ELECTROCHEMICAL RECOVERY OF RARE EARTH ELEMENTS FROM MAGNET SCRAPS- A THEORETICAL ANALYSIS

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Abstract

Recovery of rare earth elements (REEs) from secondary resources is of great environmental and economic importance. In the case of magnet scraps, multi-step hydrometallurgy and liquid metal extraction with high energy consumption are usually applied to accomplish acceptable recovery rate of REEs from the scrap. This paper aims to provide theoretical framework for using electrochemistry to selectively extract REEs into aqueous solution. Thermodynamic and electrochemical behaviour of different components in the alloy are theoretically predicted and correlated with available data from the literature. The role of microstructure and different elements in dissolution mechanism of the REE magnet is reviewed. Through understanding various factors involved in dissolution behaviour of the alloy, an electrochemical process with enhanced selectivity to recover REEs can be established.

Introduction

Rare earth elements are of great importance in modern industry for producing various functional materials like permanent magnets, rechargeable batteries, catalysts, lamp phosphors because of their unique magnetic and electronic properties. Due to the increased demand and supply shortage, REEs are listed as critical raw materials of strategic importance in many countries in the world[1,2]. This has promoted research for recovering REEs from end-of-life (EOL) products and the scrap created during production. Neodymium iron boron magnet ($Nd_2Fe_{14}B$) is one of the major usages for rare earth elements and has 62%[3]of the market share of permanent magnetic material. Apart from neodymium, REEs like dysprosium and praseodymium are used in varying amounts (in total 25-30%) for obtaining required magnetic properties[4]. Cobalt (0-10%) is often added to increase the Curie temperature and other elements like vanadium, oxygen and nitrogen can be added in trace amounts to reduce corrosion[5a,5b].

The complex composition of EOL magnets and magnet scrap makes the recovery of REEs rather difficult and demands a range of metallurgical and chemical techniques Various methods have been reported in the past for recovering neodymium and other rare earth elements from the magnets. Lyman et al.[6] used the leaching method and have obtained high recovery of neodymium (98%) by dissolving the scrap in sulfuric acid followed by using alkali hydroxides to precipitate double salts of neodymium which can be further treated to obtain neodymium oxide. Other research groups have also tried selective leaching [7], ultrasound-assisted leaching[8] and a combination of pre-roasting the scrap along with selective leaching

and solvent extraction[9] to recover the REEs from the scrap. Although the above mentioned hydrometallurgical methods have achieved appreciable recovery of REEs, they require multiple steps to enhance leaching selectivity, expensive pre-treatment techniques and consumption of large amounts of chemicals. Hence for an aqueous chemical method to be economically viable for recycling, enhanced selectivity of REEs recovery combined with low consumption of chemicals and reduced number of steps involved is of paramount importance.

In this paper, the thermodynamics and the corresponding electrochemical behaviour of various elements present in waste magnets are discussed and compared during dissolution into an aqueous solution. With improved understanding of these behaviour, a process to selectively extract REEs from waste magnet can be established.

Thermodynamic evaluations

A typical composition of commercial magnet and magnet scraps obtained from literature[9,10,11] is listed in Table 1.

Table 1: Typical composition of magnet scraps

Elements	Nd	Dy	Pr	Fe	B	Co	C	N	Others
Wt%	23-25	3.5-5	0.05-5	62-69	1	0-10	0-0.14	0-0.1	1-2

*Others- Cu, Al, Ga, Si, Gd, Mo.

The standard Gibbs energy of formation for different rare earth species are calculated from the literature[12,13] and their corresponding Nernst equation are summarized in Table 2. It can be noticed that the standard electrode potentials ($E_{RE^{3+}/RE}$ = -2.2 to -2.4 V vs SHE) of the rare earth elements are very close owing to their similar chemical nature.

Table 2: Calculated values of ΔG^0 (kJ/mol) and standard reduction potential at 298 K and the corresponding Nernst equation. Soluble species concentrations (except H^+) is $10^{-1.0}$ M

