



Microwave Exposure of Discarded Hard Disc Drive Magnets for Recovery of Rare Earth Values

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The recovery of rare earth elements from discarded electronic waste is gaining considerable interest due to the shortage of primary resources. NdFeB permanent magnets were collected from discarded hard disc drives and consist of ~ 28% rare earth values along with 65% Fe in the form of the Nd₂Fe₁₄B phase. The magnets were demagnetized, crushed and exposed to microwave irradiation for a predetermined time. It was found that, within 1.2 min of microwave exposure, significant oxidation and a temperature of ~ 600°C was attained. Recovery from the microwave-exposed product was carried out by the leaching and precipitation route. Iron values were recovered in the form of metallic iron and iron oxide in the leach residue. The process adopted is very short and yielded 56% recovery of Nd and Dy oxides with a purity of more than 98%.

INTRODUCTION

Neodymium-iron-boron (NdFeB) permanent magnets are preferred over ferrite and SmCo magnets owing to their high volume minimization and Curie temperature.¹ Rare earth elements (REEs)-based permanent magnets are of crucial importance for technological advancements and find application in small electronic devices (hard disc drives, music players, laptop,s and cell phones), and large industrial applications (electric vehicles, wind turbines, magnetic cooling).^{1–5} In general, a NdFeB magnet consists of around 25–35% REE (Nd, Dy, Pr), 1% B and the rest Fe. The addition of Dy, Tb, Nd, Co, and Al allows for the modification of the magnetic and physical properties.⁶ Hard disc drives are the single largest consumer of NdFeB magnets, with an annual production of about 600 million units. Allowing for about 10–20 g of magnet per hard disc drive, 6000–12,000 tons of NdFeB alloy is consumed annually.⁷

The major natural raw material for REEs includes monazite, xenotime, bastnasite and phosphate rock deposits. The REEs being chemically similar to each other invariably occur together in the ores, and the minimum industrial grade of REE ores varies from 0.15% to 2%. The extraction of REEs from the primary ores includes multiple processing steps such as mineral beneficiation,

leaching, fractional crystallization, ion exchange, precipitation, solvent extraction, and subsequent reduction to metals.^{8,9} The instabilities in the supply chain of REEs, especially Nd and Dy, and their increasing demand call for alternative supplies of these strategic raw materials.^{1–3,5,10}

Until now, there have been no commercial efforts in the recovery of REEs from end-of-life products, especially NdFeB magnets of hard disc drives. This can be attributed to the fact that these magnets end up in informal recycling and hence are not considered as a potential source. The REE content in a NdFeB magnet is significantly higher than natural occurring deposits and make up more than 25% of the feed compared to 0.15–2% in the primary ores.^{1,9,10} In fact, magnets from end-of-life consumer instruments can be considered as a potential source of REEs.^{5,7} From metallurgical aspects, there are various possibilities to recover the REEs from discarded NdFeB magnets, including the use of magnesium for Nd dissolution in the inert atmosphere,¹¹ hydrometallurgical,^{4,12–16} and pyrometallurgical routes,^{3,7,17–23} and dissociation in a hydrogen atmosphere.²⁴ The hydrometallurgy route involves the complete dissolution of the magnet values in acid, and iron dissolution along with REE values makes the further extraction difficult and expensive. Oxidative roasting prior to leaching provides an aid to separate Fe values.^{15,16} Oxidative

roasting of NdFeB magnets results in the transformation of all the elements present to their respective oxide (Fe_2O_3 , Nd_2O_3 , Dy_2O_3), and Fe_2O_3 being insoluble in acid is separated as a residue during the leaching step. However, this process involves significant heating, i.e., to 900°C for 6–15 h in a conventional muffle furnace followed by leaching in 0.5M HCl for 5 h.¹⁵ Pyro-metallurgical routes are generally energy-intensive since they include higher reaction temperatures and time (1000–1500 $^\circ\text{C}$, 6–24 h) along with excessive flux dosage (Si, Ti, C, B_2O_2 , Mg). Considering that iron phases are susceptible to microwave irradiation for further iron enrichment, it was therefore envisaged that microwaves can specifically target iron values and may enhance the recovery of REE values from the NdFeB phase. Microwave heating offers a number of advantages over conventional heating. Microwaves offer selective volumetric heating of ferrous minerals and the formation of a hematite phase in magnets results in high microwave susceptibility which results in a very rapid heating rate. This significantly reduces the energy consumption and makes the process energy-efficient.²⁵ The objectives of this study for the recovery of REE values from discarded hard disc drive magnets include: (1) the effect of microwaves on the recovery of RE values (Nd, Dy), (2) the evaluation of phase changes during microwave exposure, (3) a leaching and precipitation study, and (4) the recovery of REE from the leach solution.

