Selective Recovery of Rare Earth Elements by Smelting of Magnets

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Abstract

Rare earth elements (REEs) have a crucial role towards low carbon green economy and clean society. A quarter of total global REEs production is used to produce permanent magnets which have high recycling value. In this study, a high-temperature oxidation process is used to selectively oxidize REEs in the magnet using Fe₂O₃ as an oxidizing agent. B₂O₃ is added as a flux to lower the slag melting temperature and for selective recovery of REEs. In this study, the effect of flux and oxidizing agent amount was investigated on both cerium-rich NdFeB and other NdFeB magnets. At 1350 °C for 1 h with the addition of 0.8 stoichiometric amount of Fe₂O₃ and 45 wt% of B₂O₃, the slag phase was successfully separated from the metallic phase primarily metallic iron. Microstructural analysis showed that REEs in the magnet did not report to the metal phase while the REE-rich slag phase contained almost no iron or other exogen elements. After the selective removal of iron, REEs were recovered from the slag through an acid-leaching process. The process proposed in this study is reagent and energy-efficient for NdFeB and NdCeFeB magnets as iron can be removed in the initial smelting step.

Keywords: Recycling, rare earth elements, NdFeB magnets, smelting, leaching

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1. Introduction

The utilization of Rare Earth Elements (REEs) holds immense significance in the progression of clean energy and transportation technologies. Different applications use different quantities of REEs ranging from a few grams for electronic components to 1000-2000 kg for wind turbine generators. Depending on the application, life span of magnet-containing products varies from consumer gadgets that typically last 2-3 years to wind turbines and automotive applications that typically last for 20-25 years [1]. The world's primary REEs producer is China with estimated 168,000 tons in 2021 which accounts for 61% of global annual production [2]. Developing sustainable techniques for recovering REEs from secondary sources is crucial to replenish the resources required to meet future technology needs and to tackle the high demand versus low supply imbalance.

Several methods are reported in the literature to recover Nd and other REEs from NdFeB permanent magnet scrap including metallurgical processes (i.e., hydro- and pyrometallurgical). In the hydrometallurgical processes, magnet scrap is completely or selectively dissolved in strong mineral or organic acids followed by selective precipitation of dissolved REEs as double sulphates, oxalates or fluorides. A low temperature leaching with 2M H₂SO₄ and completely dissolved the NdFeB magnet with acid to magnet ratio of 2:1. From the obtained leachate, dissolved REEs were precipitated in the form of double sulphate salt and further treated to form rare earth oxides [3]. Lee et al. studied complete leaching of NdFeB magnets using H₂SO₄, HNO₃, HCl and NaOH in presence of ultrasonic oscillator. Among these solvents only H₂SO₄ and HCl gave quite good results. After complete dissolution of magnet powder in dilute H₂SO₄ solution, 98% of iron was reported to be ferrous iron which could be fully oxidized to ferric iron by addition of MnO₂ [4]. After oxidation, almost all iron could be precipitated by addition of MnO or Ca(OH)₂ and the solution can be treated for the recovery of REEs, Co and Mn with negligible losses [5].