Reaction	ΔG^0 (KJ/mol)	E^0 (V)	Nernst equation
$Nd^{3+} + 3e^- \Leftrightarrow Nd$	-671.6	-2.32	E = -2.32 + 0.020 log $[Nd^{3+}]$
$Nd+3H_2O \Leftrightarrow Nd(OH)_3+3H^++3e^-$	-563.3	-1.94	E = -1.94 +0.059 pH
$Nd^{3+}+3H_2O \Leftrightarrow Nd(OH)_3+3H^+$	108.3		3 pH = 19 – log $[Nd^{3+}]$
$Dy^{3+} + 3e^- \Leftrightarrow Dy$	-664.0	-2.29	E = -2.29 + 0.020 log $[Nd^{3+}]$
$Dy+3H_2O \Leftrightarrow Dy(OH)_3+3H^++3e^-$	-564.4	-1.95	E = -1.95+ 0.059 pH
$Dy^{3+}+3H_2O \Leftrightarrow Dy(OH)_3+3H^+$	98.6		3 pH = 17.3 – log $[Dy^{3+}]$
$Pr^{3+} + 3e^- \Leftrightarrow Pr$	-680.3	-2.35	E = -2.35 + 0.020 log $[Pr^{3+}]$
$Pr+3H_2O \Leftrightarrow Pr(OH)_3+3H^++3e^-$	-568.0	-1.96	E = -1.96 +0.059 pH
$Pr^{3+}+3H_2O \Leftrightarrow Pr(OH)_3+3H^+$	111.9		3 pH = 19.68 – log $[Pr^{3+}]$

Their very negative potential values which fall below the hydrogen evolution line indicate a strong reactivity in aqueous solutions. Experimental observation of corrosion and passivity behaviour of neodymium in different conditions have also confirmed rigorous hydrogen evolution[14]. In particular, comparison of the behaviour of iron and REEs in aqueous solution at different pH can be of importance. Koyama et al.[15] used a Pourbaix diagram (Fig. 1) to see

stability of different species of neodymium and iron in different pH and they selectively leached out Nd^{3+} by leaving out iron as Fe_2O_3 in the solution.

In contrast to selective leaching where pH plays a vital role, using scrap magnets in an electrochemical cell offers an additional advantage of controlling parameters like potential and current density to manipulate and selectively dissolve REEs. Fig. 2 shows standard electrode potentials of different components of scrap magnets vs Ag/AgCl electrode (0.25 V vs SHE). The other major elements present in the waste magnets in terms of weight percentage are iron and cobalt. The standard reduction potentials of iron and cobalt are -0.44 V and -0.28 V vs SHE respectively. EOL magnets also contain copper, as a minor additive or in the coating along with nickel to prevent corrosion.
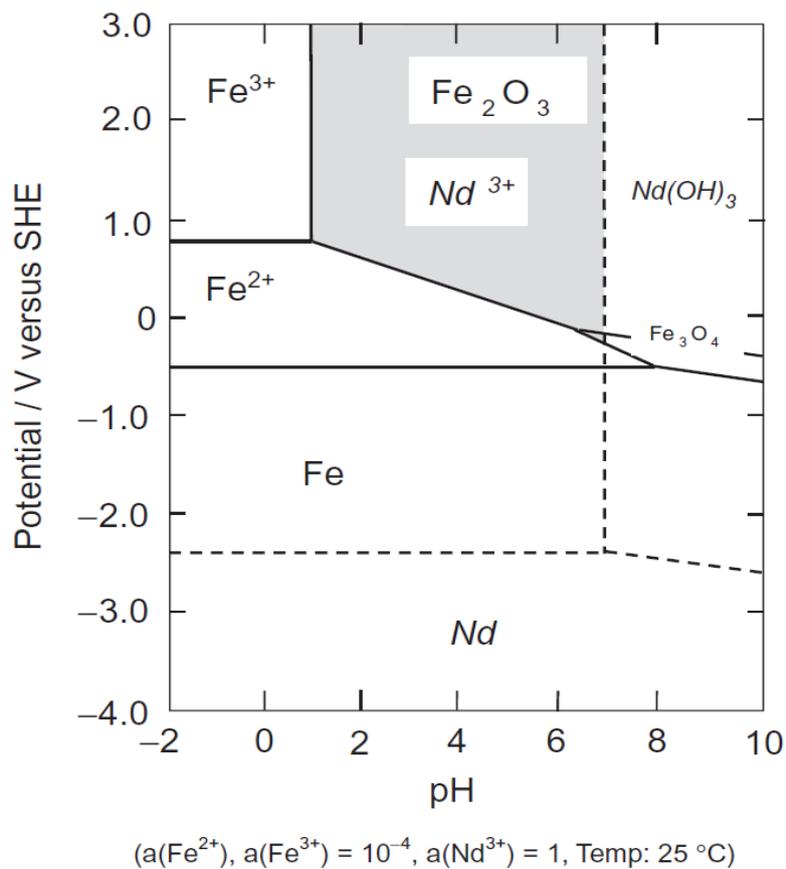

