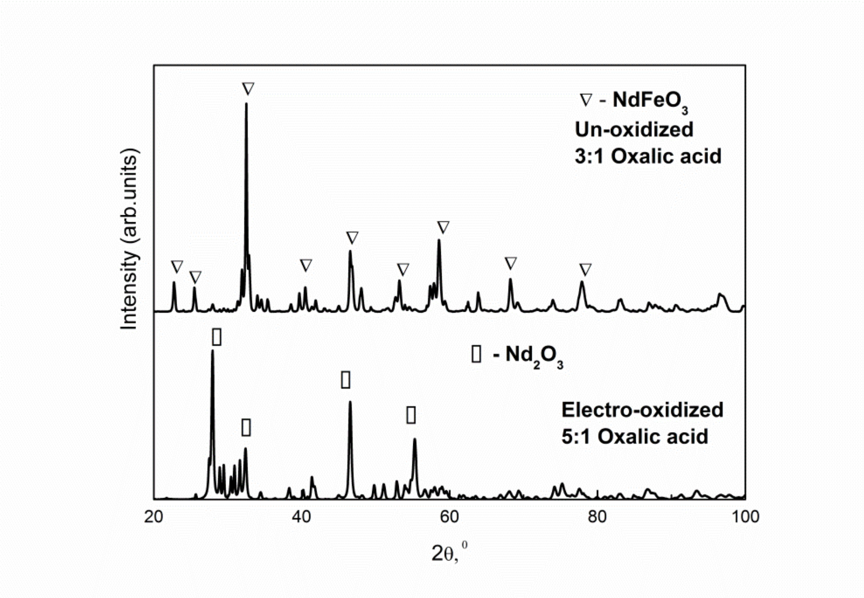

Figure 2.5 XRD pattern of oxides after calcining the oxalates of un-oxidized and electro-oxidized leachates.

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 2.2) 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 2.5 Composition of leachates and retention % 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±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 2.5. 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 (Figure 2.6).

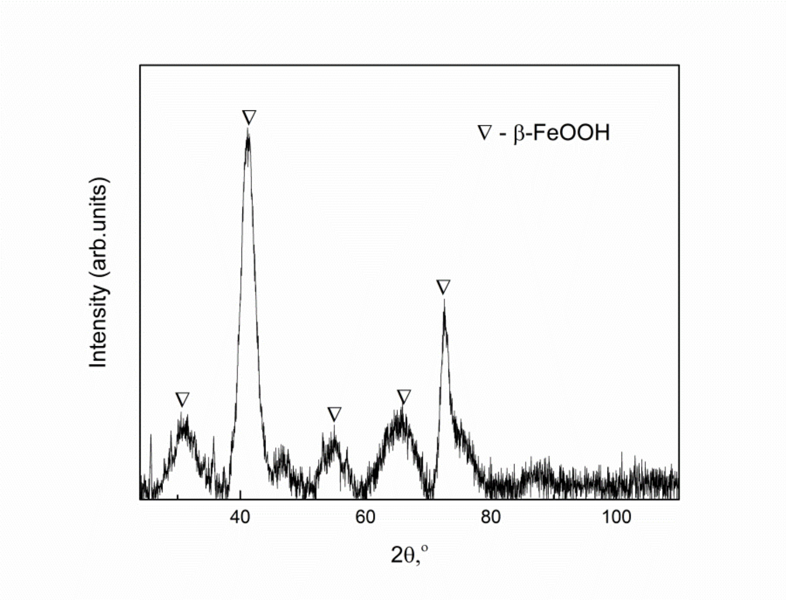

Figure 2.6 XRD pattern of β-Akagenite FeO(OH) obtained after neutralization & precipitation of electro-oxidized leachate.

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 according to

$$2\ \mathrm{FeOOH} \rightarrow \mathrm{Fe_2O_3} + \mathrm{H_2O} \tag{2.15}$$

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]

2.3.4 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 (neodymium oxalate) = 1.3×10^{-31})[41] in comparison to cobalt oxalate (Ksp= 6×10^{-8}) [42] and thus oxalic acid was added to the leachate to selectively precipitate REEs. A slight excess ($n\mathrm{C_2O_4^{2-}}$ / $n\mathrm{REE^{3+}}$ = 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, 76.7 wt% of Nd, 20.1 wt% of Dy, 3.2 wt% of Pr and 0.05% of cobalt.

2.3.5 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. 2.7(a). When scanned in negative direction, the reductive current starts around -1050 mV due to simultaneous occurrences of competing reactions (2.8) and (2.10).

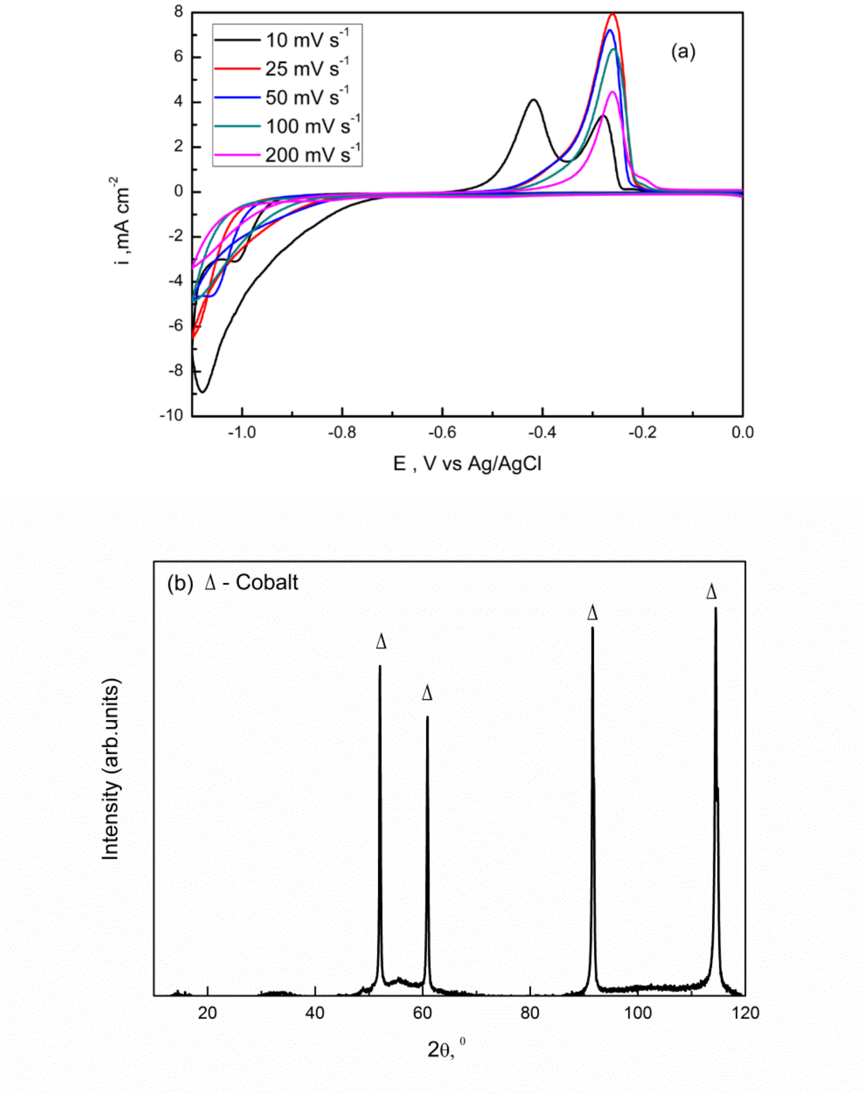

Figure 2.7. (a) Cyclic voltammetry of cobalt solution at different scan rates (b) XRD pattern of the electrodeposited cobalt at 250 Am^{-2}

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. 2.7(b)).

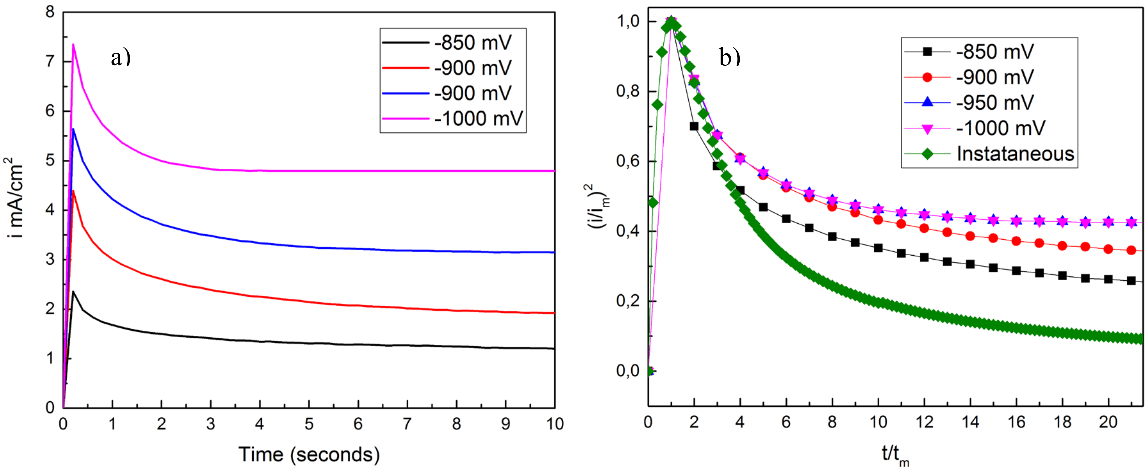

Figure 2.8. a) Chronoamperometry of cobalt during electrodeposition on glassy carbon electrode and b) corresponding Scharifker-Hills' model

Chronoamperometry was used as a tool to diagnose the nucleation mechanism of cobalt from the remnant leachate. The obtained chronoamperograms (Figure 2.8) 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]

2.3.6 Comparison of two routes

Figure 2.9 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 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.

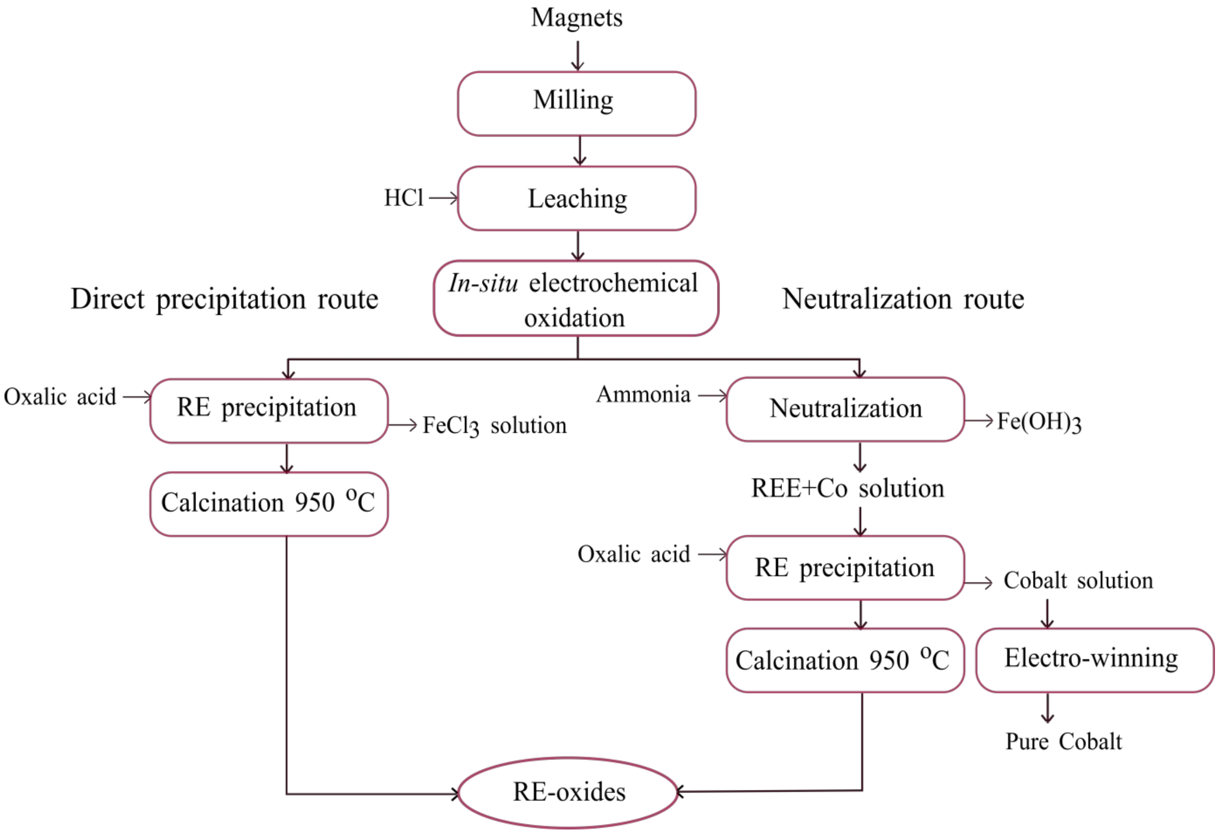

Figure 2.9 Process flowsheet of electrochemical recycling of NdFeB magnet waste illustrating the two different routes.

2.4 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 although 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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Chapter 3 A dual anode strategy to selectively extract REEs from NdFeB magnet waste at room temperature

ABSTRACT-NdFeB magnets are used in wind turbines, hybrid electric vehicles and are instrumental in progression towards a low-carbon economy. Recycling rare-earth elements (REEs) from NdFeB magnet waste is an important step towards building a sustainable REE supply chain. In this study, we describe an electrochemical process to selectively extract REEs from NdFeB magnet waste at room temperature. First, an electrolysis pretreatment step is 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 leaches into the solution leaving iron in the residue. REEs are 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 yields rare-earth oxides of high purity (99.2%), which can be used directly for producing rare-earth metals.

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3.1 Introduction

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

NdFeB magnets contain 20-30 wt% of REEs, 60-70 wt% of iron, 1 wt% boron and some admixtures of other metals in minor quantities. Selective extraction of REEs over iron is the major objective in the recycling of NdFeB magnet waste. Comprehensive reviews have summarized the approaches taken thus far to recover REEs from NdFeB magnets.[6-7] Wet chemical processes are preferred as they operate mostly at room temperature. These processes usually consist of complete and unselective dissolution of NdFeB magnets in an acid followed by selective precipitation of the rare earths as double sulfates or fluorides from the solution. Such recycling processes consume a large amount of non-recyclable chemicals such as H_2SO_4, HF, NaOH and generate considerable volumes of waste water.[8] In contrast to selective precipitation of REEs, iron can also be selectively precipitated from the leachate leaving REEs and cobalt in the solution. The speciation of iron in the solution plays an important role as Fe(II) tends to be a stable species in the solution below a pH value of 6 and thus cannot be selectively precipitated over REEs by hydrolysis. On the other hand, Fe(III) undergoes hydrolysis and can be precipitated at a pH of 2 where REEs remain as stable species in solution.[9] However, air oxidation of Fe(II) is kinetically sluggish below pH 7.[10] Recently, an electrochemical route and a chemical route were proposed where complete removal of iron from the leachate was achieved at room temperature by selective oxidation of Fe(II) in the solution. Nevertheless, both processes required complete dissolution of the magnet waste and thus, generated acid waste.[9, 11]

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

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

In this manuscript, we propose a room-temperature electrolysis pretreatment step with a similar dual anode system for recycling NdFeB magnet waste. In this electrolysis pretreatment step with NH_4Cl as the electrolyte, NdFeB magnet waste dissolves as an active metal anode (AMA) and simultaneously, a Ti/Pt inert anode (IA) oxidizes Fe(II)to $Fe(OH)_3$. At the end of this electrolysis step, the REEs and iron in the magnet can be converted into their respective hydroxides, $REE(OH)_3$ and $Fe(OH)_3$ to produce a mixed hydroxides precipitate. This insoluble mixed hydroxides precipitate is similar to the powder obtained after oxidative roasting and thus, REEs can be selectively leached from this hydroxides mixture with HCl in the ratio of (nHCl/nREE ≤ 3.5). The effect of different conditions such as the ratio of current density between the two anodes and electrolyte composition were studied and the underlying mechanisms were explored. The process produced iron-free REE-rich leachates and iron hydroxide by-product that can be used in pigment and gas sensors industries. The whole process consumes only electricity, water and oxalic acid.

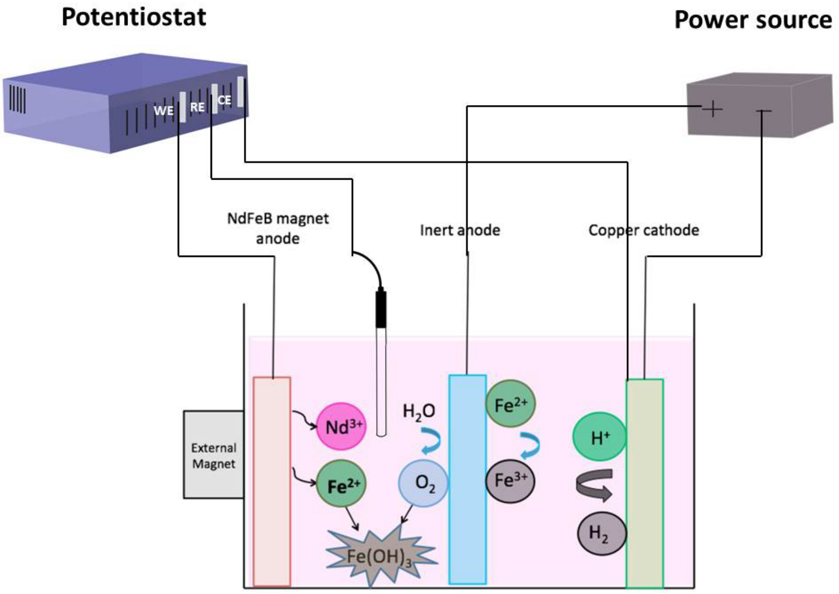

Figure 3.1 Schematic of the dual anode electrolysis process to recycle NdFeB magnet waste.