Though hydrometallurgical methods are seemingly most prominent for recovering appreciable amounts of REEs, they need costly expensive pre-treatment step(s), consume large amounts of chemicals causing environmental issues and require multiple steps which reduces the process throughput. Selectivity and reaction rates are the key challenges in this method of recycling. Contrarily, pyrometallurgical processes involved with high temperature has lesser environmental impacts [6]. The separation of REEs and iron from the magnet sludge based on the oxidation differences between REEs and iron has studied. Separation efficiency of the phases was enhanced by adding carbon as contacting material which decreases the melting temperature of iron and helps creating oxygen partial pressure over the mixing region of iron and rare earth oxides (REOs). This study also showed that the addition of B₂O₃ decreases the melting temperature of the REE-rich slag which promotes its efficient separation from the metallic phase [7]. In another study, a mechanism was proposed for extraction of REEs from magnet scrap by addition of FeO.B₂O₃ flux. The reaction sequence shown that the FeO in the flux is initially reduced by REEs forming REOs which further reacts with B₂O₃ in the flux forming REBO₃. Part of these newly formed REBO₃ is reduced by unreacted REEs in the metal bath to give REOs by supplying fresh B₂O₃ to the system for further reaction. The overall extraction rate of REEs in this study was >99% at 1500 ºC [8]. Oxidation of the NdFeB magnet scrap at temperatures
500−1100 °C under air followed by reduction at high temperatures, 1400−1500 °C leads to successful separation of the REEs to the slag phase and iron to the metallic phase [9][10][11]. In an oxidation-reduction process where waste tire rubber was used as carbon or pure graphite source to successfully separate the metal and slag phase with a clear interface. Reduction with waste tire rubber-derived carbon generated less solid carbon remnants than the case of pure graphite [12].

Most of the previous smelting studies are reported on an energy-intensive two-stage process, i.e., oxidation of the magnet followed by reduction. As mentioned earlier that there is a limited literature on smelting NdFeB magnets to separate the iron alloy and REEs-containing slag using oxidation of magnets with Fe₂O₃ or B₂O₃. However, these studies used a high temperature (>1500 °C) for slag–metal separation. Since B₂O₃ is a low boiling compound, the current study focused on metal-slag separation at lower temperatures (<1400 °C). Heating microscopy thermal analyser (HMTA) was used to study the effect of amount of B₂O₃ on melting behavior of the slag. Based on the results from HMTA, smelting experiments were conducted on cerium-rich magnets in a tubular furnace under controlled atmosphere. Based on the results obtained for cerium rich magnets, this study also investigated on the smelting of NdFeB magnets in the presence of Fe₂O₃ and B₂O₃. Moreover, the recovery of rare earths and B₂O₃ was also investigated as part of this study.

2. Materials and Method

2.1. Sample preparation

REE-bearing magnet scrap was collected and manually separated from end-of-life hard disk drives (HDDs), and commercially available magnets were purchased for the present study. These magnets were demagnetized in a muffle furnace at 450 °C for 1 h. The demagnetized magnets were then mechanically pulverized to fine particles <90 μm in a planetary ball mill (Restch-PM400, Germany) with tungsten carbide (WC) balls for 2 h at 200 rpm. Ball to powder ratio during milling was maintained at 10:1. The fine magnet powder was mixed with iron oxide (Fe₂O₃, purity >99%, LOBA CHEMIE PVT.LTD.) and boron oxide (B₂O₃, purity >98%, LOBA CHEMIE PVT.LTD.) in an agate mortar pestle and made pellets using a hydraulic press with a pressure of 30 MPa. Images from the collection of spent HDDs to the pellet fabrication is listed in Figure 1.
Figure 1. Images from the collection of spent HDDs to the pellet fabrication, (a), (b) spent HDDs, (c), (d) spent NdFeB magnet dismantled from HDDs (e) magnet powder and (f) fabricated pellet composed of NdFeB magnet powder, Fe$_2$O$_3$ and B$_2$O$_3$.

Since lack of data available for FeO-B$_2$O$_3$-REE oxide contained slag system in Factsage® or any other commercially available thermodynamic modelling softwares, the phase diagram of the B$_2$O$_3$-Nd$_2$O$_3$ system is considered to understand the slag melting behaviour as shown in Figure 2 [12]. NdFeB magnets were smelted in presence of Fe$_2$O$_3$ for oxidation of rare earth elements and B$_2$O$_3$ for slag formation. From the phase diagram, it is evident that there are two eutectic regions for Nd$_2$O$_3$-B$_2$O$_3$ system: the first one being at ~1250 °C and the other at ~1120 °C which are the chosen slag systems of the present study.
2.2. Thermal study using heating microscopy thermal analysis (HMTA)