(a(Fe^{2+}), a(Fe^{3+}) = 10^{-4}, a(Nd^{3+}) = 1, Temp: 25 °C)

Fig. 1: Pourbaix diagram of Fe-H_2O and Nd-H_2O system[9]

It can be noted that, when magnets are deployed as anodes in a 3-electrode electrochemical cell (Ag/AgCl reference electrode), selective dissolution can be accelerated by controlling the potential and maintaining it in the region between dissolution of rare earths and the region in which metallic iron, cobalt and other elements are stable. Further anodic polarization of the scrap magnets can accelerate the dissolution process.

$$E^0_{(Cu^{2+}/Cu)} = 0.09 \qquad Cu^{2+} + 2e^- \Leftrightarrow Cu$$

$$E^0_{(Co^{2+}/Co)} = -0.54 \qquad Co^{2+} + 2e^- \Leftrightarrow Co$$

$$E^0_{(Ni^{2+}/Ni)} = -0.5 \qquad Ni^{2+} + 2e^- \Leftrightarrow Ni$$

$$E^0_{(Fe^{2+}/Fe)} = -0.65 \qquad Fe^{2+} + 2e^- \Leftrightarrow Fe$$

$$E^0_{(B(OH)3/B)} = -1.14 \qquad H_3BO_3 + 3H^+ + 3\,e^- \Leftrightarrow B + 3H_2O$$

$$E^0_{(RE^{3+}/RE)} = -2.44 \qquad RE^{3+} + 3e^- \Leftrightarrow RE$$

Fig. 2: Standard reduction potential (V vs Ag/AgCl) of different elements in scrap magnet[9a]

Analyzing elements individually can theoretically form a basis for selective dissolution but dissolution of individual components from an alloy is governed by their partial thermodynamic properties. Partial potential of an individual component in an alloy can be written as [16]

$$E^M_i = -\left(\frac{RT}{z_i F}\right) \ln N_i \quad (1)$$

where E^M_i is the difference between equilibrium electrode potential of the component *i* in the alloy and the corresponding potential of the same component in the individual phase. *R, T, F ,Z$_i$, N$_i$* are molar gas constant, temperature, Faraday's constant, number of electrons transferred and molar fraction of the component respectively. By definition mole fraction is less than one and hence the partial potential of a component in the alloy will always be more positive than the individual component potential. Hence experimental determination of the extent of positive shift for individual components in the $Nd_2Fe_{14}B$ alloy in different electrolytic environments is vital.

An electrolyte environment which is non-inhibiting and encouraging free corrosion process is essential. Passivity is in principle possible in highly alkaline solutions and Song et al.[17] observed that NdFeB magnets form passive hydroxide layers in sodium hydroxide and in oxalic acid. Jingwu et al.[18] observed similar type of passive behaviour in phosphoric acid with low corrosion current. However the alloy freely dissolves in other acids such as sulfuric acid, nitric acid and hydrochloric acid with high current density and is also susceptible to attack by chloride and other ions even in the solutions in which they exhibit passivity. Hence for active dissolution of the magnets it is preferred to have an acidic conditions with strong acids having high corrosion current.