3.2 Experimental section

3.2.1 Materials and Methods

Solid sintered magnets used as electrodes were supplied by Magneti Ljublijana (Slovenia) and their composition as measured with ICP-OES is listed in Table 3.1. HCl (37%), NH_4Cl (99.95%) were purchased from Sigma Aldrich (Zwijndrecht, The Netherlands). External hold magnets (EHM) were purchased from Supermagnete, (Okeo Germany). A dimensionally stable cylindrical platinum coated titanium anode (DSA, fully platinum coated, Magneto B.V. Schiedam) of 3 cm in diameter and 3 cm in height was used as inert electrode. Copper plates 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. Universal 320R centrifuge was used to separate the leachate from the precipitate. The solution analysis was done with inductively coupled plasma- optical emission spectrometry (ICP-OES, PerkinElmer Optima 3000DV). Chloride concentration was measured using DX-120 Ion Chromotograph. The leach residue and rare-earth oxides were characterized with XRD using Bruker D8 diffractometer with Cu Kα radiation operated at 45 kV.

Table 3.1 Chemical composition of the magnet (wt%)

Element	Fe	Nd	Dy	Co	B	Pr	Cu	Ga	Al	Gd	Ni	Nb	Total
Wt %	64.38	23.14	6.05	2.86	1.10	0.84	0.17	0.22	0.06	0.02	0.02	0.01	98.86

3.2.2 Experimental set up and procedure

A PMMA reactor (10 × 10 × 7 cm^3) was used as an electrochemical cell and the electrolyte volume was kept constant at 200 ml during the experiment. Solid sintered magnet (2.5 × 1.5 × 0.55 cm^3) was soldered to a wire and the soldered portion was carefully covered with a polymer resin to prevent solder material from contaminating the leachates. A copper plate with an area of 23 cm^2 (10 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 (3M KCl) was used as a reference electrode and both the reference electrode and pH meter were immersed in the electrolytic cell throughout the experiment. A PTFE overhead stirrer was used to agitate the electrolyte at a constant rotating speed of 500 rpm. A separate power source was used to connect inert platinized titanium (Ti/Pt) anode and copper cathode (Figure 3.1). A water bath was used to maintain the temperature of electrochemical cell and the accuracy of it was found to be ±2 ^{o}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 cm^2 exposed area. Samples were mechanically polished up to 1200 silicon carbide paper and 1 µm with diamond paste, then ultrasonically cleaned in ethanol. All the experiments were conducted using potentiostat Versastat 4 (Ametek, UK) and the data was obtained using Versastudio software

3.2.3 Iron removal using dual anode system

The dependency of Fe(II) oxidation on the ratio of current passed between active magnet anode (AMA) and inert anode (IA) was studied by drawing out 1 mof sample over the duration of experiment. The current in AMA was kept constant at 0.5 A while the current at IA was changed to see the effect of iron oxidation. The samples were centrifuged at 5500 rpm for 10 minutes and the aqueous phase was filtered using a syringe filter (0.45 µm) leaving out the residue. The leachate was diluted using concentrated HCl (37%, 12 M).

3.2.4 Solution measurement and calculations

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

$$E\ (\%) = \frac{\mathrm{M_L\ x\ V_L}}{\mathrm{X_M\ X\ M_T}}\ \mathrm{X}\ 100 \tag{3.1}$$

where *E* is the percentage of extraction of metal M (%), $\mathrm{M_L}$ is amount of metal M present in the leachate (mg/l), $\mathrm{V_L}$is the volume of the leachate in liters, $\mathrm{X_M}$ is the fraction of metal M in the magnet waste and $\mathrm{M_T}$is the total amount of magnet waste used (mg).

Anodic dissolution efficiency (ŋ) for the dissolution of NdFeB alloy is calculated as follows.

$$\text{ŋ} = \frac{M_0}{M_t}\ \mathrm{x}\ 100\ (\%) \tag{3.2}$$

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

$$M_t = \frac{It}{FN_{EQ}} \tag{3.3}$$

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

$$N_{EQ} = \sum \frac{f_i n_i}{a_i} \tag{3.4}$$

where $f_{i,}n_{i,}a_i$ are mass fraction, electrons exchanged and atomic weight respectively of the i^th^ alloying element.

Power consumption, P (kWh/kg) is calculated as

$$P = \frac{V_{MA} + V_{IA}\, x\, (I_{MA} + I_{IA}) \mathrm{x}\, t}{m} \tag{3.5}$$

where V_{MA} and V_{IA}, are the voltage (V) measured between magnet anode and 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 electrolysis and m is the amount of magnet dissolved. Thus the reported values are kWh per kilogram of magnet waste.

3.3 Results and Discussion

3.3.1 Anodic dissolution behavior of magnet scrap

The electrochemical dissolution behavior of NdFeB magnets was characterized by anodic polarization measurements (Figure 3.2) at different concentrations of NH_4Cl over a constant pH of 4±0.3. The electrochemical dissolution reactions of major elements from the magnet anode are

$$\mathrm{Nd} \rightleftharpoons \mathrm{Nd}^{3+} + 3\mathrm{e}^- \ (E^0 = -2.323 \text{ V}) \tag{3.6}$$

$$\mathrm{Dy} \rightleftharpoons \mathrm{Dy}^{3+} + 3\mathrm{e}^- \ (E^0 = -2.295 \text{ V}) \tag{3.7}$$

$$\mathrm{Fe} \rightleftharpoons \mathrm{Fe}^{2+} + 2\mathrm{e}^- \ (E^0 = -0.477 \text{ V}) \tag{3.8}$$

$$\mathrm{Co} \rightleftharpoons \mathrm{Co}^{2+} + 2\mathrm{e}^- \ (E^0 = -0.28 \text{ V}) \tag{3.9}$$

Over the scanned potential range, the polarization curves show an increase in current with increasing potential. This indicates an active dissolution behavior of NdFeB magnets without any passivation. Increase in the NH_4Cl concentration resulted in higher dissolution current densities and is consistent with the fact that chloride ions act as pitting agents promoting dissolution.[21]

NdFeB magnets have a matrix phase ($Nd_2Fe_{14}B$) as well as Nd-rich and B-rich phases in the grain boundaries. Due to galvanic coupling, the Nd-rich and B-rich phases preferentially dissolve creating voids in the microstructure which facilitates the mechanical degradation of matrix phase. El Moniem et al., anodically dissolved NdFeB magnets at different current densities and found that the actual mass loss was higher than the theoretically calculated faradaic mass loss.[22] 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.

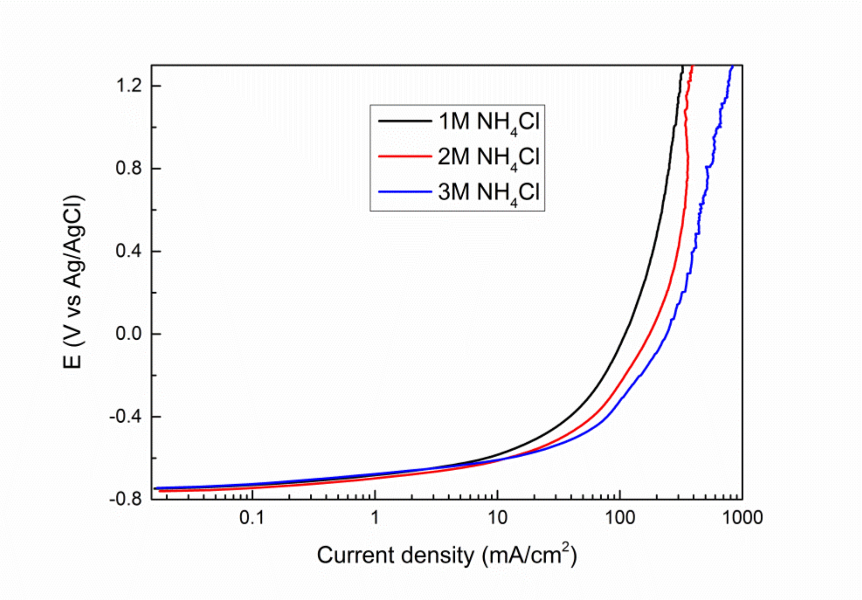

Figure 3.2. Potentiodynamic polarization curves of NdFeB magnets in 1 ,2 and 3 M NH_4Cl, scan rate 2 mVs^{-1} at temperature 25±2 °C.

3.3.2 Oxidation of iron at inert anode

Anodic dissolution of NdFeB magnets produces Fe(II) ions which need to be oxidized to Fe(III) to achieve effective separation between REEs and iron. To study the effect of current on the oxidation of Fe(II), a constant current (I_{NdFeB}) of 0.5 A was maintained at the AMA and four different currents (0 A, 0.06 A, 0.12 A, 0.2 A) were applied to the inert anode. The experiments were conducted at pH 2 and between 6 with periodic addition of HCl to keep the un-oxidized Fe(II) as soluble species. Platinized titanium (Ti/Pt) was chosen for this study as the inert anode as it was found to have high exchange current density for oxidation of Fe(II) and has been applied for treatment of pickling effluents.[23,24] The control experiment (0 A) showed the highest dissolution of iron into the leachates(Figure.3.3).

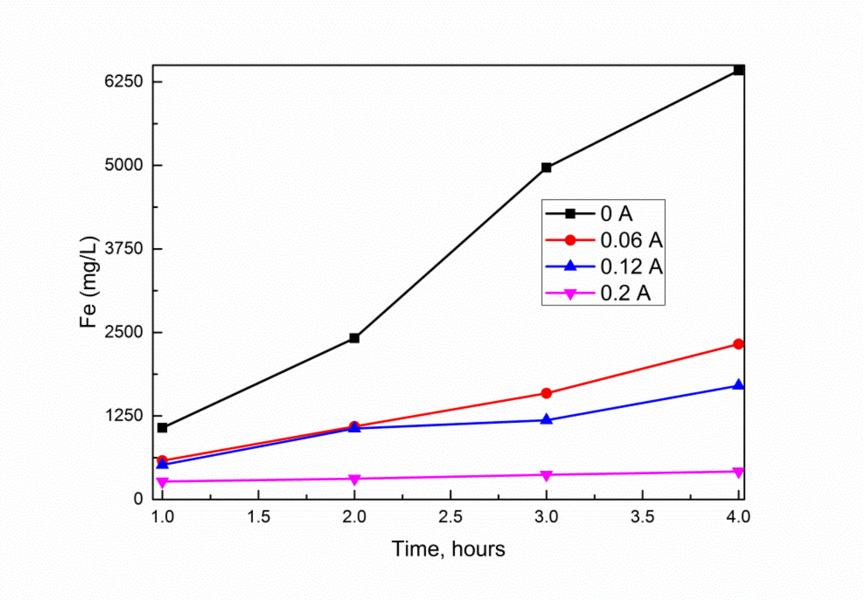

Figure 3.3 Influence of current density over Fe(II) elution into the leachatein 3 M NH_4Cl, at temperature 25±2 °C and at a stirring rate of 500 rpm. Relative standard deviation < 6.4%

With increase in current density at the IA, elution of Fe(II) 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[25-26]or by indirect electrochemical oxidation through dissolved oxygen.

$$\mathrm{Fe}^{2+} + 3\,\mathrm{H_2O} \rightleftharpoons \mathrm{FeOH_3} + 3\mathrm{H^+} + 3\mathrm{e^-} (E^0 = 0.931\ \mathrm{V}) \tag{3.10}$$

$$2\,\mathrm{H_2O} \rightleftharpoons 4\mathrm{H^+} + 4\mathrm{e^-} + \mathrm{O_2} (E^0 = 1.23\ \mathrm{V}) \tag{3.11}$$

The drop in Fe(II) elution was accompanied by presence sludgy $Fe(OH)_3$ precipitates. Around 0.2 A in the IA, more than 94% of Fe(II) was removed in comparison with the control experiment. Further increase in current density did not result in substantial removal of Fe(II) and hence, 0.2 A was chosen as current density at the inert anode.

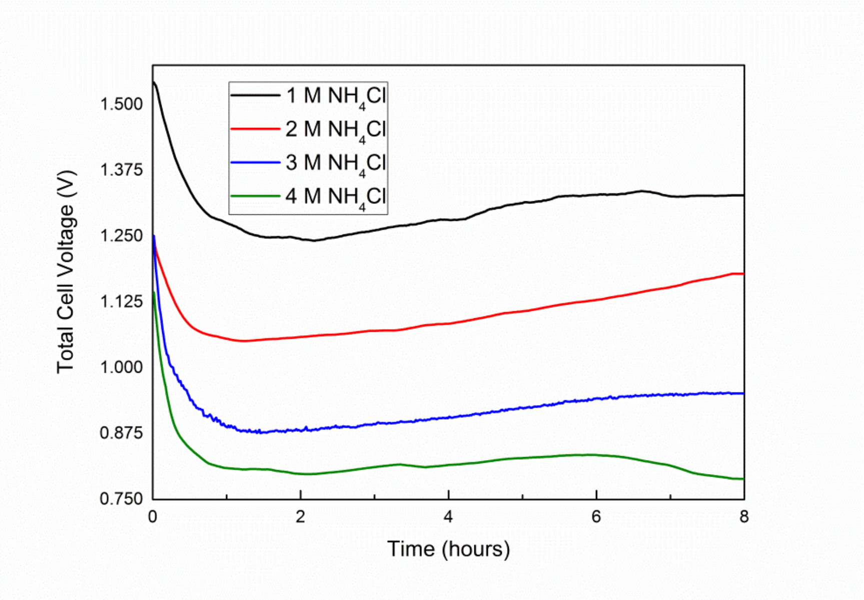

Figure 3.4 Effect of ammonium chloride concentration on the total cell voltage supplied between active magnet anode and the copper cathode at 25±2 °C and at a stirring speed of 500 rpm.

3.3.3 Effect of NH_4Cl concentration

The effect of the concentration of ammonium chloride salt on the galvanostatic electrolytic process was investigated by keeping currents on the AMA and IA constant at 0.5 A and 0.2 A respectively. The electrolysis experiments were carried out for 8 hours at room temperature, 25±2 °C.

Table 3.2 Effect of NH4Cl concentration on anode potential, magnet dissolution, anodic current efficiency and energy consumption in kWh/kg of magnet.

NH4Cl molarity (M)	Anode potential (V vs Ag/AgCl)	Mass of magnet dissolved (g)	Anodic current efficiency (%)	Mass gain at cathode (g)	Energy consumption (kWh/kg)
1M	-0.34 to -0.23	4.7±0.1	97.2±0.4	0.12	3.6
2M	-0.29 to -0.20	4.85±0.15	98.1±0.2	0.20	3.3
3M	-0.30 to -0.22	4.9±0.1	99.3±0.4	0.13	3.0
4M	-0.28 to -0.21	5±0.1	99.8±0.1	0.22	2.9

In order to understand the behavior of NdFeB anode and inert anode, a potentiostat and power supply was used separately to connect them in this study. However, industrially, a single power source could be used to supply current to both the anodes. The current supplied can be partitioned between the two anodes equally or different current densities can be maintained by connecting a resistor between the electrode and power supply. Alternatively, the area of the inert anode can also be varied to maintain the requisite current density. No acid was added during the electrolysis pretreatment step. The anodic potential for all NH_4Cl concentrations remained well below 0 V (vs Ag/AgCl), hinting a highly efficient dissolution process without any parasitic reactions consuming the supplied charge (Table 3.2). The anodic dissolution efficiency was more than 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.[27]The total cell voltage and the energy consumption decreased with the increase in concentration of the ammonium chloride salt (Figure 3.4). High concentration (1M and above) of Cl^- ion enhances metal dissolution via chloride adsorption mechanism and can therefore be the reason behind the voltage drop .[28]An initial drop of cell voltage was also observed which can be attributed to introduction of ions from magnet dissolution which enhances the conductivity of the electrolyte. The cell voltage between the inert anode and the copper cathode remained around 1.8-2.1 V for the whole of the experiment. Hydrogen gas evolution was the predominant cathodic reaction combined with deposition of a small amount of metallic iron.

$$2H^+ + 2e^- \rightleftharpoons 2\,H_2 (E^0 \;=\; 0\,\mathrm{V}) \tag{3.12}$$

$$Fe^{\,2+} + 2e^- \rightleftharpoons\; Fe\;(E^0 = \text{-}0.44\,\mathrm{V}) \tag{3.13}$$

At the end of electrolysis, a sludgy precipitate was obtained. The end pH of the leachate after electrolysis was 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 3.3.