Mixture of (Nd, Ce) FeB magnet, Fe$_2$O$_3$ and B$_2$O$_3$ powders were compacted in a cylindrical shape of 3 mm diameter and 3 mm height using a hand press (EM-HP209Z). Thermal behaviour of the powder mixtures was studied using a heating microscopy thermal analyser (HMTA) (EM301, Germany). The compact sample was placed on an alumina substrate and inserted in the analyser. The compact samples were examined optically using a noncontact method in the heating microscope from room temperature to 1500 °C with a heating rate of 10 °C per minute. The images of each sample were automatically analysed by the EMI software which establishes geometrical parameters and characteristic temperature. The melting behavior of the sample was observed using a heating microscope recording camera and automatic image analyzer. By measuring the projected area of the sample at various temperatures during the experiment, the geometrical changes of the samples during sintering were estimated. For every 1 °C, the projected area of the sample was photographed using a camera and its geometrical changes (i.e., height, width, projected area, and shape factor) were quantified using image analyzing software. The values of the flow temperature was determined from the measured geometrical changes.

2.3. Smelting Study

A horizontal tube furnace was used for conducting smelting studies with optimum experimental conditions obtained from HMTA to extract the REEs in the magnet scrap into a molten slag. The powder mixture was placed in the furnace and the furnace was heated to the desired temperature with 10 C min$^{-1}$ rate under argon atmosphere to avoid any pre-oxidation of the magnet sample. Reduction temperature and reduction duration were both kept constant at ~1350 °C and 60 min respectively. The first eutectic region in Figure 2 at ~ 1250 °C is very narrow by means of B$_2$O$_3$ content. Because of its light molecular weight, achieving the eutectic B$_2$O$_3$ composition
experimentally was difficult. Hence, the second low melting region (>40 wt% B$_2$O$_3$) was chosen for smelting, which is close to 1120 °C. B$_2$O$_3$ was added to the pellet to attain this. The effect of Fe$_2$O$_3$ (0.6 – 1.0 stoichiometry) and B$_2$O$_3$ addition on the slag-metal separation was investigated on (Nd,Ce)FeB magnets.

### 2.3. Leaching and precipitation studies

After smelting, the slag sample was grounded to -90 μm size and leached with 2N sulphuric acid (H$_2$SO$_4$, purity 98%, purchased from Merck Life Science Private Limited) at 90 °C for 4 h in a 3-neck flask with condenser and temperature probe was connected to one of its necks to maintain solution temperature within ±1 °C. REEs were selectively recovered as double sulphates by sodium sulphate (Na$_2$SO$_4$, purity 99.5% purchased from LOBA CHEMIE PVT. LTD.) addition at pH about 2. The double sulphate precipitate was filtered and washed using watman paper followed by drying it in an oven at 120 °C for 6 hrs. The filtrate was evaporated to partially crystallise the H$_3$BO$_3$ followed by filtration, washing and drying. The RE double sulphate was further treated with NaOH at 120 °C for 30 min in order to get RE oxide/hydroxide.

### 2.4. Characterization

Phase analysis of the samples was examined using X-ray diffraction (Philips-PANalytical PW3040/60, Netherlands) with Cu Kα (λ = 0.15406 nm) radiation. Composition of the initial magnet powder was analysed using X-ray fluorescence (XRF) technique (model no, etc). The slag and metallic phases were analysed using scanning electron microscopy (SEM)−Energy Dispersive X-ray spectroscopy (EDS) (model no etc.).