Microstructure of the magnet and dissolution mechanism

Another crucial aspect of selective dissolution is to understand the correlation between microstructure of the alloy and the corresponding dissolution mechanism. NdFeB magnets have a matrix ferromagnetic phase (Φ) of $Nd_2Fe_{14}B$ tetragonal compound and is surrounded by intergranular regions containing a neodymium rich phase (n) and a boron rich phase (η) [19]. The complexity of the intergranular region in the microstructure of the neodymium magnets depend upon the additional elements such as cobalt, aluminum and gallium . In order to selectively dissolve rare earths, an understanding of dissolution mechanism in different environments is thus necessary. Several authors[19,20,23] have proposed that neodymium rich phases (n) corrode preferentially due to the formation of a galvanic couple owing to negative standard potential of rare earths. This is followed by the boron rich phase dissolution and this renders the matrix loose finally creating disruption of the matrix phase. Corrosion in Nd-Fe-B alloy is a natural process and can even result in the pulverization of the magnet. The scheme of step by step dissolution process presented by Schlutz[19] et al. is given in Fig. 3.
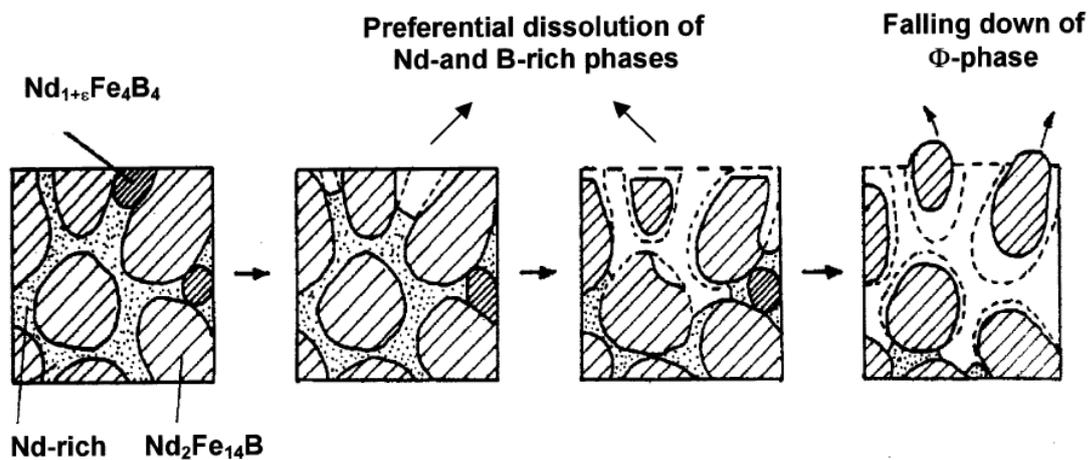

Fig. 3: Schematic illustration of dissolution process of Nd-Fe-B magnets by corrosion[19]

Mao et al.[20] observed the dissolution process of individual phases by synthesizing them separately and subjecting them to different corrosion tests. The Nd rich phase had the most negative open circuit potential followed by matrix phase and the boron rich phase, indicating that the Nd rich phase has the highest electrochemical reactivity. These results further strengthen the conclusion that selective dissolution of rare earths are feasible and is in fact a naturally occurring corrosion process.

The composition of different components in the alloy also play a crucial role in dissolution process. Corrosion studies of magnets with higher weight percent of iron in phthalate buffer showed reduced current density, indicating formation of passive layers like iron oxide preventing corrosion[21]. Aluminum, gallium and copper have reduced the corrosion as they reduce the strength of galvanic coupling among magnetic phases[22] and cobalt has been observed to improve corrosion resistance as it prevents magnetic pulverisation[23]. High rate of dissolution is observed in low carbon and oxygen alloy when the nitrogen content exceeds

0.1 wt%. Oxygen impedes corrosion when it is added between 0.6-1.2 wt% and the optimum amount of carbon was found to be 0.1wt% as anything above that facilitates corrosion[5a]. Dysprosium and niobium have been said to have formed stable intermetallic phases which retards corrosion[24] but also high amount of dysprosium (16 %) has been deemed as disadvantageous [25]. On the whole, it is important to know the nature of the scrap to accelerate the dissolution process by various means and by altering the environment.

Electrochemical cell: cathode products and anode slime

Table 2 lists the possible anodic reactions in the electrochemical cell. Besides dissolution of rare earth metals, co-dissolution of iron and cobalt by chemical or electrochemical means is also possible although not desirable.

Rare earths, due to their very negative potential liberate hydrogen on the cathode in aqueous solutions from an electrochemical process. Due to the same, the rate determining step becomes mass transport as the charge transfer is relatively fast. The cathodic reactions in such case are

$$2H^+ + 2e^- \Leftrightarrow H_2 \quad (2)$$

$$M^{n+} + ne^- \Leftrightarrow M \quad (3)$$

$$2H_2O + 2e^- \leftrightharpoons H_2 + 2\,OH^- \quad (4)$$
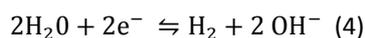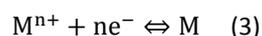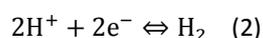
Hydrogen evolution reaction though inevitable, can be kinetically slowed down with proper choice of a cathode as it will hinder deposition of non-REEs as well as modify the pH. Schlutz et al.[14] observed water reduction to be the prominent cathodic reaction for pure neodymium at lower concentrations (≤0.01 M) and at higher concentrations they observed hydrogen evolution. In addition to just acting as counter electrode, the cathode can also be chosen in such a way that it allows deposition of co-dissolved non-REEs. In order to have a cathode to allow deposition of non-REEs, it should a) be inexpensive b) have slow kinetics and low exchange current density for hydrogen evolution reaction c) favor the deposition of non-REEs like iron, nickel or cobalt. Besides if such a deposit from scraps can also be attractive in terms of commercial applications (such as FeNi alloys) it can be an added benefit.