Table 3.3 Extraction % of cobalt and REEs after electrolysis step.

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

The near complete extraction of cobalt at the end of electrolysis can be explained by cobalt's tendency to form stable ammoniacal complexes.[29-30] 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.[31]

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

$$2Cl^- \rightleftharpoons Cl_2 + 2e^- \tag{3.14}$$

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.

3.3.4 Selective acid leaching

Following the electrolysis step, an acid leaching step was carried out at different concentrations of HCl to selectively extract the REEs from the mixed hydroxide precipitate.

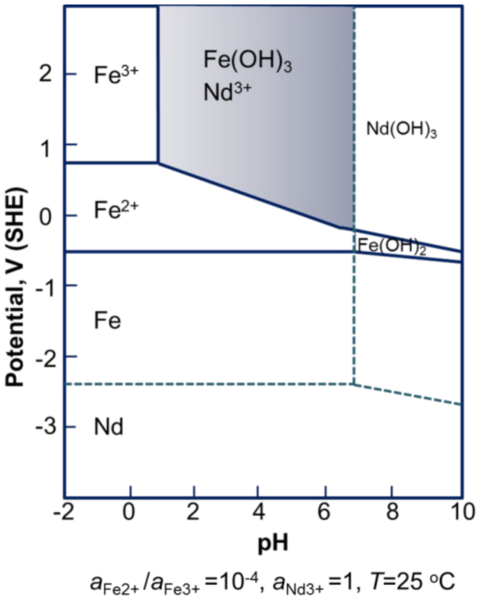

Figure 3.5 Potential–pH diagram of the Fe–H_2O and Nd–H_2O systems (regenerated according to data from [32] and HSC chemistry 6)

The potential-pH diagram for Nd-H_2O system and the Fe-H_2O system is shown in Figure 3.5. REEs are stable in the solution below a pH of 7 (K_{sp} $Nd(OH)_3 = 1.9 \times 10^{-21}$) while iron remains as $Fe(OH)_3$ precipitate at a pH of around 3 and above.[33] 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 that no Fe(III) was extracted into the solution.

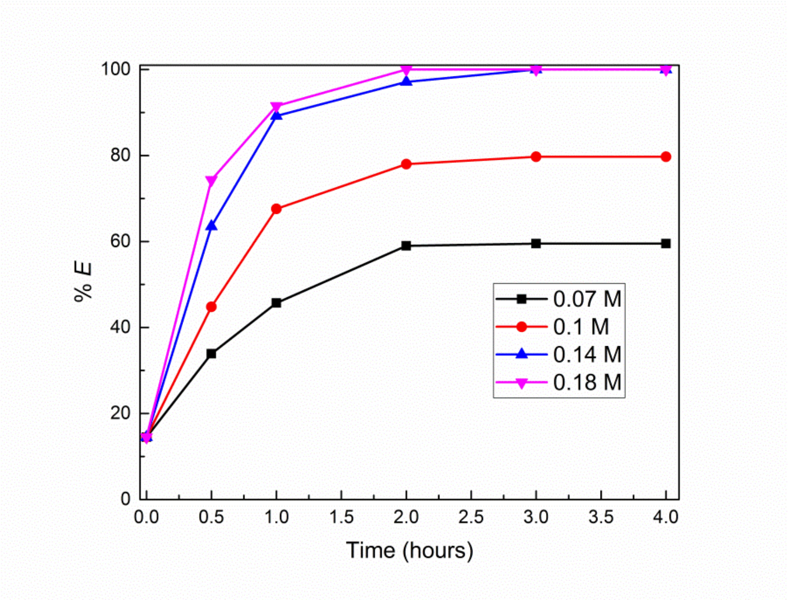

Figure 3.6 Percentage of extraction of REEsas a function of concentration of HCl after the electrolysis step at 25±2 ^{o}C and at a stirring rate of 500 rpm. Relative standard deviation < 2.9%

A pink leachate was obtained where REEs were completely and selectively extracted within three hours at a concentration of 0.14 M HCl and above (Figure 3.6). The number of moles of acid required per mole of REEs present in the mixed hydroxide precipitate (nHCl/nREEs) was only 2.5, lower than the stoichiometric requirement of 3. This lower than stoichiometric consumption of HCl is due to the fact of partial extraction of REEs at the end of electrolysis step. Additionally, in comparison to selective leaching step after acid roasting that took five days, the selective leaching step from mixed hydroxide precipitates is remarkably faster.

The composition of the leachate obtained after the acid leaching step is given in table 3.4. The concentration of cobalt decreased with increase in concentration of ammonium chloride whereas the concentration of REEs were more or less the same. It can be seen that Fe(II) oxidation by inert anode was effective and no iron was leached into 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. Leach residue after the acid leaching process consisted mainly of β-FeO(OH) (Figure 3.7) akaganeite that can be potentially used in gas sensors, as pigments or in water treatment industry. [34]

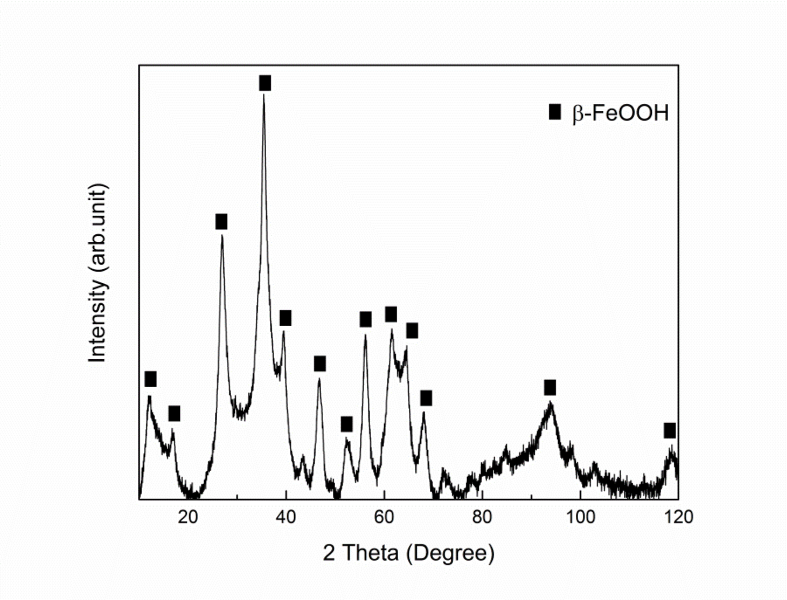

Figure 3.7 XRD pattern of Akaganeite FeOOH, leach residue obtained after acid leaching step.

Similar to Recai et al.,[15] around 10±4% of boron was extracted into the leachate and most of the boron was present in the residue. Iron hydroxides have the capacity to act as metal scavengers and boron is often removed from the leachate by coagulation or electrocoagulation with ferric hydroxide.[35-36] Nevertheless, further analysis is necessary to completely understand the boron chemistry in this recycling process. Though a relatively pure magnet waste is investigated here, this pretreatment process can also be used for complex end-of-life magnet waste. The other minor elements such as nickel, copper can be co-extracted into the leachate while aluminium can be precipitated along with iron. [37]

Table 3.4 Composition of leachates after acid leaching step in mg/L

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

3.3.5 Oxalic acid precipitation of REEs

Oxalic acid is traditionally used for stripping REEs from the solution [38], by

$$2\,RECl_3 + 3H_2C_2O_4 \rightarrow RE_2(C_2O_4)_3 + 6HCl \qquad (3.14)$$

When comparted with cobalt oxalates (Ksp = 6 x 10^{-8})[39], neodymium oxalate is highly insoluble (Ksp = 1.3 x 10^{-31}) [40] and this difference can be used to selectively precipitate REEs over cobalt.[9, 11] A small excess of oxalic acid ($nC_2O_4^{2-}$ / nREE^{3+} = 2) was sufficient to precipitate 99% of REEs from the solution as rare-earth oxalates while less than 0.5% of cobalt co-precipitated.. Then the rare-earth oxalates were calcined at 950 ^{o}C (Figure 3.8) to obtain rare-earth oxides of remarkable purity (99.2±0.2%). Importantly, the acid used in the selective acid leaching step is regenerated forming the basis for a closed loop process. The overall process flowsheet is illustrated in Figure 3.9.

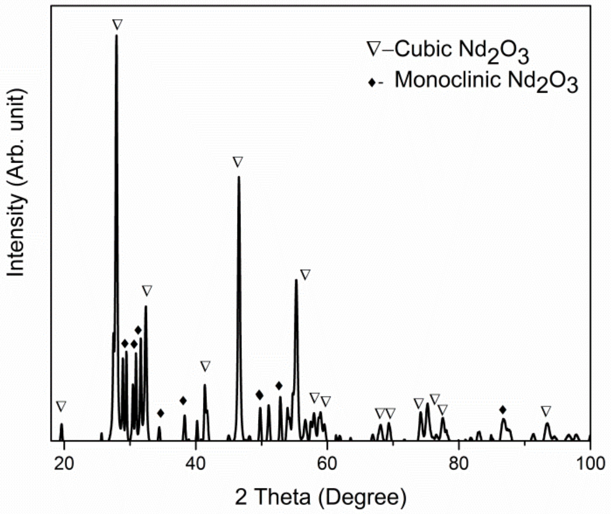

Figure 3.8: XRD pattern of the rare-earth oxides obtained after the calcination step.

3.4 Conclusion

We developed an environmentally friendly route to selectively extract REEs from NdFeB magnet at room temperature. The magnet waste was first subjected to an electrolysis pretreatmet step where the solid sintered magnet was made as an anode together with Ti/Pt inert anode in which all the components of the magnet waste were converted into a mixed hydroxide precipitate. The ratio of current supplied between magnet anode and inert anode was optimized to ensure efficient oxidation of Fe(II) to $Fe(OH)_3$. Ammonium chloride was used as the electrolyte and increase in ammonium chloride concentration increased the anodic dissolution efficiency and decreased the energy consumption. REEs and cobalt were selectively leached with HCl from the mixed hydroxides precipitate leaving iron out in the solid 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. The calcined rare-earth oxalates produced rare-earth oxides of remarkable purity (99.2%). The whole process consumes only current, water and oxalic acid and happens entirely at room temperature. The electrolysis pretreatment step has enhanced kinetics and can be easily scaled-up with an acceptable energy consumption of 3 kWh/kg of NdFeB magnet waste.

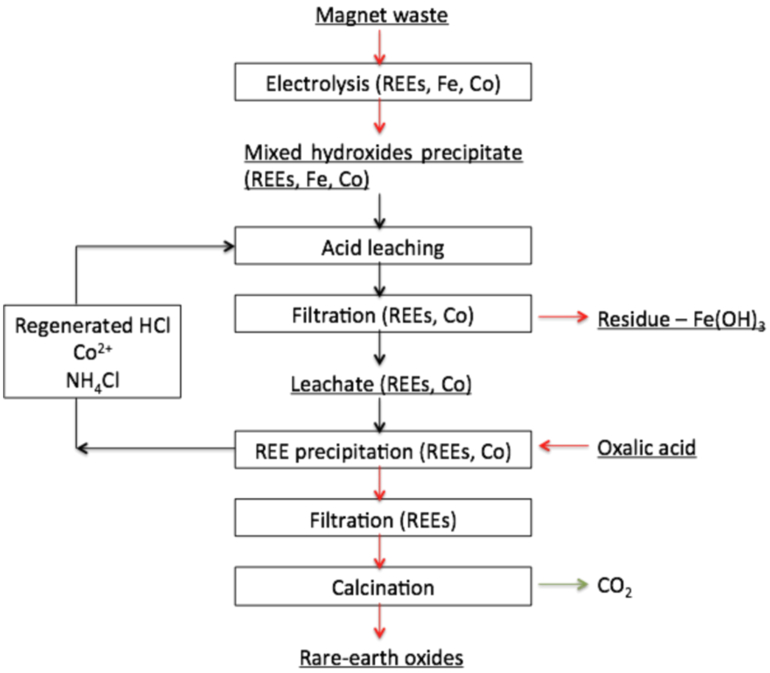

Figure 3.9 Process flowsheet for the proposed recycling scheme. Red arrows: solid stream, black arrows: liquid stream, green arrow: gaseous stream.

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Chapter 4 Selective electrochemical extraction of REEs inside a two chambered membrane reactor from NdFeB magnet waste at room temperature

ABSTRACT-NdFeB magnet waste is one of the important secondary resources from which rare earth elements can be recovered. An electrochemical route was developed to selectively extract REEs from the magnet waste at room temperature. First, the magnet waste was partially leached with HCl. The partial leachate along with undissolved magnet particles were taken in the anolyte side of a two compartment reactor separated by an anion exchange membrane whereas the catholyte consisted of sodium chloride solution. The Fe(II) present in the leachate was oxidatively precipitated as $Fe(OH)_3$ while more than 95% of REEs were extracted into the solution. Subsequently, oxalic acid was used to selectively precipitate REEs as rare-earth oxalates. Hydrochloric acid liberated during the oxalic acid precipitation process can be directly reused in the partial leaching step. Sodium chloride was the only chemical consumed during the electrolysis and the effect of anolyte and catholyte concentration of NaCl on the extraction of metals were investigated. From magnet waste to rare-earth oxides, the developed recycling process is environmentally friendly and consumes only current, NaCl and oxalic acid.

This chapter is based on the published scientific paper**-** Prakash Venkatesan, Tom Vander Hoogerstraete, Tom Hennebel, Koen Binnemans, Jilt Sietsma, Yongxiang Yang, Green Chemistry, 2018, 20, 1065-1073.

4.1 Introduction

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

NdFeB magnets have superior magnetic properties, consisting of 20-30 wt% of REEs and are an important secondary resource containing REEs.[9] In 2014, 22% of rare-earth oxides produced globally were consumed for the production of NdFeB magnets making them one of the largest applications among all REEs.[10] Several reviews have summarized the recycling processes that have been developed thus far for recycling NdFeB magnets.[11-13] Hydrometallurgical recycling processes designed for NdFeB magnets are promising as they operate at room temperature, do not require complex setups and can be applied irrespective of the composition of the magnets.[14-16] In hydrometallurgical processes, NdFeB magnets are completely leached with acid. These processes are unselective and iron, which is the major component of NdFeB magnets (60-70%), is co-extracted into the solution along with REEs. The leaching step is followed by precipitation step where REEs are selectively precipitated as rare-earth double sulfates or rare-earth fluorides. Complete acid dissolution of the industrial magnet waste requires around 15 moles of HCl per mole of REEs (nHCl/nREE) whereas complex end-of-life magnet waste requires 40 moles of HCl per mole of REEs.[17] The whole process has many steps, consumes excess acid, alkali and other precipitation agents, that cannot be recycled.[11] The lack of selectivity between REEs and iron in the hydrometallurgical routes is due to the fact that iron leaches into the solution as Fe(II) which is a stable species until a pH of 6 and cannot be selectively precipitated. Recently, a chemical process[15] and an electrochemical route[18] were proposed to oxidize Fe(II) to Fe(III) at room temperature. After oxidation, Fe(III) was selectively and completely precipitated from the solution at a pH around 3 leaving only REEs in the solution. However, both the processes required complete and unselective dissolution of NdFeB magnets as the first step after which oxidation of Fe(II) to Fe(III) was performed.

In contrast, in a pyrometallurgical process, REEs can be selectively leached from NdFeB magnet waste after a roasting pretreatment step.[19-20] Vander Hoogerstraete et al.[21] designed a closed loop process in which magnets were oxidatively roasted to convert iron into Fe_2O_3 and REEs into rare-earth oxides. The roasted powder was then leached in near stoichiometric equivalent of acid for REEs (nHCl/nREE = 3.5) in which only REEs were selectively leached leaving out the iron as $Fe(OH)_3$. Subsequently, the acid used in the leaching step was recovered by precipitating REEs with oxalic acid. There was no net consumption of HCl in the whole process flow sheet. However, the roasting pretreatment step operates at 900 °C and is energy-intensive. Moreover, the selective leaching step was sluggish and required 5 days to completely extract the REEs even at 100 °C.

In this paper, we describe an electrochemical process to selectively recover REEs from NdFeB magnet waste. The proposed process happens at room temperature, with enhanced kinetics and with no net consumption of

HCl. The magnet waste was treated in a simple two chamber membrane reactor separated by an anion exchange membrane. We investigated the effect of concentration of sodium chloride in both the anolyte and catholyte on the metal extraction and net energy consumption. The end product of mixed rare-earth oxides showed excellent purity (>99%) and can be directly used for metal production.