### 3. Results and Discussion

#### 3.1 Characterization of rare earth magnet powder

Table 1 gives chemical composition of both NdCeFeB and NdFeB magnets used in this study. The results show that cerium rich magnet contains 35.0% of REEs with around 20% Ce content and only Fe, Ni and Al as noticeable other elements. The NdFeB magnet sample contains more Nd of about 29.3% along with other REEs (Pr, Dy, Gd, Eu) of about 6.1%. The XRD study shows only the major phase Nd$_2$Fe$_{14}$B (reference code 98-060-2637) in Figure 3. The peaks corresponding to the Nd-rich grain boundary phase and the minor Nd$_{1.1}$Fe$_{0.4}$B$_{0.3}$ phase are not visible as their peaks overlap with those of Nd$_2$Fe$_{14}$B phase. Table 1. Composition of the NdCeFeB and NdFeB magnet powder (mass %)

<table>
<thead>
<tr>
<th>Element</th>
<th>Fe</th>
<th>Ce</th>
<th>Nd</th>
<th>Pr</th>
<th>Gd</th>
<th>Ni</th>
<th>Al</th>
<th>Cu</th>
<th>Y</th>
</tr>
</thead>
<tbody>
<tr>
<td>NdCeFeB</td>
<td>57.4</td>
<td>19.7</td>
<td>10.1</td>
<td>2.5</td>
<td>2.3</td>
<td>0.8</td>
<td>0.5</td>
<td>0.4</td>
<td>0.4</td>
</tr>
<tr>
<td>NdFeB</td>
<td>60.9</td>
<td>29.3</td>
<td>4.3</td>
<td>1.1</td>
<td>1.2</td>
<td>1.1</td>
<td>0.4</td>
<td>0.3</td>
<td>0.3</td>
</tr>
</tbody>
</table>
3.2 Selective oxidation and slag-metal separation

Iron and REEs in (Nd, Ce)FeB magnets can be separated by selective oxidation of REEs with Fe$_2$O$_3$ followed by phase separation of slag and metallic phases with addition of B$_2$O$_3$ flux. Both reagents were chosen as they cannot contaminate the metal or slag phase during smelting.

Ellingham diagram in Figure 4 lists thermodynamic feasibility of thermal oxidation for major elements in an NdFeB magnet. The standard Gibbs free energy of formation for Nd$_2$O$_3$ is much more negative than the other listed oxides. This means that the oxidation reaction of Nd is thermodynamically more feasible than the other oxidation reactions. Then, in the presence of an oxidizing agent like Fe$_2$O$_3$, the reaction in Equation (1) should occur giving oxides of REEs and B with metallic iron.

$$2 \text{Nd}_2\text{Fe}_{14}\text{B}_{(s)} + 3 \text{Fe}_2\text{O}_3_{(s)} \rightarrow 34 \text{Fe}_{(s)} + 2 \text{Nd}_2\text{O}_3_{(s)} + \text{B}_2\text{O}_3_{(s)} \quad (1)$$
Oxidation-reduction reaction in Equation (1) is only the first step of REE-Fe separation in the permanent magnets. For the physical separation of these components, both the metal and slag phases should be in liquid form. Figure 5 shows that an Fe-C alloy can melt at a eutectic point of 1153 °C. A small addition of carbon at the bottom of the mixture pellet can then help to have an efficient separation of the metallic phase from the slag by decreasing the melting point of iron and increasing the fluidity of the alloy. According to the Ellingham diagram in Figure 5, addition of carbon can reduce the iron oxide into metallic iron at a temperature of 1000 °C or more where it is impractical to reduce REOs at such temperatures.

**Figure 4. Oxide stabilities of different oxides**

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For better separation of the slag from the metallic phase, B\textsubscript{2}O\textsubscript{3} was added to the pellet in order to form a low-melting REE-rich slag. Since there is lack of data for REE-containing slag systems in FACTSage\textsuperscript{®} or other commercially available software, B\textsubscript{2}O\textsubscript{3}-Nd\textsubscript{2}O\textsubscript{3} system in Figure 2 is considered to understand the slag melting behaviour [12]. The binary oxide system has a liquidus at two regions of approximately at 1250 °C and 1120 °C, respectively. Therefore, B\textsubscript{2}O\textsubscript{3} was chosen as fluxing agent to be added to the pellet to produce a liquid slag of Nd\textsubscript{2}O\textsubscript{3}-B\textsubscript{2}O\textsubscript{3} through Equation (2).

