



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



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ABSTRACT

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

1. Introduction

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

The various approaches investigated hitherto to recycle NdFeB magnets have been summarized in detail by many authors [7–9]. The recycling approaches can be broadly classified into pyrometallurgical and hydrometallurgical routes. Some examples of the pyrometallurgical routes include liquid metal extraction [10], selective chlorination [11,12] and roasting [13]. However, these pyrometallurgical processes operate at a temperature of around 750–950 °C and are thus energy

intensive. In hydrometallurgical routes, magnets are completely leached with acid followed by direct precipitation of REEs as their double sulfate salts [14,15]. Rare-earth double sulfates need to undergo an additional conversion step to rare-earth fluorides by reacting with HF. Oxalic acid was also reported as a selective precipitation agent by [16]; however, the role of oxalic acid as precipitation agent is unclear as Fe(II) has been reported to interfere with the selective precipitation [17]. Iron, the major component of NdFeB magnets, is seldom recovered in the hydrometallurgical processes in a useful form. These processes typically consume non-recyclable chemicals such as excess acid, ammonia and sodium hydroxide, involve multiple steps and generate a large amount of waste water. Irrespective of whether the magnet waste is treated at room temperature or high temperature, the speciation of iron plays a major role. Fe(II) tends to be stable in the solution until a pH of 6 and Fe(II) oxalates are highly insoluble, whereas in contrast, Fe(III) precipitates at a pH around 2–3 and Fe(III) oxalates are highly soluble [18,19].

In this paper, we describe an environmentally friendly electrochemical approach to selectively recover REEs from NdFeB magnet waste. The magnet waste was acid leached with HCl and subsequently *in-situ* electro-oxidation was performed to selectively oxidize Fe(II) to Fe(III). Once the electro-oxidation was complete, rare-earth ions in the solution were selectively precipitated using oxalic acid. More than 98%

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of REEs present in the magnet was recovered as rare-earth oxides with a product purity higher than 99%. The remaining solution is composed mainly of FeCl_3 , which can be used in water treatment plants or in mineral ore leaching [20]. The whole process is environmentally friendly as it is carried out in a single reactor, at room temperature and consumes only oxalic acid and current without generating waste.

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

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

2. Experimental

2.1. Materials

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

2.2. Experimental set-up and procedures

A cylindrical plexiglass electrochemical reactor (Fig. 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 $25 \pm 2^\circ\text{C}$ 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 (3 M 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 (3 M KCl) reference electrode and a glassy carbon counter electrode. All experiments were conducted using either the potentiostat Versastat 4 or Parstat 4000 (Ametek, UK) and the data was obtained using Versastudio software.

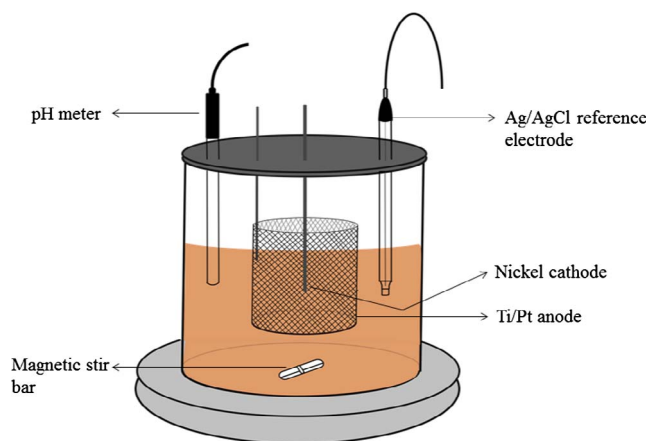


Fig. 1. Schematic illustration of the electrolysis set-up.

2.3. Analyses

Elemental concentrations in solution were analyzed 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 ($0.45\ \mu\text{m}$) 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

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

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

3. Results and discussion

3.1. Leaching of the magnet waste

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

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 g and liquid volume of 300 ml. Ammonium chloride (Concentration, $C_{\text{NH}_4\text{Cl}} = 3\text{ M}$) 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

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