4.2 Experimental

4.2.1 Materials and methods

All chemicals are of analytical grade and were used without further purification. Sodium chloride (≥99%), ammonium acetate, ammonia solution (25% NH_3 in water), hydrochloric acid (37%), oxalic acid dihydrate (≥99%), 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). The pH was measured by an Inolab 7310 pH meter (WTW, The Netherlands) with a Sentix 81 tip. A Universal 320R centrifuge (Hettich, The Netherlands) was used to separate the leachate from the precipitate. The magnet waste used in this study was supplied by Magneti (Slovenia). These bulk magnets are uncoated and failed the quality control step before getting magnetized. Thus, no demagnetization step was required. Ball-milling was performed at Umicore (Olen, Belgium) using a Retsch RS100 ball-mill for two hours to mill the bulk sintered magnets. Immediately after milling, the powder samples were directly divided into 3 gram subsamples and stored in a plastic vial to offset the effect of oxidation on the extraction efficiency calculations.[19]

4.2.2 Electrochemical reactor

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

4.2.3 Analytical methods

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

$$E\ (\%) = \frac{\mathrm{M_L\ x\ V_L}}{\mathrm{X_M\ X\ M_T}}\ \mathrm{X}\ 100 \tag{4.1}$$

where E is the percentage of extraction of metal M (%), $\mathrm{M_L}$ is amount of metal M present in the leachate (mg/l), $\mathrm{V_L}$is the volume of the leachate in liters, $\mathrm{X_M}$ is the fraction of metal M in the magnet waste and $\mathrm{M_T}$is the total amount of magnet waste used (mg).

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

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

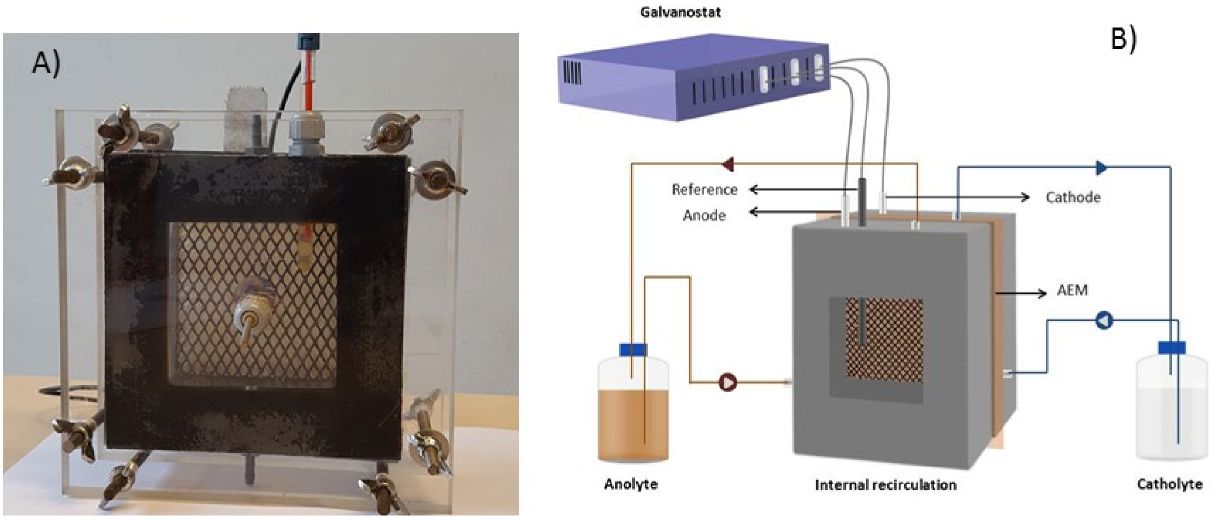

Figure 4.1 A) Photo and B) schematic illustration of the membrane electrochemical reactor

4.3 Results and Discussion

4.3.1 Partial leaching of NdFeB magnets with HCl

The chemical composition of the NdFeB magnet waste is given in Table 4.1. The industrial magnet waste has high dysprosium and low praseodymium content and is typically used for hybrid electric vehicles and electric motors. Neodymium, dysprosium, praseodymium, iron and cobalt form more than 98 wt% of the magnet waste, and are thus, the focus of this study. Several inorganic and even organic acids have been investigated for leaching NdFeB magnets.[14, 16, 23]The solubility limits of rare-earth sulfates are low and thus, chlorides and nitrates are the preferred anions for downstream solvent extraction process.[19] However, the oxidizing nature of nitrate anions was reported to interfere with the leaching process of NdFeB magnet waste with release of NO_x gases.[21] Hence, HCl and a chloride system were chosen for this study.

Table 4.1 Elemental composition of NdFeB magnets in wt%

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

A sample of 3 grams of magnet waste was first leached with HCl at a constant molar ratio of 3.5 between HCl to REEs (nHCl/nREE). The acid leaching was unselective and around 23.0±1.2 % of total magnet waste was extracted into the solution (Table 4.2). The partial leaching was complete within 60 minutes and was accompanied by a pH rise to 6.5±0.5. Speciation measurements of the obtained leachate with a UV-Vis spectrophotometer showed that ≥ 98.7% of iron leached was in the form of Fe(II).

Table 4.2 Percentage of extraction of different metals after partial leach of magnet waste with (nHCl/nREE = 3.5)

Elements	Fe	Nd	Dy	Co	Pr	Total magnet waste
E (%)	23.2	28.9	21.18	19.13	36.4	23.1

The dissolution reactions of the important elements are

$$2\,\mathrm{RE} + 6\,\mathrm{HCl} \leftrightarrow 2\mathrm{RECl_3} + 3\mathrm{H_2} \tag{4.2}$$

$$\mathrm{Fe} + 2\,\mathrm{HCl} \leftrightarrow \mathrm{FeCl_2} + \mathrm{H_2} \tag{4.3}$$

$$\mathrm{Co} + 2\,\mathrm{HCl} \leftrightarrow \mathrm{CoCl_2} + \mathrm{H_2} \tag{4.4}$$

Iron is the major component of the magnet waste and separation of REEs from iron forms the major part of NdFeB recycling. It is important to determine the speciation of iron in the leachate because first of all, Fe(II) remains in the solution as soluble species until a pH of 6.[20] Selective precipitation of the REEs by addition of a neutralizing agent is not possible as both REEs and Fe(II) can undergo hydrolysis and co-precipitate. Secondly, addition of precipitating agents like oxalic acid is also problematic as iron(II) oxalate is also highly insoluble.[18, 24]

Table 4.3 Amount of iron extracted and percentage of Fe oxidized under different experimental conditions.

Current density (Am^{-2})	Anolyte NaCl concentration (M)	Catholyte NaCl concentration (M)	Fe extracted (%)	Fe Oxidized (%)
40	0.2	0.6	27.1 ± 2.2	89.2 ± 1.6
50	0.2	0.6	39.2 ± 3.6	95.6 ± 0.7
75	0.2	0.6	52.3 ± 3.4	99.9 ± 0.3
125	0.2	0.6	54.1± 3.5	99.9 ± 0.3
125	-	0.6	56.2 ± 2.9	2.3 ± 0.6
125	0.2	0.05	0.1 ± 0.1	-
125	3.5	0.05	0	-
125	4.5	0.05	0	-

In contrast to Fe(II), Fe(III) can undergo hydrolysis at a pH of about 2 whereas REEs are stable until a pH of 6. To study the oxidation of Fe(II) under ambient conditions, a control experiment of leaching was performed where air was purged into the leachate for 24 hours. The leachate turned green over time with slight precipitation of $Fe(OH)_2$ and air oxidation did not result in oxidation of Fe(II) or further extraction of metals. This is due to the fact that oxidation of Fe(II) by air is an extremely sluggish reaction with its kinetics heavily dependent on the pH.[25] Thus, electrochemical oxidation of Fe(II) to Fe(III) was formulated as the basis for removal of iron from the leachate.

4.3.2 Electrochemical extraction of REEs

Membrane electrolysis has been successfully employed in various fields including metal recovery.[26-28] For all the electrolysis experiments, 3 grams of magnet waste was first partially leached with HCl at (nHCl/nREE = 3.5). In this study, a membrane electrochemical reactor with two chambers separated by an anion exchange membrane was used to treat the magnet waste (Figure 4.1). The partially leached solution (Table 4.2) was passed into the anolyte compartment while the undissolved magnet particles stayed in the Scott bottle along with the magnetic stirrer. The catholyte consisted of sodium chloride solution. Both the catholyte and anolyte were internally recirculated. The following reactions are possible at the anode:

$$\mathrm{Fe^{2+} + 3H_2O \rightleftharpoons Fe(OH)_3 + 3H^+ + 3e^-}\ (E^O = 0.931\ \mathrm{V}) \tag{4.5}$$

$$\mathrm{2\,H_2O \rightleftharpoons 4H^+ + 4e^- + O_2}\ (E^O\ =\ 1.23\ \mathrm{V}) \tag{4.6}$$

Cathodic reaction is reduction of water to produce hydroxyl ions, by

$$\mathrm{2\,H_2O + 2e^-\ \rightleftharpoons 2OH^- + H_2} \tag{4.7}$$

The anion exchange membrane not only prevented migration of Fe(III) to the catholyte where it can be reduced to Fe(II) butalso ensured capture of acid released from reaction (4.5) to be utilized for leaching undissolved magnet particles. In all the electrolysis experiments, the metals were leached exclusively inside the anolyte loop. ICP-OES analysis of catholyte after the electrolysis showed no presence of metals and thus, it can be concluded that the anion exchange membrane served as an effective physical barrier.

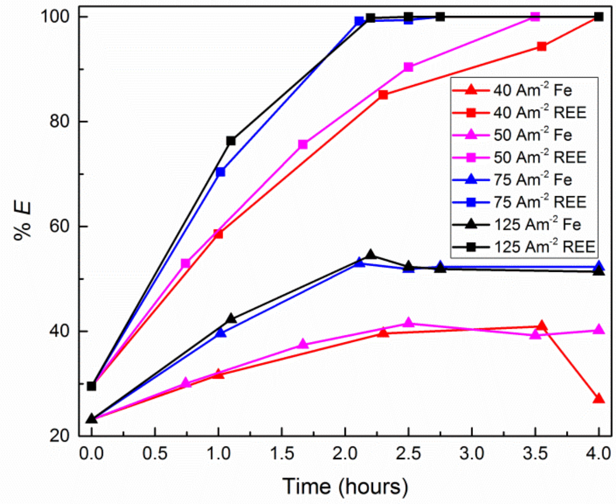

Figure 4.2 Influence of current density on percentage extraction of REEs and iron with 0.2 M NaCl in the anolyte and 35 g/L NaCl in the catholyte a) 40 A Am^{-2} b) 50 Am^{-2} c) 75 Am-2 d) 125 Am^{-2}. Relative standard deviation < 4.5%.

4.3.3 Influence of current density over metal extraction

To investigate the kinetics of magnet leaching under different current densities, an artificial brine solution (0.6 M, 35 g/L NaCl). was used as a catholyte and 0.2 M NaCl was added to the anolyte as a supporting electrolyte. The kinetics of REEs leaching into the solution increased with increase in current density (Figure 4.2). At current densities above 50 Am^{-2}, more than 97% REEs and cobalt were extracted into the solution within three hours. Around 50% of iron was removed from the leachate as $Fe(OH)_3$ due to electrochemical oxidation of Fe(II). In acidic pH, the kinetics of oxidation of Fe(II) by dissolved oxygen is very sluggish[25] and direct anodic oxidation of Fe(II) was found to be the predominant mechanism.[29] However, ≥30% of iron was also co-extracted into the leachate. This is due to formation of acid by migration of chloride ions to anolyte.

$$\mathrm{z}Cl^{-}_{Catholyte} \rightarrow \mathrm{z}Cl^{-}_{Anolyte} \tag{4.8}$$

Chloride anions migrated from catholyte to the anolyte through the anion exchange membrane and reacted with protons produced from water electrolysis (eqn (4.6)) to form HCl thereby leaching metals unselectively.[30]Loss of around 3.5±1 wt % of chloride ionsfrom catholyte was measured by ion chromatography. After complete treatment of the waste, water electrolysis and subsequent acid formation happens at the anolyte which was also observed as a drop in pH.

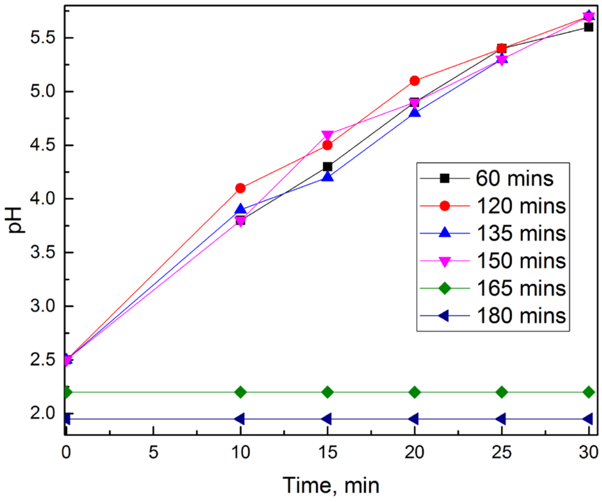

Figure 4.3 Evolution of pH of the anolyte in time after electrolysis reactor is switched off at various intermittent time intervals with 0.2 M NaCl in anolyte, 0.6 M NaCl in catholyte and at 50 Am^{-2}.

The pH of the anolyte served as an important parameter for indicating the end point of the electrolysis. During the electrolysis, a constant pH of 2.5±0.2 was observed. This constant pH reflects the dynamic equilibrium existing between two competing reactions in the anolyte, chemical dissolution of the magnet (eqn (4.2)-(4.4)) and Fe(II) oxidation (eqn (4.5)). The cell was switched off at intermittent time intervals and the pH of the anolyte was subsequently monitored over time when no energy was supplied. Two distinct profiles of the anolyte pH were observed. In a first profile, at intermittent time intervals 60, 120, 135 and 150 minutes, the pH gradually increased to 6±0.5 (Figure 4.3). This increase of pH when the cell was turned off indicates that there were still magnet particles that remained undissolved and reaction was still incomplete. In the second profile, at intermittent time intervals 165, 180 minutes the pH of the anolyte remained stable at 2±0.2 and continuation of the electrolysis resulted in a further decrease of pH. This stable profile can be attributed to complete treatment of all magnet waste and further acid formation resulting from migration of chloride ions from catholyte.

Table 4.4 Composition of leachates after electrolysis at 125 Am^{-2} and neutralization with ammonia.

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

Despite co-extraction of iron, ≥99% of the iron that was extracted into the leachate existed in Fe(III) state (Table 4.3). It has to be noted that this Fe(III) from these leachates can easily be removed by neutralization and precipitation to obtain a REE-rich solution.[15] Thus, ammonia was added dropwise to increase the pH of the leachate to 4.5±0.2. Table 4.4 presents the composition of leachate after electrolysis and after neutralization. It can be seen that the electrolysis step removes around 50 % of iron from the original magnet. The neutralization step resulted in precipitation and complete removal of iron in the form of iron(III) hydroxide precipitate. The obtained iron(III) hydroxide precipitate was filtered and the XRD of the precipitate showed that it consisted of β-FeO(OH), akagenite.

4.3.4 Effect of catholyte NaCl concentration

To understand the migration of chloride ions from the catholyte, the effect of catholyte NaCl concentration on the extraction of different metals was investigated first at a constant current density of 50 Am^{-2} (Fig 4.4.). No NaCl was added to the anolyte. Low concentration of NaCl (0.05 and 0.01 M) in the catholyte resulted in incomplete leaching of the metals. A saturation point for extraction was reached at 2-3 hours and further electrolysis resulted even in a slight decrease of metal concentration signifying precipitation of metals due to migration of hydroxide ions to the anolyte.

$$zOH^-_{Catholyte} \rightarrow zOH^-_{Anolyte} \tag{4.9}$$

However, complete extraction of REEs was observed at a NaCl concentration similar to that of brine solution and higher (0.6 M and 1 M NaCl). Nevertheless, more than 40% of iron was still co-extracted into the leachate. However, in contrast to the previous experiments where 0.2 M NaCl was present in the anolyte, almost all of the iron extracted into the leachate was Fe(II) in the absence of NaCl in the anolyte (Table 4.2). This shows that the presence of sodium chloride additive salt in the anolyte plays a role in Fe(II) oxidation.

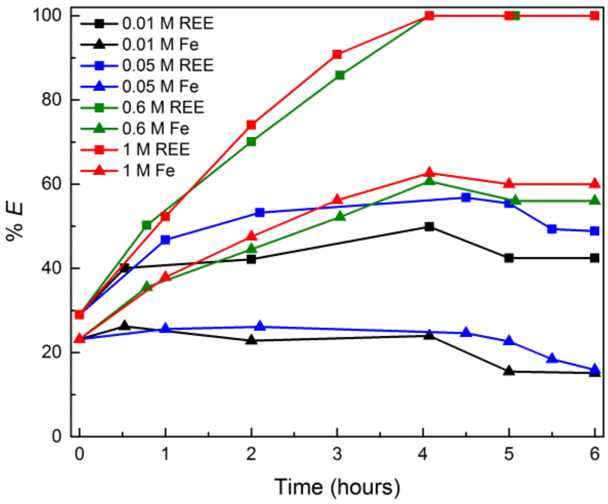

Figure 4.4 Percentage extraction of REE and iron over different concentrations of sodium chloride in catholyte at constant current density of 50 Am^{-2}, after initial leaching at (nHCl/nREE = 3.5). Relative standard deviation < 5.9%

4.3.5 Influence of anolyte NaCl concentration

The role of NaCl concentration in anolyte on the speciation and extraction was investigated further at a constant current density of 125 Am^{-2}. The catholyte concentration of NaCl was kept constant at 0.05 M to minimize the influx of chloride ions into the anolyte. Similar to the previous set of experiments, in the absence of NaCl in the anolyte, the leach was incomplete and unselective with co-extraction of iron. However, with the addition of NaCl in the anolyte, around 94±2 % REEs and cobalt were selectively extracted into the leachate with almost complete removal of iron (Figure 4.5). This selective extraction of REEs and cobalt can be attributed to two different factors. First, by reducing the NaCl amount in the catholyte (0.05 M), the excess acid formation by migration of chloride ions was prevented.