\[
\text{Nd}_{2}\text{Fe}_{14}\text{B}_{(s)} + \text{Fe}_{2}\text{O}_{3(s)} + \text{B}_{2}\text{O}_{3(s)} \rightarrow \text{Nd}_{2}\text{O}_{3(l)} + \text{B}_{2}\text{O}_{3(l)} + \text{Fe}_{16}\text{B}_{(l)} \quad (2)
\]

### 3.2.1. HMTA studies

To understand melting characteristics of the mixture samples, heating microscopy studies were conducted with varying B\textsubscript{2}O\textsubscript{3} amount for the slag formation. Table 2 shows the effect of B\textsubscript{2}O\textsubscript{3} amount on flow temperature of samples. If the sample height is decreased to one-third of its initial height, that would mean the mixture has reached its flow (melting) temperature. The software determines and records the flow temperature as the first temperature when this requirement is met. The flow temperature obtained at first low melting region of Nd\textsubscript{2}O\textsubscript{3}-B\textsubscript{2}O\textsubscript{3} binary system in Figure 2 (at ~1250 °C with 15 wt% B\textsubscript{2}O\textsubscript{3}) is recorded at more than 1400 °C and the second low melting region (~1120 °C) is recorded above 1350 °C for the actual magnet mixtures. This discrepancy in the temperature with the phase diagram may be due to presence of REEs other than Nd and presence of other elements present in the magnet, which can alter the melting point of the slag. The mixture sample with 45% B\textsubscript{2}O\textsubscript{3} shows the flow temperature at

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Figure 5. Binary phase diagram of the Fe-C system
1372 °C. This composition was used for the smelting and slag-metal separation. The flow temperature of different samples is depicted in Figure 6 for further details.

**Table 2. Geometrical changes of the samples during heating microscope study before (left) and after (right) heating:** Slag composition of the samples from top to bottom, S1) 9%B$_2$O$_3$−91%RE$_2$O$_3$, S2) 11%B$_2$O$_3$−89%RE$_2$O$_3$, S3) 14%B$_2$O$_3$−86%RE$_2$O$_3$, S4) 38%B$_2$O$_3$−62%RE$_2$O$_3$ and S5) 40%B$_2$O$_3$−60%RE$_2$O$_3$.
3.2.2. Smelting studies

Smelting and slag-metal separation studies were conducted for cerium rich magnets in a horizontal tubular furnace under Argon atmosphere. Initial smelting experiment was conducted with 45 wt% $B_2O_3$ and stoichiometric $Fe_2O_3$ addition according to the equation 2. The sample could be melted partially and there was no clear slag-metal separation as seen in Figure 6, as there were still slag portion attached to the alloy. The SEM-EDS analysis of the slag sample in the same figure shows presence of FeO in the REE-rich slag.

Figure 6. Photograph and SEM-EDS analysis of cerium rich magnet with stoichiometric $Fe_2O_3$ and 45 wt% $B_2O_3$ in the slag

According to the Ellingham diagram depicted in Figure 5, the reduction of $Fe_2O_3$ by elemental boron is thermodynamically feasible. However, the low reactivity of boron within the magnet alloy limits its effectiveness in participating in the reduction reaction. This limitation was
confirmed through XRD analysis of the iron alloy, which shows the presence of boron (XRD image). As boron fails to efficiently reduce Fe₂O₃, a portion of FeO is generated and reports to the slag phase. Consequently, the composition of the slag is altered, resulting in an increased melting point and hinders the separation of the slag from the metal. In order to overcome this issue, further investigations were conducted to reduce the initial Fe₂O₃ content in the sample.