A simple schematic is illustrated in Fig. 4 for the conceptual framework of the electrochemical cell described in the paper. Fig. 4 a) shows the scrap magnets placed as anodes in a simple 2-electrode electrochemical cell. Fig. 4 b) shows an in-progress dissolution. Although it is preferred to selectively dissolve only rare earth ions, chemical dissolution and the complex microstructure of the alloy might also encourage co-dissolution of non-REEs. These co-dissolved non-REEs can be further deposited back on the cathode which results in a partially purified solution enriched in rare earths which is suitable for further elemental recovery and the rest of undissolved elements can be collected as anode slime. The proof of principle experiments are currently in preparation.
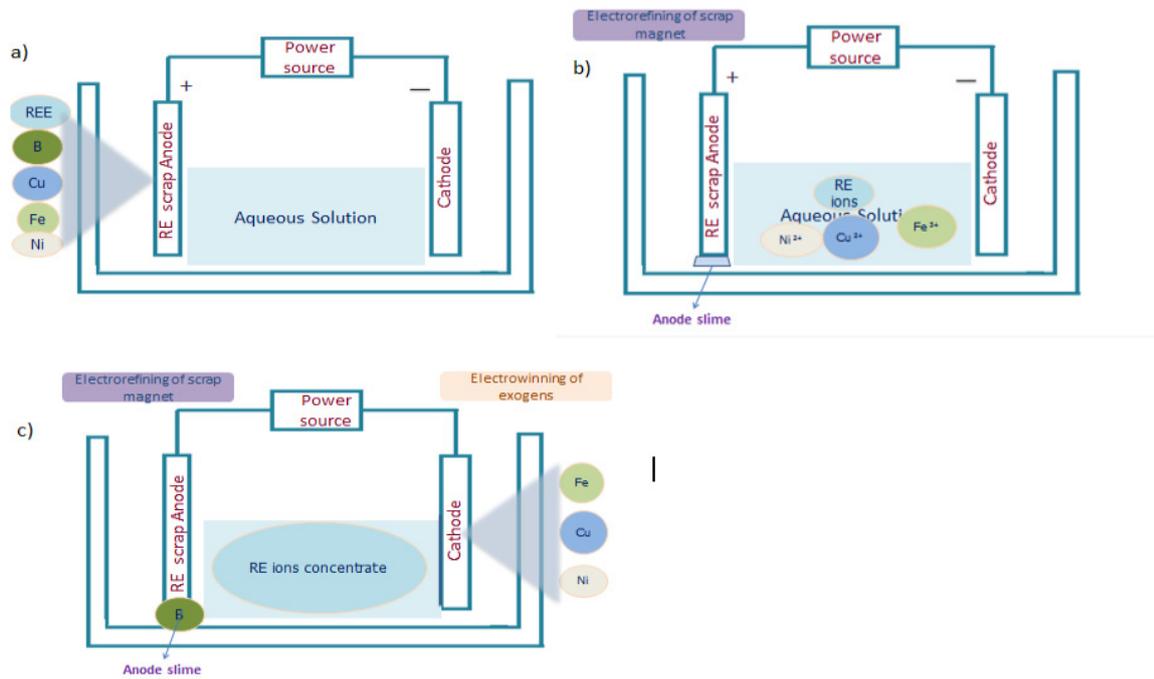
Fig.. 4 Simple schematic of the proposed electrochemical method for REE recovery

Conclusion

This paper establishes the theoretical framework required to perform an electrochemical recycling of end-of-life scrap NdFeB magnets. By drawing ideas from different fields such as electrodeposition, selective dissolution, corrosion and also by projecting thermodynamic predictions for different rare earths of our interest, it can be observed that not only enhanced selective recovery of rare earths is possible but also it is, to an extent, a naturally favored process. The next step of this research will be to build up a 3-electrode electrochemical cell which can help establish the proof of concept described in the paper.

A more detailed look into the dissolution mechanism and kinetics of scrap magnets by using complimentary tools such as electroanalytical techniques and microscopy will be essential. Once the dissolution mechanism is understood, influence of different parameters such as pH, temperature, potential difference and electrolyte composition can be analyzed and optimized. The further goal will be to build up a lab scale cell which can handle few hundreds of grams of scrap in an efficient manner.

Acknowledgment

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