Secondly and most importantly, chlorine gas was generated from the oxidation of chloride ions at the anode. Subsequently, Fe(II) is oxidized also by reaction with chlorine. It has to be noted that even in the experiments where no NaCl was presented in the anolyte, more than 50% of iron present in the magnet was removed as $Fe(OH)_3$. Thus, Fe(II) oxidation at the anolyte happens directly at the anode surface as well as by electrochlorination. Generation of chlorine gas by *in-situ* electrochlorination has been used in water disinfection as a safe alternative to transporting chlorine gas to the sites of water treatment.[31-32]

$$2Cl^- \rightleftharpoons Cl_2 + 2e^- \tag{4.10}$$

$$Cl_2 + 2Fe^{2+} \rightleftharpoons 2Fe^{3+} + 2\,Cl^- \tag{4.11}$$

Chlorine gas is also used in organic industries to oxidize Fe(II) to Fe(III).[33]Electrogenerated chlorine was reported to play a dual role of oxidizing Fe(II) as well as leaching metals from the waste.[34-35] High concentrations of chloride ions (3.5 M and 4 M) were investigated here mainly because they can be used as salting agents for environmentally friendly downstream solvent extraction processes to separate different REEs from each other.[21] The whole extraction process was complete within 3 hours. This is marked improvement over other selective leaching processes which required 5-7 days for complete extraction of REEs.[21, 36] Prolonging the reaction time further decreased the extraction of REEs due to possible precipitation of REEs as hydroxides due to migration of hydroxide ions from the catholyte (eqn. 4.9). On average, the leachate contained 3600 mg/L of REEs and 310 mg/L of cobalt. The concentration of REEs can be remarkably increased by treating a large amount of magnet waste in a single batch or by reusing the leachate obtained at the end of the electrolysis over and over again in the subsequent electrolysis runs.

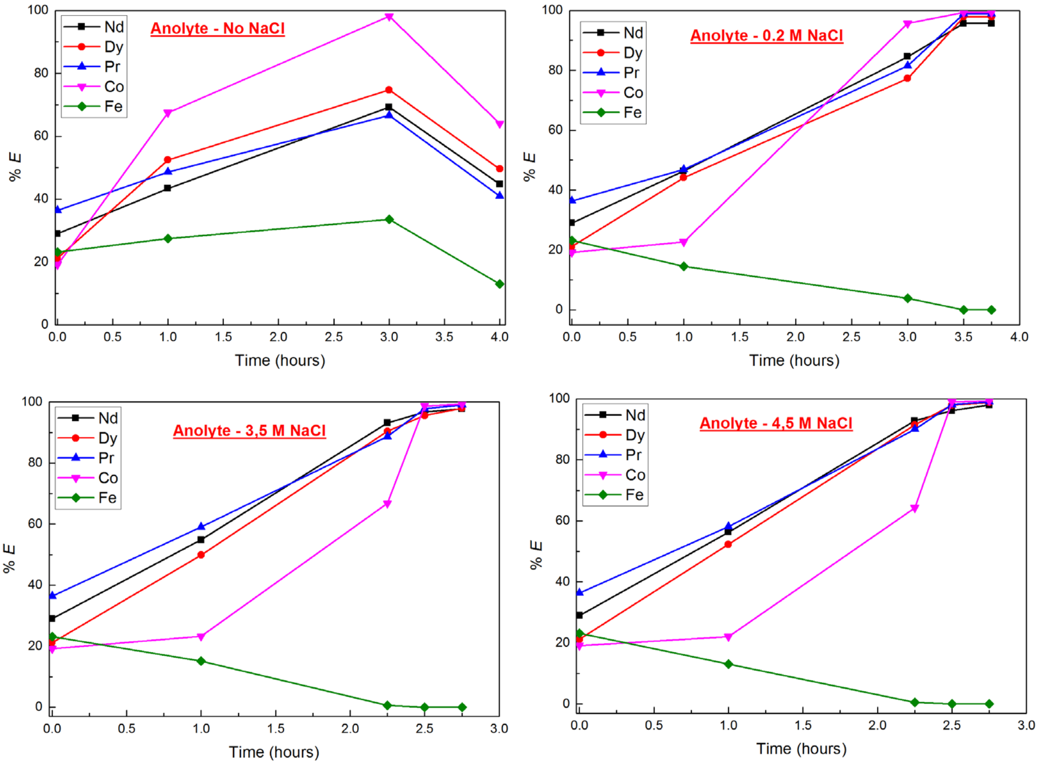

Figure 4.5 Percentage of extraction of metals (Nd, Dy ,Pr, Fe and Co) over different concentrations of NaCl in the anolyte at constant current density of 125 Am^{-2} . Relative standard deviation < 4.8%

4.3.6 Selective oxalate precipitation of REEs

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

$$2\ RECl_3 + 3H_2C_2O_4 \rightarrow RE_2(C_2O_4)_3 + 6HCl \qquad (4.12)$$

Rare-earth oxalates are highly insoluble ($K_{sp} = 1.3 \times 10^{-31}$ for neodymium oxalate)[38] in comparison to cobalt(II) oxalate ($K_{sp} = 6.3 \times 10^{-8}$)[39] and thus oxalic acid was added to the leachate to selectively precipitate the REEs. As in Figure 4.6, at the ratio of moles of oxalic acid to REEs of 2:1, almost all REEs were precipitated while only less than 1% of cobalt was precipitated. The obtained rare-earth oxalates were calcined further at 950 °C to obtain rare-earth oxides. The XRD pattern of the obtained rare-earth oxides showed the pattern of two different phases of Nd_2O_3 (Figure 4.7). The obtained oxides were dissolved in HCl and analysed with ICP-OES. The oxide was found to be quite pure (99.5 % of REEs) with only minor impurities from cobalt and aluminium. The remnant leachate was rich in cobalt. Recently we demonstrated that the remnant leachate can be directly used, after possible up concentration step, in an electrowinning process to recover the valuable cobalt metal.[18]

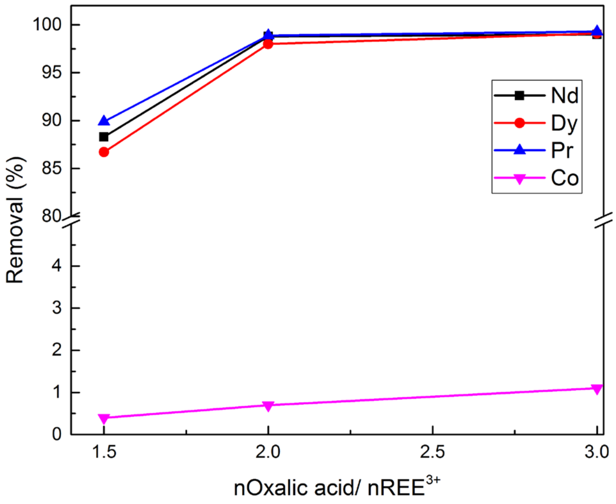

Figure 4.6 Removal of REEs as rare-earth oxalates by addition of oxalic acid.

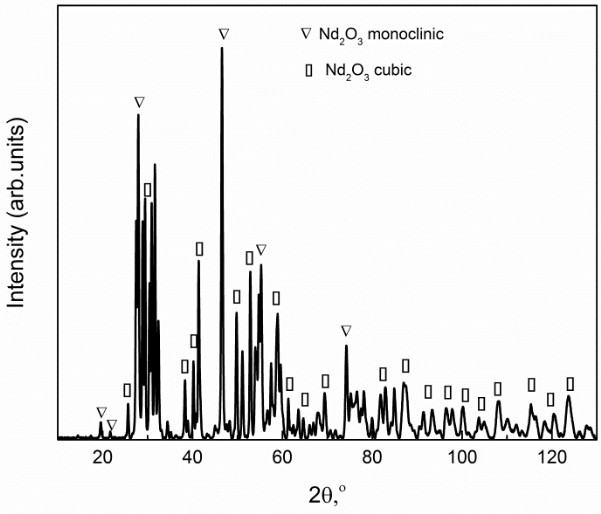

Figure 4.7 XRD pattern of the obtained rare-earth oxide**.**

4.3.7 Overall process and energy consumption

The overall recycling process for NdFeB magnet waste contains five distinctive steps (Figure. 4.8). First, the NdFeB magnet was partially leached with HCl at a ratio of (n HCl/n REE = 3.5) with 3.5 M NaCl as an additive salt. Then, the leachate was fed into the anolyte compartment of the two chambered electrochemical reactor separated by an AEM while the unreacted magnet powder stuck to the magnetic stirrer in the anolyte Scott bottle. The catholyte contained a NaCl solution of low concentration (0.05 M). Upon electrolysis, iron was oxidatively precipitated as $Fe(OH)_3$ while ≥95% REEs and cobalt were extracted into the leachate. The pH played an important role in indicating the end point of the electrolysis process. During the electrolysis, the pH was constant at 2.5±0.2 and was a result of competing reactions of magnet dissolution by acid and oxidative precipitation of Fe(II).

The electrolysis process was switched off intermittently and as long as unreacted magnet waste remained, the pH raised to 6.5±0.3. Complete treatment of NdFeB magnet waste resulted in decrease of pH to a value below 2. Thus the pH served as an effective indicator for the end point of the reaction. At the end of electrolysis step, the leach residue was removed by filtration. Subsequently, the leachate was treated with oxalic acid to further precipitate REEs as rare-earth oxalates. The acid that was consumed in the partial leaching step was regenerated in this precipitation step. The rare-earth oxalates were further calcined at 950 ^{o}C to produce rare-earth oxides. The acid along with cobalt ions and a highly concentrated NaCl solution can be fed again into the anolyte resulting in a closed-loop process without net consumption of HCl. Cobalt can be separated using a solvent extraction step[40] or it can be recovered as cobalt metal through an electrowinning step.[41] For the 3 grams of magnet waste treated in the process, 1.2±0.1 gram of rare-earth oxides was obtained as the main product. The iron hydroxide residue (3.6±0.2 gram) produced was found to be in the form of β- FeO(OH) akaganeite and can be potentially used in pigment industries, ion exchangers and gas sensors. Residual cobalt (0.09 gram) present in the solution can be used in the subsequent electrolysis step to increase the cobalt concentration until it is suitable for direct electrowinning.

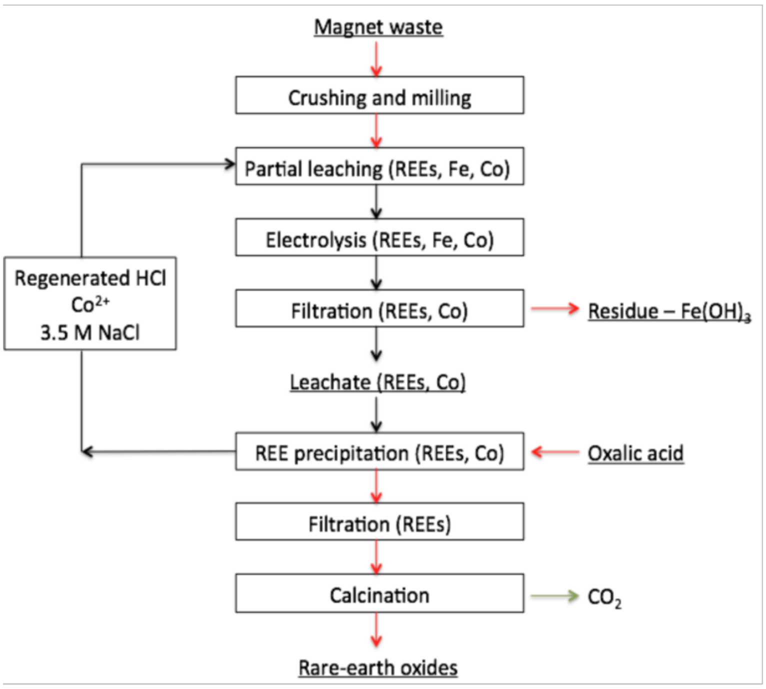

Figure 4.8 Flowchart of the recycling process. Red arrows: solid stream, black arrows: aqueous stream, green arrow: gaseous stream

The average cell voltage and energy consumption (kWh/kg) calculated per kilogram of magnet for different experimental conditions are tabulated in Table 4.5. Increase in concentration of NaCl in the catholyte decreases the energy consumption significantly. However, at high concentration of NaCl in the catholyte almost half of the iron present in the magnet waste was co-extracted into the leachate. The speciation of the extracted iron into the solution depended upon the presence of NaCl in the anolyte. Nevertheless, the best suited conditions for selective extraction of REEs with iron removal are 3.5 M of anolyte NaCl and 0.05 M of catholyte NaCl (condition G). Both conditions C and G can provide iron-free leachates rich in REEs and cobalt. However, condition C requires an additional neutralization step for iron removal. In terms of energy consumption, condition G requires almost 3.5 times more energy than condition C. At an energy cost of €0.12 per kilowatt hour, these results indicate that the magnet waste can be processed at an energy cost of €0.7/kg in a scaled up set-up. Assuming an average of 30% of REEs in magnet waste, the power cost of the developed electrochemical process to produce a kilo gram of rare-earth oxides would be less than three euros. In 2014, the price of Nd_2O_3 was €50 per kilogram.[10] Thus, despite additional capital and operational costs, the developed recycling process is still commercially attractive. Although the focus of this manuscript is on treatment of NdFeB magnet waste, the concept of *in-situ* electrochemical oxidative-precipitation of iron from waste feed can be extended and used in treatment of ferrous fraction of a generic WEEE stream(Waste Electrical and Electronic Equipments) which contains substantial amount of REEs.[42-44] The electrochemical oxidative-precipitation process not only removes iron from the leachate but also simultaneously regenerates the acid that can be used by other metals present in the feed to dissolve into the solution.

Table 4.5 Average cell voltage and energy consumption per kg of magnet waste under different conditions

Condition	Current density (Am^{-2})	Anolyte NaCl concentration (M)	Catholyte NaCl concentration (M)	Average Cell Voltage (V)	Energy consumption (kWh/kg)
A	40	0.2	0.6	2.79	0.95
B	50	0.2	0.6	2.91	1.24
C	75	0.2	0.6	3.1	1.65
D	125	0.2	0.6	3.31	2.2
E	125	-	0.6	3.89	4.15
F	125	0.2	0.05	6.45	6,02
G	125	3.5	0.05	6.24	5.82
H	125	4.5	0.05	6.1	5.7

4.4 Conclusions

An environmentally friendly electrochemical process was developed to recover REEs from NdFeB magnet waste at room temperature. REEs were selectively extracted from NdFeB magnet waste through partial leaching followed by membrane electrolysis. Fe(II) was oxidized in the anolyte to be precipitated as $Fe(OH)_3$. The acid liberated from Fe(II) oxidation was captured in the anolyte *in-situ* and leached the undissolved magnet waste further until ≥ 95% REEs were leached into solution and all iron was removed as ferric hydroxide precipitate. Concentration of sodium chloride in the anolyte and catholyte was shown to play an important role in the recovery process. The kinetics of metal extraction was shown to increase with increase in current density. Oxalic acid was used as a selective precipitating agent to separate REEs from cobalt. The whole process is environmentally friendly and consumes only sodium chloride, oxalic acid and energy of 5.8 kWh/kg of magnet waste.

4.5 References

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Chapter 5 An acid and CO_2 free process for recycling Rare Earth Elements from NdFeB magnet waste inside a three compartment electrochemical reactor

Abstract

Recycling is one of the important strategies to forge a sustainable supply chain for critical metals. This manuscript presents an efficient process to recover rare earth elements (REEs) from NdFeB magnet waste at room temperature. A three compartment electrochemical reactor was used where 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 were calcined to obtain rare-earth oxides. More than 95% REEs and cobalt were extracted into the solution and more than 85% of iron was removed as $Fe(OH)_3$ precipitate in the same step. Subsequently, the leachate was neutralized to remove more than 99% iron. This process combines leaching and precipitation in a single step and the reagents are generated *in-situ* in the electrochemical reactor. The leachate produced at the end rich in REEs can be fed again into the middle compartment to continue the process, thus forming a completely closed loop process. Overall, the process consumes no acid, but only electricity, ammonium sulfamate and is CO_2 free.

5.1 Introduction

Rare earth elements (REEs) are considered as critical metals due to substantial frailties in supply chain and an increasing demand from high-tech sector.[1-2] 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.[3-4] 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 in creating 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.[5-6] 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.[6-9] Direct recycling of NdFeB magnet waste to new NdFeB magnets using hydrogen gas is effective, however, the process is sensitive to the composition of the magnet waste.[7, 10-11] Alternatively, NdFeB magnets can be indirectly recycled by selectively recovering REEs as rare-earth oxides. NdFeB magnets consist of 20-30% of REEs, 60-70% of iron, 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.[12-16] However, wet-chemical routes are unselective between REEs and iron, consume excess acid and precipitating agents that cannot be recycled, and requires an additional step to discharge metal containing acid waste.