Figure 7. shows SEM-EDS analysis of the slag sample after the addition of 0.8 times the stoichiometric need of Fe₂O₃. It shows a clear slag-metal separation with EDS analysis confirming no iron presence in the slag phase and no rare earths in the metallic phase. On further decrease in the added Fe₂O₃ content in the sample there is once again no clear slag-metal separation as shown in Figure 8. That is due to the change in the chemistry of metallic and slag phases resulting in no separation once again. SEM-EDS analysis of 0.6 stoichiometric Fe₂O₃ sample gives the presence of rare earths in the metallic phase which reduces the REEs concentration in the slag phase.

![Images of the sample and EDS analysis of (a) metal (b) slag sample of the cerium rich magnet with 0.8 stoichiometric Fe₂O₃ and 45 wt% B₂O₃ addition](https://doi.org/10.26434/chemrxiv-2023-zlb7d)
Figure 8. Photograph and SEM-EDS analysis of cerium rich magnet with 0.6 stoichiometric Fe₂O₃ and 45 wt% B₂O₃ in the slag.

Similar smelting studies were conducted for NdFeB magnets with addition of 45 wt% B₂O₃ and varying Fe₂O₃ content. It was observed that at about 0.8 stoichiometric amount of Fe₂O₃, a clear slag-metal separation was observed as shown in the Figure 9.
Figure 9. Photograph and SEM-EDX analysis of NdFeB magnet with 0.8 stoichiometric Fe$_2$O$_3$ and 45 wt% B$_2$O$_3$ in the slag (a) metal (b) slag

3.3 Leaching and REEs recovery studies

After smelting, the slag sample was ground to -90 µm size and leached with 2N sulphuric acid solution at 90 °C for 4 h. The sample was completely soluble during leaching. Rare earths were selectively recovered as double sulphates by sodium sulphate addition. The sulphate precipitate after washing and drying was analysed with SEM and XRD (Figure X). The XRD analysis shows only the peaks RE double sulphates in Figure 10. These double sulphates were further treated with NaOH to remove sodium and precipitate RE oxide/hydroxides selectively using conventional process and analysed by XRD. XRD result shows the presence RE oxide and hydroxide which is shown in Figure 11. The filter after the removal of RE double sulphates is subjected to evaporation crystallisation to recover boric acid. The recovered boric acid was analysed with XRD, which is shown in the Figure 12.
Figure 10. XRD pattern of RE double sulphate

Figure 11. XRD pattern of RE oxide/hydroxide obtained from RE double sulphate
4. Conclusion

An energy efficient pyrometallurgical process for the selective recovery of iron in the form of an alloy and REEs in the form of slag was developed for recycling of discarded permanent magnets containing REEs. The process flowsheet is given in Figure 13. The process consists of selective oxidation of REEs from magnet for selective separation of iron and REEs. The waste magnets were initially subjected to ball milling to make fine powders. Melting behaviour of the magnet powder (with the addition of B$_2$O$_3$ and Fe$_2$O$_3$) was first studied HMTA. The sample composition with low melting point was further investigated in a tubular furnace for slag-metal separation. The slag generated from the process was subsequently ground and leached with sulphuric acid. The REEs present in the solution was selectively recovered by double sulphate precipitation. Boron was recovered by evaporation and crystallisation as boric acid. It was found that at stoichiometric Fe$_2$O$_3$, some amount of FeO is reporting to slag which affects the slag-metal separation. No REEs in the metallic phase and no iron in the slag phase was detected when the slag was mixed with 0.8 stoichiometric Fe$_2$O$_3$ and 45 wt% B$_2$O$_3$ amount. The results obtained with cerium rich magnets were successfully reproduced with NdFeB magnets.

Figure 13
Acknowledgements

SERB

References


[9] Y. Bian *et al.*, “RECOVERY OF RARE EARTH ELEMENTS FROM NDFEB MAGNET SCRAPS BY PYROMETALLURGICAL PROCESSES.”