In contrast to wet chemical routes, high temperature pyrometallurigcal processes offer improved selectivity between REEs and iron.[17-19] In 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, HCl used in this selective leaching step can be recovered through selective precipitation of REEs as rare-earth oxalates, forming a closed-loop process. Nevertheless, pyrometallurgical processes have high operational temperatures, can release toxic gases that need to be captured with additional set-ups and are energy intensive.[17-18, 20]

Alternatively, closed-loop corrosion and electrochemical processes have been developed in which REEs were selectively extracted over iron at room temperature.[21-23] However, to recover REEs from the solution, oxalic acid was used to precipitate rare-earth ions as rare-earth oxalates.[24-26] Oxalic acid is an expensive chemical and the rare-earth oxalates produced from the precipitation step need to be calcined at around 800 ^{o}C which releases CO_2 gas and is energy intensive.[27]

In this chapter, we propose a room-temperature electrochemical process in which the REEs can be selectively extracted from NdFeB magnet waste without consuming HCl or oxalic acid. A rare-earth salt solution is taken in the middle compartment of a three compartment electrochemical reactor separated by an anion and a cation exchange membrane. The salt was electrochemically split into acid in the anolyte which simultaneously extracted REEs from the magnet waste. The rare-earth hydroxide in the catholyte was calcined to produce rare-earth oxides. After electrolysis and neutralization, an REE-rich salt solution is obtained from the anolyte which can be fed again into the middle compartment in the next run, thus formulating 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 electrolysis process combines leaching and precipitation in a single step. The whole flowsheet is acid free, does not emit CO_2 and consumes only electricity, water and a salt such as ammonium sulfamate.

5.2 Experimental

5.2.1 Materials

Sodium chloride (NaCl ≥99%), ammonium sulfamate ($(NH_3)_2SO_3$ ≥99%), ammonium acetate, hydrochloric acid (HCl 37%), ammonia solution (25% NH_3 in water), oxalic acid dihydrate (≥99%), ferrozine (monosodium salt hydrate of 3-(2-pyridyl)-5,6-diphenyl-1,2,4-trazine-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 two hours to mill the bulk sintered magnets. Immediately after milling, the powder samples were divided into 1 gram subsamples and stored in a plastic vial to offset the effect of oxidation on the extraction efficiency calculations.[17]

5.2.2 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 (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 is used as the cathode (Solana, Belgium) and a mixed metal oxide (35% TaO_2 & 65% IrO_2) coated titanium electrode was used as the anode (Magneto Special Anodes BV, Schiedam, The Netherlands). The anode and cathode had a projected electrode surface area of 64 cm^2 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 was obtained using Versastudio software. An Ag/AgCl (3M KCl) reference electrode was placed in the anode compartment. All three compartments were operated in batch mode at an internal recirculation rate of 50 ml min^{-1} and heated to a temperature of 30±2 ^oC with a water bath. The anolyte and catholyte consisted of 250 ml of 0.05 M ammonium sulfamate solution. The liquids were pumped from three different Scott bottles that were stirred constantly at 300 rpm with a magnetic stirrer.

5.2.3 Analytical methods

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

$$E\ (\%) = \frac{M_L \times V_L}{X_M \times M_T} \times 100 \qquad (5.1)$$

where E is the percentage of extraction of metal M (%), M_L is amount of metal M present in the leachate (mg/l), V_L is the volume of the leachate in liters, X_M is the fraction of metal M in the magnet waste and M_T is the total amount of magnet waste used (mg).

The oxidation state of Fe in the leachate was measured using the ferrozine colorimetric method.[28] The concentration of Fe(II) was measured at wavelength 562 nm using UV-Vis spectrophotometer (Hitachi, U-2900). ICP-OES was used to measure the total concentration of Fe. The concentration of Fe(III) was calculated as the difference in concentration between total iron and that of Fe(II). After the electrolysis step, the precipitate was removed from the leachate by centrifugation. The iron(III) hydroxide precipitate was washed thoroughly and was completely dissolved in HCl (37%) for analysis. 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 °C – 800 °C with steps of 50 °C.

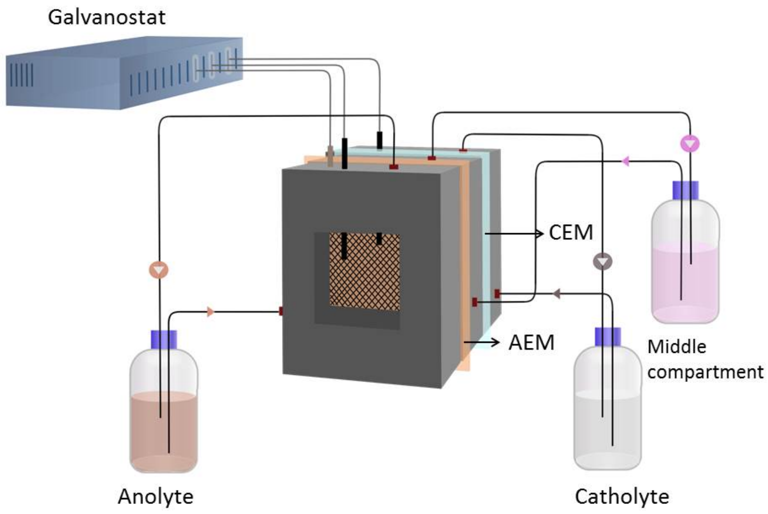

Figure 5.1: Schematic illustration of the three chamber membrane electrochemical reactor. AEM- Anion exchange membrane and CEM- Cation exchange membrane.

5.3 Results and discussion

5.3.1 Electrochemical leaching

The elemental composition of the magnet waste is given in Table 5.1. The magnet scrap investigated here has a high dysprosium content and is generally used in electric vehicles.

Table 5.1: Chemical composition of the NdFeB magnet waste

Element	Fe	Nd	Dy	Co	B	Pr	Ni	Gd	Si	Cu	Ni	Al	Total
Wt %	66.75	21.14	5.9	3.0	1.1	0.62	0.18	0.16	0.08	0.08	0.02	0.1	99.09

Various leaching studies have been carried out on NdFeB magnets using HCl, H_2SO_4, HNO_3 and organic acids such as acetic acid and ionic liquids.[14-15, 29-30] The solubility of rare-earth sulfates is low and the formation of highly insoluble rare-earth double sulfates is deemed problematic as they require further conversion steps.[12] Nitrates are chosen over chlorides in this study to eliminate the possibility of anodic chlorine evolution in the electrochemical reactor.[31]

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.[32-34] The three compartment electrochemical reactor used in this study is illustrated in Fig 5.1. The anolyte and the middle compartment are separated by an anion exchange membrane (AEM). The catholyte and the middle compartment are separated by a cation exchange membrane (CEM). Rare-earth nitrate salt that is only slightly excess to the stoichiometric amount of REEs and cobalt present in the magnet waste is fed into the middle compartment. During electrolysis, water is oxidized at the anolyte compartment by the reaction

$$2\,H_2O \rightleftharpoons 4H^+ + 4e^- + O_2 \tag{5.2}$$

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

$$2\,H_2O + 2e^- \rightleftharpoons 2OH^- + H_2 \tag{5.3}$$

The REEs can be precipitated as rare-earth hydroxides which can be further calcined to produce rare-earth oxides.

5.3.2 Effect of $Nd(NO_3)_3$ concentration

1 g of NdFeB magnet waste was taken in the Scott bottle that is in circulation with the anolyte compartment (Fig 5.1). 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, 1.2*n*, 4*n* and 6*n* where *n* is the mass of REEs and cobalt together in grams in the magnet waste. All experiments were done at 30 Am^{-2} except a control experiment where no electrolysis was performed. Figure 5.2A) shows the effect of 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.

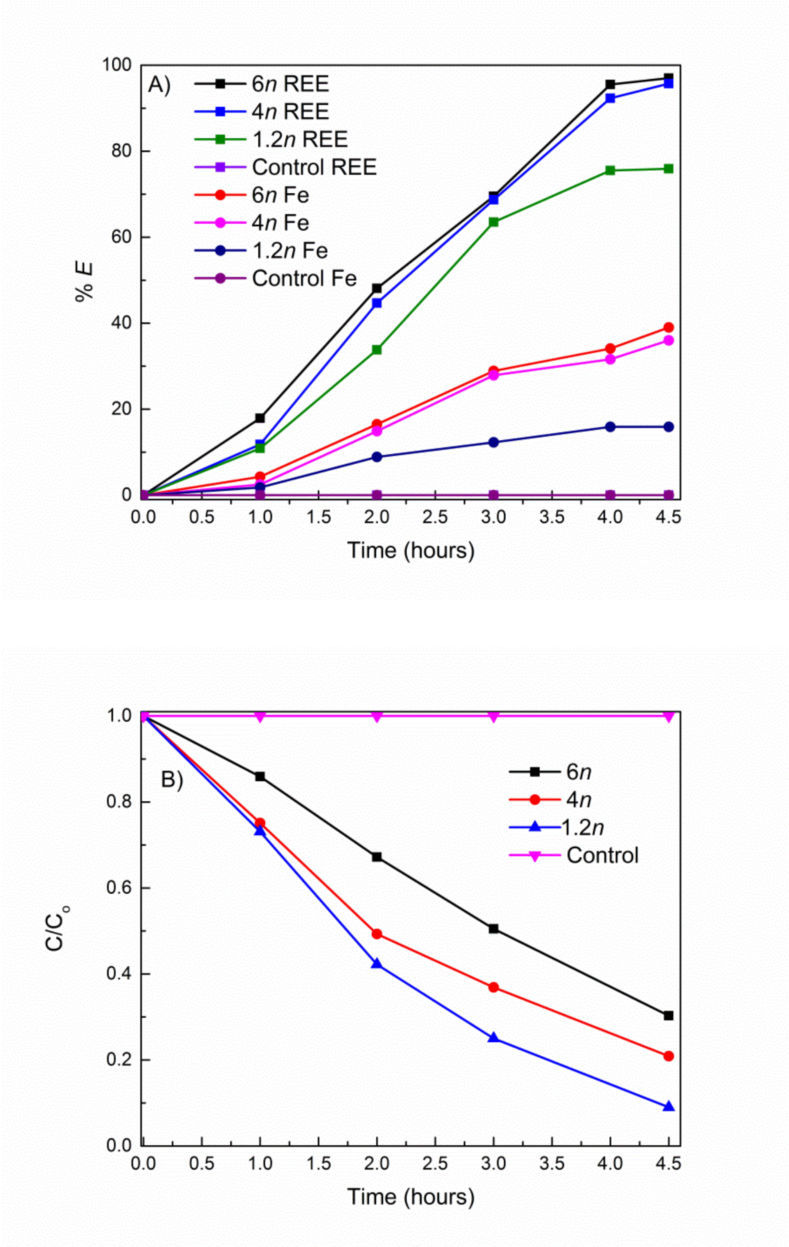

Figure 5.2 A) Influence of Nd concentration in the middle compartment over the extraction of metals from the magnet waste B) Removal of Nd from the middle compartment at different concentrations where C_o is the initial concentration of Nd and C is the concentration of Nd at time t. Relative standard deviation < 3.6%

It can be seen that at all different concentrations, REEs and Fe were dissolved from the magnet waste into the leachate due to nitric acid formation in the anolyte (Figure 5.2A). Nitric acid leached REEs, Fe and cobalt from the magnet waste into the solution by the reactions

$$2\ \mathrm{REE} + 6\ \mathrm{HNO_3} \rightleftharpoons 2\ \mathrm{REE(NO_3)_3} + 3\mathrm{H_2} \tag{5.4}$$

$$\mathrm{M} + 2\ \mathrm{HNO_3} \rightleftharpoons \mathrm{M(NO_3)_2} + \mathrm{H_2} \tag{5.5}$$

where M is either Fe or Co

Dissolution of metals in concentrated nitric acid can produce NOx gases, however, under dilute concentrations, eqns (5.4) and (5.5) are valid.[35] 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 decrease in concentration of Nd in the middle compartment, the conductivity of the solution dropped which was accompanied with sharp increase in voltage towards the end of the experiment. Secondly, there was back diffusion of OH^- co-ions from the catholyte compartment into the middle compartment which increased the pH and caused partial precipitation of REEs in the middle compartment.[36] With increase in concentration in the middle compartment to 4n and 6n, more than 95% of REEs from the waste were extracted into the leachate. Around 65±2% of iron was removed from the leachate in the same step by precipitation as $Fe(OH)_3$. This oxidative precipitation of iron is primarily due to anodic oxidation of Fe(II) in the anolyte compartment as

$$\mathrm{Fe^{2+}} + 3\mathrm{H_2O} \rightleftharpoons \mathrm{Fe(OH)_3} + 3\mathrm{H^+} + 3\mathrm{e^-}\ (E^O = 0.931\ \mathrm{V}) \tag{5.6}$$

It has to be noted that the oxidative-precipitation reaction also releases acid back which can be also used in-situ to leach magnets further. The pH of the anolyte was around 2 during the electrolysis due to the competing reactions of iron leaching from the waste (eqn 5.5) and Fe(II) oxidation (eqn 5.6).[21] The pH decreases to 1.6±0.2 at the end of the electrolysis. The end pH of the catholyte was marked by a sharp increase to 12.5±0.5 indicating the production of OH^- ions. Neodymium from the middle compartment is transported through the CEM and is mainly precipitated as $Nd(OH)_3$ in the catholyte. Similar to 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.[34]

Decrease of concentration of Nd from the middle compartment is presented in Figure 5.2B. At 1.2n, more than 92% of Nd was removal 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 given in table 5.2.

Even though around 35±3% of iron was present in the leachate at 4*n* and 6*n* runs, more than 83% of Fe(II) is oxidized. Thus, by increasing the pH above 3, more than 80% of iron from the magnet scrap could be removed as $Fe(OH)_3$ residue. The residual iron which is in Fe(II) form can be removed by oxidation in air at a pH around 6.5.[37] In order to effectuate a complete closed loop process, the amount of neodymium fed into the middle compartment in the form of $Nd(NO_3)_3$ should be stoichiometrically equivalent to that of REEs present in the magnet waste. Thus, the excess requirement of $Nd(NO_3)_3$ salt to leach the magnet waste here is problematic. In order to overcome this issue, the excess requirement of $Nd(NO_3)_3$ was compensated by adding an inexpensive additive salt ammonium sulfamate.

Table 5.2: Average cell voltage, energy consumption and percentage of Fe oxidized under different concentrations of Nd (C_{Nd}) in the middle compartment.

C_{Nd}	Fe extracted (%)	Fe Oxidized (%)	Average cell voltage (V)	Energy consumption (kWh/kg)
1.2*n*	15.9±0.4	88 ± 2	5.44	4.65
4*n*	36.0±1.2	83± 3	4.53	3.88
6*n*	39.3±0.6	81± 2	4.48	3.83

5.3.3 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 in the middle compartment, electrochemical splitting of ammoniacal salts can produce ammonia gas which can be captured by the conventional stripping process.[38] The effect of ammonium sulfamate concentration on metal extraction was investigated by keeping the concentration of Nd constant at 1.2*n* and at constant current density of 30 Am^{-2}.

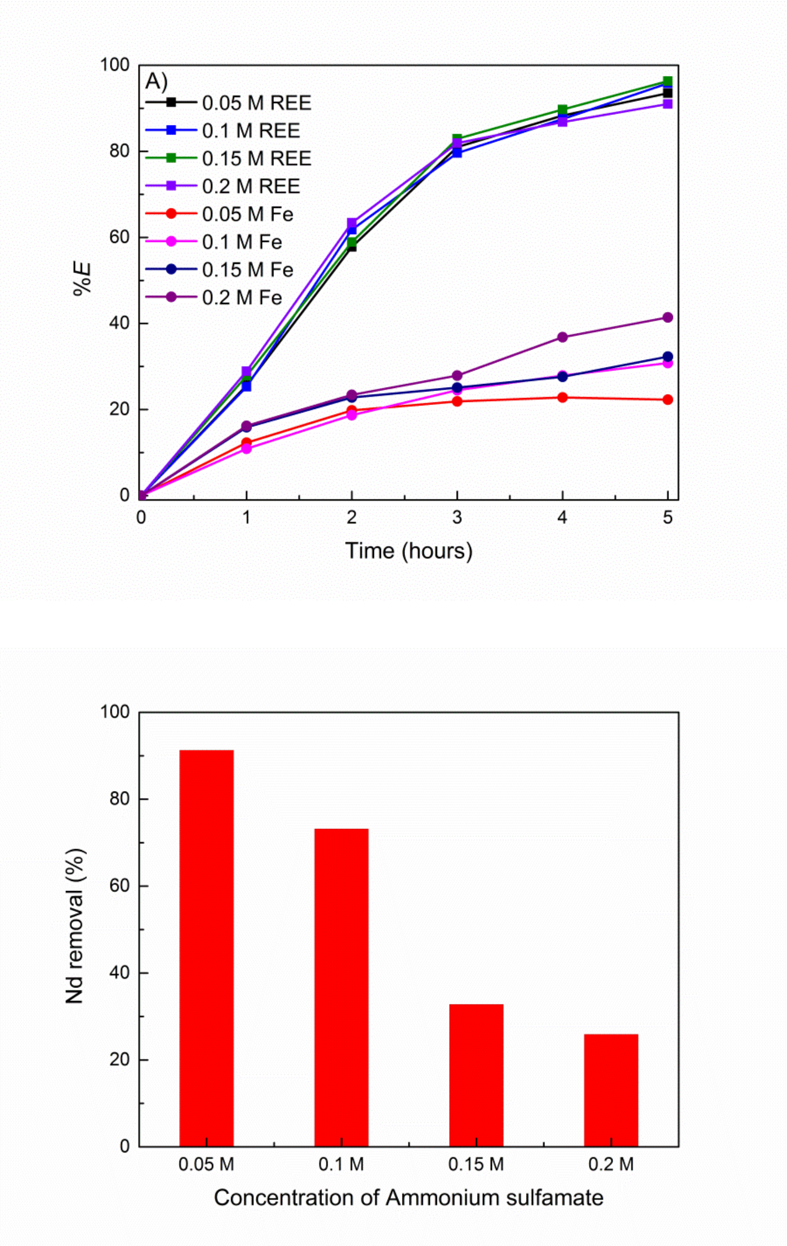

Figure 5.3 A) Percentage of extraction of REEs and Fe at different concentrations of ammonium sulfamate B) Percentage removal of Nd from the middle compartment at 30 Am^{-2} and at 1.2*n*. Relative standard deviation < 4.4%

It can be seen from Figure 5.3A that 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 5.3B) 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. Experiments performed with sodium nitrate (results not shown) in place of ammonium sulfamate yielded similar results as well. However, in contrast to the previous run with pure neodymium nitrate solutions, increase in ammonium sulfamate concentration lowered the oxidation of Fe(II). This can be explained by the oxidizing capacity of nitrate ions to convert Fe(II) to Fe(III). 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 5.3).

Table 5.3: Average cell voltage, energy consumption and percentage of Fe oxidized under different concentrations of ammonium sulfamate (C_{ams}) in the middle compartment at 30 Am^{-2} and 1.2*n*

Current density Am^{-2}	C_{ams} (M)	Fe extracted (%)	Fe Oxidized (%)	Average cell voltage (V)	Energy consumption (kWh/kg)
30	0.05	22.3±0.2	83±2	6.9	6.6
30	0.1	30.8±1.1	75±2	6.5	6.2
30	0.15	32.3±0.5	70±1	6.4	6.0
30	0.2	41.4±1.2	66±2	5.7	5.4
20	0.05	19.1±1.5	85±1	4.8	4.6
50	0.05	27.5±1.6	81±1	8.1	7.7

5.3.4 Effect of current density

One of the important advantages of electrochemical leaching over other hydrometallurgical processes is the ability to extract metals at enhanced kinetics at high current densities. Figure 5.4 shows the effect of different current density over extraction of REEs and Fe at 1.2*n* and 0.05 M ammonium sulfamate in the middle compartment.

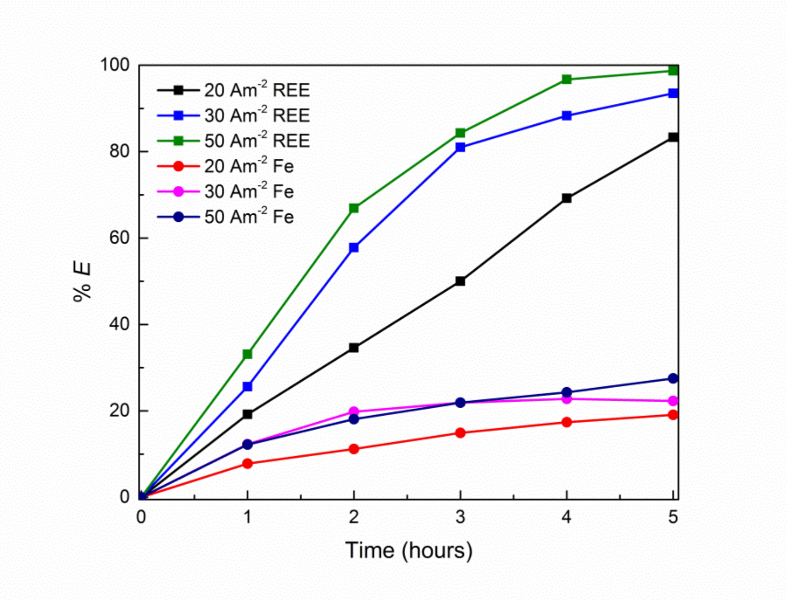

Figure 5.4: Effect of current density over extraction of REEs and Fe at 1.2*n* and 0.05 M ammonium sulfamate in the middle compartment.

At 20 Am^{-2}, the extraction of REEs is incomplete at five hours whereas with increase in current density, the rate of metal extraction increased. At 50 Am^{-2}, more than 97% of REEs are extracted into the solution with simultaneous removal of 80% of iron from the waste as $Fe(OH)_3$. However, with increase in current density, the net cell voltage as well as the energy consumption increased. Under 30 Am^{-2} and 50 Am^{-2}, around 91±2% of Nd was removed from the middle compartment and was recovered as $Nd(OH)_3$ in the catholyte, indicating an effective one step process.

5.3.5 Neutralization and residual Fe removal

The electrolysis step removed more than 80% iron. However, complete removal of iron is necessary for creating the closed-loop process and to obtain REE-rich leachates. The residual 20% of iron was removed by rising the pH of the leachate to 6.5±0.2 with the neutralizing agent, ammonium hydroxide. The pH was increased every hour for the first 6 hours and the leachate was then stirred in air for 48 hours to completely remove iron from the leachate with centrifuging and filtering. The final leachate was rich in REEs and cobalt with around 95% of total recovery for REEs and cobalt after the electrolysis and neutralization steps (Table 5.4). Cobalt can be recovered from the leachate using electrowinning or solvent extraction processes.[39-40]

Table 5.4. Composition of the leachates after electrolysis and neutralization at 30 Am^{-2}.

Elements	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

Total recovery [%]	94 ±1	93±1	96.0 ±0.5	97±0.5	-

5.3.6 Obtention of rare-earth oxides

The rare-earth hydroxides obtained were heated up stepwise until 800 °C in order to study the transformation of rare-earth hydroxides to oxides and XRD measurement was made for every 50 °C. The unchanging peaks at 2ϴ values 40° and 46° were from the Pt-Rh strip on which the powder was heated up (Figure 5.5 A and B). The crystalline $Nd(OH)_3$ disappeared at intermediate temperatures and at around 650 °C, crystalline peaks of hexagonal Nd_2O_3 phase were obtained.

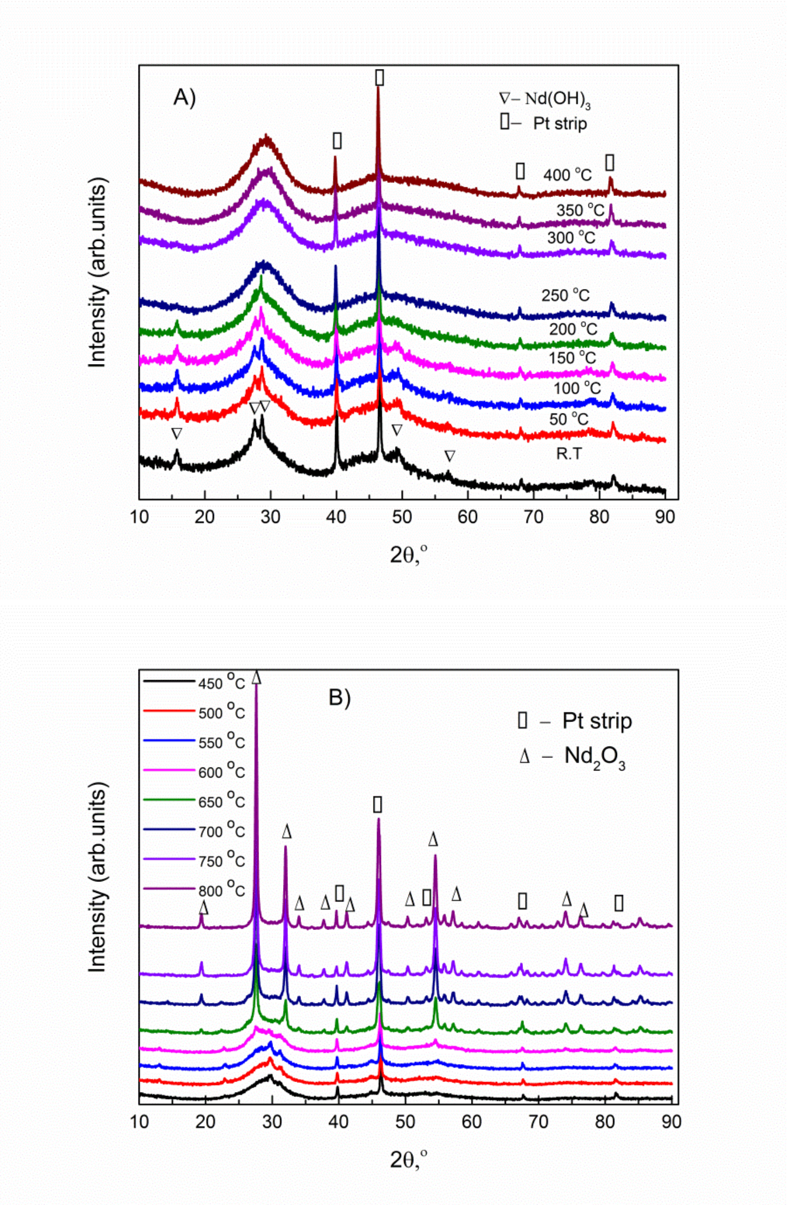

Figure 5.5: XRD of the obtained rare-earth hydroxides at different temperatures from A) R.T- 400 °C and B) 450 °C - 800 °C with steps of 50 °C.

5.3.7 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 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 magnet waste from the solution. Around 95±1 % of REEs were dissolved into the solution with over 80% of removal of iron as $Fe(OH)_3$ precipitate. The iron removal during the electrolysis step was caused by anodic oxidation of Fe(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 5.6. The average cell voltage decreases with 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 0.05M ammonium sulfamate is 6.6 kWh/kg. The magnet scrap can be processed at an operational cost of €0.8 kg^{-1} assuming an average energy cost of €0.12 per kilowatt hour. It is important to note that avoiding usage of oxalic acid not only cost saving but also avoids carbon emissions and lowers the global warming potential of the process.[41] Rare-earth oxides can 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.

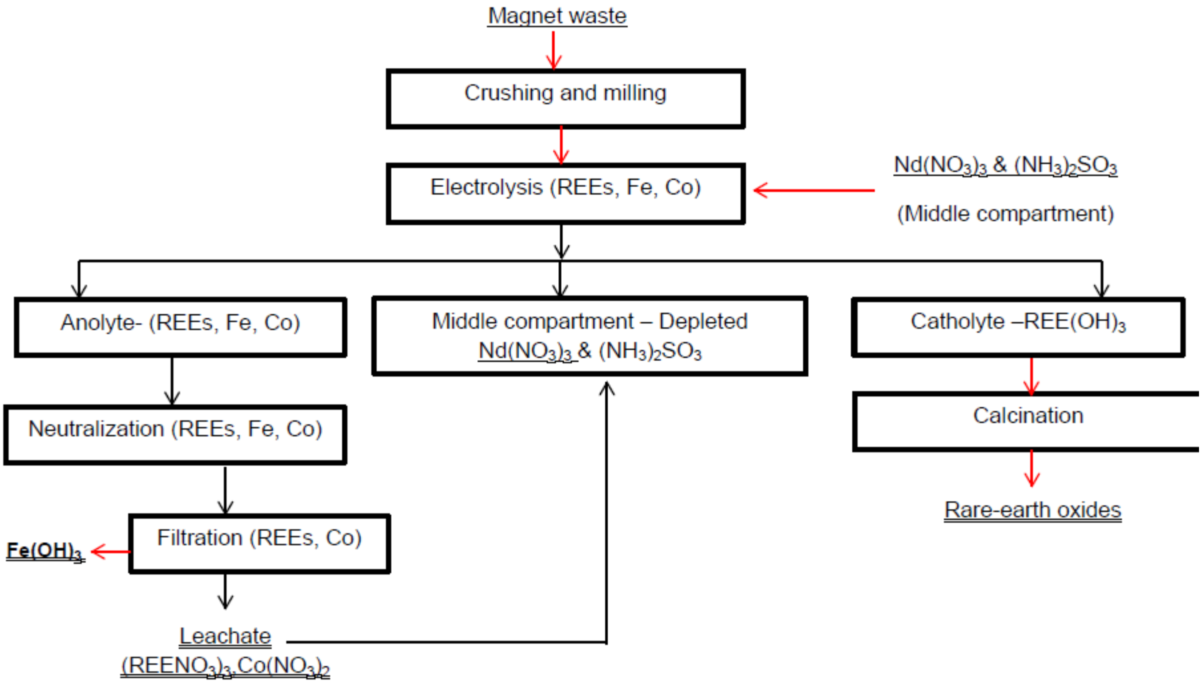

Figure 5.6: Flowsheet of the proposed recycling scheme. Black arrow: liquid streams, red arrow: solid streams.

5.4 Conclusion

An acid free process was developed to recover REEs from NdFeB magnet waste at room temperature. We demonstrate that REEs can be recovered 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 electrolysis step. Complete iron removal was achieved by neutralizing the leachate. In the same step, 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 oxalic acid as the precipitating agent and combines the extraction and precipitation steps into a single one. The overall process can be performed at a reasonable energy consumption of 6 kWh/kg. The whole flowsheet is environmentally friendly as it consumes no acid and is CO_2 free.

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Chapter 6 Conclusions and Outlook

6.1 Conclusions

Critical metals such as REEs are an integral part of a future low-carbon economy because of their usage in clean-tech devices. The supply chain of REEs is fragile due to China's monopoly over production. To effectuate a circular economy, recycling REEs from end-of-life waste products is crucial. NdFeB magnets is the leading consumer of the produced REEs and thus, an important secondary resource to recover REEs. NdFeB magnets typically contain around 25-30% REEs, 60-70% iron and the rest consists of admixtures of various metals to impart magnetic and other properties.

This dissertation is mainly focussed on developing electrochemistry based routes to recycle NdFeB magnet waste. Four different electrochemical processes were developed to recover REEs. a) Electro-oxidative approach b) Selective extraction through a room-temperature electrolysis pretreatment with dual anodes c) Selective extraction in a two-chambered membrane reactor with an AEM d) Acid-free extraction of REEs in a three-chambered membrane reactor.

In the electro-oxidative approach, the magnet waste was completely dissolved in HCl. Subsequently, Fe(II) in the leachate was selectively oxidized electrochemically using a large anode to cathode area. Anodic oxidation was found to be the predominant mechanism. Later, the oxidized leachate was subjected to two different routes to recover REEs. In the first route, oxalic acid was directly added to the leachate which selectively precipitated more than 97% of REEs in the leachate as rare-earth oxalates. The oxalates were calcined to produce rare-earth oxides of high purity (99.2%). It was also shown that a similar selective precipitation of REEs with oxalates was not possible if Fe remains unoxidized in the Fe(II) form. Thus, speciation of iron is shown to play a key role in formulating a process to recover REEs. As an alternative, ammonia was added to the electro-oxidized leachate in the second route. Addition of ammonia caused the iron to precipitate from the leachate as $Fe(OH)_3$ leaving REEs and cobalt in the leachate. It was also shown that cobalt can be selectively recovered from the leachate as metallic cobalt using electrowinning. Despite efficient recovery of REEs and cobalt, this approach required complete dissolution of magnet waste in acid. The excess consumption of non-recyclable HCl and oxalic acid is problematic. Thus, the later processes were created to be more sustainable and closed loop.

In order to selectively recover REEs from NdFeB magnet waste, an electrolysis pretreatment route was investigated. Solid sintered NdFeB magnet was used as an anode along with an inert Ti/Pt anode. While the components of the magnet waste could be anodically dissolved, the inert anode ensured simultaneous conversion of Fe(II) to Fe(III). At the end of this electrolysis pretreatment step, the components in the magnet waste are completely converted into the respective hydroxide form. Subsequently, the mixed hydroxides precipitate was leached with HCl. Only REEs and cobalt leached into the solution, leaving iron as $Fe(OH)_3$ in the residue. Then, oxalic acid was added to the leachate to selectively precipitate REEs as rare-earth oxalates. The oxalic acid precipitation step also regenerates HCl using in the leaching step resulting in a closed loop process.

In the third flowsheet, a two chambered electrochemical reactor separated by an anion exchange membrane was used to selectively extract REEs from the magnet waste. The magnet waste was first milled and partially leached with HCl. The amount of HCl used was equal to the stoichiometric requirement for REEs and cobalt. The leachate along with the undissolved magnet waste was internally circulated as the anolyte. Sodium chloride was used in both anolyte and catholyte and the effect of NaCl was systematically investigated. It was shown that Fe(II) was oxidized and the acid generated by Fe(II) oxidation simultaneously dissolved the magnet waste. The process went on until all REEs and cobalt were leached into solution and iron was converted into ferric hydroxide residue. Similar to the dual anode pretreatment process, the oxalic acid precipitation step regenerated HCl. Though the second and third flowsheets are closed loop, both these processes still consume oxalic acid. Oxalic acid is an expensive chemical and calcination of rare-earth oxalates result in emission of carbon dioxide.

In the final process presented in this thesis, a three chambered membrane electrochemical reactor with anion and cation exchange membranes was used. An acid free process was developed to recover REEs from NdFeB magnet waste at room temperature. We demonstrate that REEs can be recovered in a three chamber electrochemical reactor by obtaining acid from its own salt. Around 95% of REEs are recovered from the magnet waste with partial removal of iron during electrolysis step. Complete iron removal was achieved by neutralizing the leachate. In the same step, 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 oxalic acid as the precipitating agent and combines the extraction and precipitation steps into a single one. The overall process can be performed at a reasonable energy consumption of 6 kWh/kg. The whole flowsheet is environmentally friendly as it consumes no acid and is CO_2 free.

6.2 Outlook

This thesis presents for the first time an electrochemical approach to recycling REEs from NdFeB magnet waste. The focus of this thesis is on the development of innovative strategies and to understand the fundamental reaction mechanisms involved in recycling. There are two fronts upon which this thesis can be built up further.

6.2.1 Applicability of developed flowsheets to complex waste

It is important to note that currently in the WEEE recycling plants, the predominant philosophy is that of “material based recycling”. Different products are collected and shredded together after which the shredded waste is divided into ferrous and non-ferrous components. However, an alternative philosophy is “product based recycling”. This involves careful dismantling, separation and collection of products from the different appliances after which specific routes can be applied to recover important metals. One of the important examples of exclusive collection of products is nickel metal hydride and lithium ion batteries. In this thesis, a relatively clean production magnet scrap was used in all the processes in order to understand the fundamental mechanisms and to be consistent with the philosophy of product based recycling. However, some of the chemistries developed here can be extended to magnets extracted from EoL waste and complex shredder waste as well.

In the dual anode flowsheet, in addition to production scrap, magnets extracted from EoL waste can also be used. Alternative to the solid sintered magnets that were used in the process, the waste can be pulverized and the powders can be directly used and slurry electrolysis can be performed to convert the magnet components into the hydroxide form. The electro-oxidiative process can be easily applied to dismantled EoL magnets as the process requires pulverization and complete acid dissolution of the waste as initial steps. However, careful screening needs to be done before using complex shredder scrap. Significant amount of copper in the scrap can bring down the efficiency of electro-oxidation of Fe(II) due to parasitic reaction of Cu(I) oxidation in the anode. However, base metals can also be removed by simultaneous electrodeposition in the cathode during electrolysis.

The flowsheets developed based on the membrane electrolysis offer the best possibility to deal with complex waste. The chemistry of iron removal and simultaneous acid generation presented here can be used for complex waste stream containing significant amount of iron. Especially, the third flowsheet with two-chambered membrane reactor with AEM is best suited for dealing with contaminant elements such as copper, aluminium, nickel and lead. The electrochlorination reaction can circumvent the problem of Cu(I) electro-oxidation that often brings down extraction efficiencies. The complex waste can be stored in separate extraction tanks where the electrogenerated chlorine leaches the waste into solution along with oxidation of Fe(II). After leaching, iron and aluminium can be separated by precipitation. REEs can be recovered by selective precipitation with oxalic acid and the residual metals can be separated using solvent extraction.

In three chamber membrane process with AEM and CEM, iron and aluminium can be precipitated in the anolyte leaching other metals like copper, nickel, cobalt, REEs etc into the solution with acid. The complex solution with REEs and other metals can be reused in the middle compartment. This will result in complex hydroxide precipitate in the catholytic compartment. The base metals such as nickel, copper and to an extent zinc can be extracted from the hydroxide precipitate with ammoniacal leaching. A relatively pure rare-earth oxide can be then used for metal production.

6.2.2 Combinatorial processes

One of the significant unchartered territories in this thesis is design of combinatorial processes. With the recent stabilization of REE prices, the incentive for opening recycling plants for REEs has diminished. One of the ways to make REE recycling possible is to combine it with other existing recycling process, such as copper recycling. In a simple two chambered membrane process with an AEM, copper can be electrodeposited in the catholyte and the acid generated from this electrodeposition process can be utilized to leach REEs from the waste in anolyte.

The membrane processes demonstrated in this thesis allows combining metal recycling with water treatment. For instance, sea water has been treated in a three chambered membrane process where NaCl was split up into NaOH, HCl and pure water. One of the issues plaguing their water treatment process is electrogeneration of chlorine which decreases the efficiency of HCl generation. This disadvantage can be conveniently used by metal recyclers by capturing the chlorine gas to leach metals from the waste. The generated NaOH can be used for precipitating different metals. There are myriad of possibilities to combine electrodeposition, electroleaching, electro-oxidation, electrochemical splitting of salts to develop environmentally friendly multipurpose processes.

Finally, bridging the gap between recycling and energy storage could prove crucial. There are already efforts undertaken in this direction. Incorporating iron chemistry into a fuel cell can create significant breakthroughs in environmentally friendly recycling.

Summary

Rare earth elements (REEs), along with other metals, will play a pivotal role in the transition towards a low-carbon economy. Primary mining of REEs consists of multiple steps, is energy intensive and has an adverse environmental impact. Thus, the current scenario of "use and throw" of REEs after a single use in a product is untenable. Furthermore, the REEs are classified as *critical metals* by the US and EU due to the monopoly of China over REE production. Thus, recycling REEs from secondary resources and end-of-life (EOL) waste products can help effectuate a circular economy by a) reducing the environmental impact of primary mining, b) reducing the dependency on imports and formulating a secure supply chain, c) avoiding landfilling and incineration.

One of the important products produced from REEs are NdFeB magnets. NdFeB magnets have excellent magnetic properties and consists of 20-30 wt% of REEs, 1 wt% boron, 60-70 wt% of iron with other elements in minor quantities. Several recycling processes have been proposed hitherto to recover REEs from NdFeB magnet waste. An efficient and environmentally friendly NdFeB recycling process has several constraints. Such a process should a) selectively recover more than 95% of REEs over iron and other additives, b) operate at room temperature as high temperature processes are energy intensive, c) be a closed-loop process with minimum consumption of chemicals and ability to regenerate the used chemicals again, d) produce little or no waste that has to be discarded or treated further e) be scalable and economically feasible.

This thesis consists of four different electrochemical flowsheets that were developed to recycle NdFeB magnet waste in an environmentally friendly manner. In the first flowsheet, an electro-oxidative approach was used where the magnet waste was first completely dissolved in acid and then the Fe(II) was electrochemically oxidized into Fe(III). After the electro-oxidation step, more than 95% of REEs could be recovered either by direct addition of oxalic acid or by removal of iron by addition of a neutralizing agent, ammonia. In the former case, the remnant solution predominantly contains $FeCl_3$ which can be directly used for water treatment. In the latter case, in addition to REEs, the feasibility of recovering cobalt in the metallic form was also demonstrated. However, this flowsheet required unselective dissolution of magnet waste in the acid as the pre-requisite step and thus consumed excess acid. To overcome this disadvantage, a second flowsheet was developed with a "dual-anode" strategy. The magnet waste was completely converted into a mixed hydroxide form by a electrolysis pretreatment step. Eventually, REEs were selectively leached with HCl from the mixed hydroxide precipitate while iron remained in the residue. The HCl used in the leaching step could be regenerated by precipitating the REEs with oxalic acid resulting in a "closed-loop" process.

In the third flowsheet, a two chambered membrane electrochemical reactor with an anion exchange membrane was used to selectively extract REEs from the NdFeB magnet waste. In the first step, the magnet waste was partially and unselectively leached with HCl corresponding to the amount of REEs present in the waste. The Fe(II) present in the leachate was electrochemically oxidized in the anolyte which simultaneously precipitated iron and liberated the acid consumed by iron in the partial leaching step. This process was continued until all iron was collected in the residue and more than 95% of REEs were extracted into the leachate. The cathodic

reaction was production of hydrogen gas through reduction of water. This process consumed only electricity, water and oxalic acid. In all the three flowsheets, oxalic acid was used to recover REEs from the leachate as rare-earth oxalates. The rare-earth oxalates were calcined to obtain rare-earth oxides. However, oxalic acid is expensive and calcination process produces carbon dioxide. The fourth flowsheet overcomes this challenge by use of a three chambered electrochemical reactor. A rare-earth salt solution was fed into the middle compartment and was split into anions and cations. The anions passed through an anion exchange membrane and generated acid in the anolyte compartment which leached the magnet from the waste into the solution. The cations passed through a cation exchange membrane and were precipitated as rare-earth hydroxides. The rare-earth hydroxides were calcined to obtain rare-earth oxides. Thus, for the first time, this thesis demonstrates an acid-free extraction process for REE recovery from waste.

Samenvatting

Zeldzame aardmetalen hebben, samen met andere metalen, een belangrijke rol in de overgang naar een koolstofarme economie. De primaire mijnbouw van zeldzame aardmetalen bestaat uit meerdere stappen, is energie-intensief en heeft een nadelige impact op milieu. Dus is de actuele scenario van ''gebruiken en weggooien'' van zeldzame aardmetalen, na eenmalig gebruik van een product, onhoudbaar. Bovendien zijn de zeldzame aardelementen geklasseerd als kritieke metalen door Verenigde staten en Europa, gezien de monopolie van China op deze metalen. Derhalve is het van belang om de zeldzame aardmetalen te recyclen uit secundaire grondstoffen en afgedankte (end-of-life) producten om een kringloopeconomie te creëren. Dit zal a) de milieu-impact van primaire mijnbouw verminderen, b) afhankelijkheid van import te verkleinen en hierdoor een veilige supply chain garanderen en c) het vermijden van het storten van afval en afvalverbranding.

Een van de belangrijke producten geproduceerd uit zeldzame aardmetalen zijn NdFeB magneten. De NdFeB legering heeft uitstekende magnetische eigenschappen en bestaat uit zeldzame aardmetalen (circa 20-30%), boor (circa 1%) en ijzer (60-70%), alsook andere elementen in kleine hoeveelheden. Tot heden zijn er meerdere werkwijzen voorgesteld om zeldzame metalen uit NdFeB magneet afval te recyclen. Een doeltreffend en milieuvriendelijk proces moet aan bepaalde randvoorwaarden voldoen. Zo'n proces moet a) >95% van de zeldzame metalen selectief kunnen herwinnen ten opzichte van ijzer en andere additieven, b) op kamertemperatuur plaatsvinden, omdat hoge temperatuur processen energie-intensief zijn, c) een gesloten kringproces zijn waar minimale hoeveelheden chemische reactanten gebruikt worden en de gebruikte chemicaliën geregenereerd worden, d) minimaal of geen afval produceren dat gestort of verder behandeld moet worden en e) opschaalbaar en economisch haalbaar zijn.

Vier verschillende electrochemische behandelingsrouten(flowsheets) worden beschreven in dit proefschrift om NdFeB magneet afval te recyclen. In de eerste behandelingsroute werd elektro-oxidatie gebruikt, waarbij het magneet afval eerst volledig in zuur werd opgelost en hierna werd het Fe(II) tot Fe(III) geoxideerd in een electrochemische reactor. Meer dan 95% van de zeldzame aardelementen kunnen herwonnen worden door het toevoegen van oxaalzuur aan de loogoplossing waarbij een onzuivere $FeCl_3$ overblijft die kan ingezet worden voor waterbehandeling. Een alternatief tot oxaalzuur is het toevoegen van ammoniak om ijzer te verwijderen. Hierdoor is het mogelijk om naast op zeldzame aardmetalen, ook het kobalt te herwinnen in zijn metallische vorm. Maar gezien het magneet afval volledig is opgelost, heeft dit proces een hoge zuur consumptie. Om dit te overwinnen werd een dubbele anode systeem gebruikt in de tweede flowsheet. Eerst werd het magneet afval geëlektrolyseerd tot gemengd hydroxide doormiddel van een voorbehandeling stap. Daarna werden de zeldzame metalen selectief uitgeloogd uit het gemengd hydroxide precipitaat met HCl, waarbij ijzer in de residu achterbleef. Het gebruikte HCl kan dan geregenereerd worden met een gesloten kringproces waarin zeldzame aardmetalen worden geprecipiteerd met oxaalzuur.

In de derde flowsheet werd een tweekamerig-membraan-elektrochemische reactor met een anionuitwisselingsmembraan gebruikt voor de selectieve extractie van zeldzame aardelementen. Eerst werd het magneet afval gedeeltelijk en niet-selectief uitgeloogd met een hoeveelheid HCl overeenkomend met de stoichiometrische hoeveelheid van zeldzame elementen in het afval. Fe(II) in de loog oplossing werd hierna in het anolyte elektrochemisch geoxideerd, waarbij gelijktijding het ijzer werd geprecipiteerd en het verbruikte HCl geregenereerd. Dit proces werd gecontinueerd tot alle ijzer werd geprecipiteerd in het residu en tot meer dan 95% van de zeldzame elementen werden uitgeloogd naar de oplossing. Aan de kathode vond reductie van water plaats. Alleen water, elektriciteit en oxaalzuur werden verbruikt in dit proces. In alle drie flowsheets werd oxaalzuur gebruikt om zeldzame aardelementen te herwinnen als zeldzame aard-oxalaten. Deze werden hierna gecalcineerd om zeldzame aard oxiden te krijgen. Echter is oxaalzuur duur en produceert calcinatie koolstofdioxide. In de vierde flow sheet werden deze problemen overwonnen door het gebruik van een driekamerig elektrochemische reactor. Een zeldzame aarde-zout oplossing werd gesplitst in anionen en kationen in het middelste compartiment. Door transport van de anionen door het anionuitwisselingsmembraan werd zuur gegenereerd in het anolyte compartiment. Dit zuur werd dan gebruikt om het magneet afval te oplossen. De zeldzame aard kationen, die door het kationuitwisselingsmembraan werden getransporteerd, werden geprecipiteerd als zeldzame aarde-hydroxiden. Deze hydroxiden werden omgezet tot zeldzame aarde-oxiden doormiddel van calcinatie. Dus in dit proefschrift wordt een zuurvrij extractieproces voor het herwinnen van zeldzame aardelementen uit magneet afval voor de eerste keer gedemonstreerd.

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List of publications

1. Prakash Venkatesan, Zhi Sun, Jilt Sietsma, Yongxiang Yang, An environmentally friendly electro-oxidative approach to recover valuable elements from NdFeB magnet waste, Separation and Purification Technology, 2018, 191, 384-391.

2. Prakash Venkatesan, Tom Vander Hoogerstraete, Tom Hennebel, Koen Binnemans, Jilt Sietsma, Yongxiang Yang, Selective electrochemical extraction of REEs from NdFeB magnets at room temperature, Green Chemistry, 2018, 20, 1065-1073.

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Conference presentation and proceedings

1. Prakash Venkatesan, Zhi Sun, J.Sietsma and Y.Yang, Recovery of Neodymium from NdFeB magnet scrap by selective electrolytic dissolution, Proceedings of the 1st European Rare Earth Resources Conference, Milos (Greece), 4-7 September 2014, 163-170

2. Prakash Venkatesan, Zhi Sun, J. Sietsmaa, Y. Yang, An electrochemical approach to recover valuable elements from the NdFeB magnet waste 2nd European Rare Earth Resources Conference (ERES 2017), Santorini (Greece), June 2017.

3. A. Abbasalizadeh, S. Seetharaman, P. Venkatesan, E. Haccuria, J. Sietsma, and Y. Yang. Novel reactive anode for electrochemical extraction of rare earth metals from rare earth oxides. TMS 2017, San Diego, USA, Feb. 2017.

4. Sebastian Peelman, Prakash Venkatesan, Shoshan Abrahami, Yongxiang Yang, Recovery of REEs from End-of-Life Permanent Magnet Scrap Generated in WEEE Recycling Plants. TMS 2018.

About the author

Prakash Venkatesan was born in 1988 in India. He has a bachelors in technology (B.Tech) in Chemical and Electrochemical engineering from Central Electrochemical Research Institute(CECRI), India (2005-2009). He received an Erasmus Mundus scholarship award to pursue his masters in “Materials for Energy Storage and Conversion”. He did his MS from 2009 to 2011 at three different universities- University of Paul Sabatier, Warsaw University of Technology and University of Picardie Jules Vernes. His MSc thesis project “Synthesis and characterization of structured cathode materials for all solid state Lithium-Sulfur batteries” was carried out at Robert Bosch, Stuttgart. He worked on Li/S batteries as a research assistant in Unviersity of Waterloo, Canada in 2012. In 2014 he received the Marie Curie scholarship to pursue the PhD in the group of Metal Production and Resource Recycling (MPRR) under the supervision of Prof. Yongxiang Yang and Prof. Jilt Sietsma at TU Delft. His PhD was focussed on developing environmentally friendly electrochemical processes to recover rare-earth elements from NdFeB magnet waste. He did two brief internships in Stena Metall and Umicore during his PhD. From February 2018, he is working as a postdoc under Prof. Arjan Mol in the QUALIFY project in field of adhesion and interfacial delamination.