MATERIALS AND METHODS

Feed Preparation and Characterization

The REE magnets used in this study were collected from end-of-life hard disc drives of desktop computers of different manufacturers. The Curie temperature of NdFeB magnets is around 312°C ,^{6,9} therefore, the samples were demagnetized at 350°C for 1 h in a muffle furnace and were further pulverized using a mortar and pestle to obtain a magnet powder with a particle size below $100\ \mu\text{m}$. The elemental composition of the pulverized magnets was determined using x-ray fluorescence (XRF) technique (Rigaku Supermini 200). The morphology of the powder sample was studied by scanning electron microscopy (SEM) with an attached electron dispersive x-ray technique (EDS) (Fe-SEM; Zeiss EVO18). The x-ray diffraction study of the sample was carried out by an x-ray diffractometer (XRD; Rigaku Smart Lab) using $\text{Cu-K}\alpha$ radiation. The diffraction peaks were recorded in the 2θ range of 10° – 90° with a step size of 0.02° and a scanning rate of $2^\circ/\text{min}$ to identify the different phases. The quantitative phase analysis of the powder sample was carried out by assuming all the peaks are a triangle and that the respective peak area reflects the amount of phase present. The amount of any phase (i) was calculated by the formula, % of phase = A_i/A , where A_i is the area of the peak of a

particular phase (i) and A is the total area of all the peaks. Thermo-gravimetric analysis (TGA) of the sample was carried out in a temperature range of 20 – 1150°C in an air atmosphere with a flow rate of $200\ \text{ml}/\text{min}$ and heating rate of $10^\circ/\text{min}$ to check the effect of temperature on the oxidative character of the magnets. The magnetic character of the sample was studied using a vibratory sample magnetometer.

Microwave Exposure and REE Extraction

The complete experimental flowsheet adopted in this study is shown in Fig. 1. The pulverized NdFeB magnet was placed inside a refractory grade crucible in a 900-W microwave (LG model) for a pre-determined time and was then cooled to room temperature in air atmosphere. It is important to mention that temperature measurement is a tedious task during microwave irradiation because an external probe (metallic thermocouple) can also cause significant interference with the microwaves. Therefore, immediately after exposure, the surface temperature was determined using an infrared thermometer (Extech model). The treated magnet was further leached in 0.5M HCl to dissolve the associated Nd and Dy values. The leaching experiments were carried out in a 250-mL glass beaker using a magnetic stirrer (C-Mag HS-7, IKA) at 70°C with a solid–liquid ratio and a stirring speed of 1:25 (g/ml) and 900 rpm, respectively. The leaching parameters were selected based on the literature.¹⁵ The subsequent leach residue was separated from the leach solution by vacuum filtration and was oven-dried at 110°C . Two fractions of the leach residue were obtained, i.e., from filtration (non-magnetic) and from magnetic beads (magnetic). The leach solution was further processed for REE precipitation using stoichiometric oxalic acid (0.015 g/ml). The precipitation process was carried out with a continuous magnetic stirring at 600 rpm for 20 min at 70°C . The obtained precipitates were further heated in a muffle furnace at 900°C for 1 h to obtain rare earth oxides (REO). The corresponding REE extraction was calculated using Eq. 1.

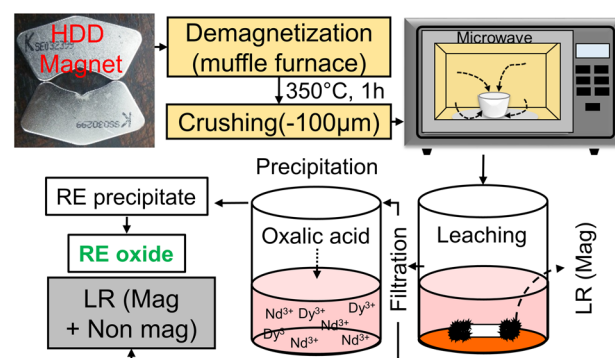


Fig. 1. Experimental flowsheet followed in the study.

$$\% \text{REO extraction} = \frac{(W_{\text{REO}} \times \% \text{REE}_{\text{REO}}) \div (W_{\text{FEED}} \times \% \text{REE}_{\text{FEED}})}{\times 100} \quad (1)$$

where W_{FEED} and W_{REO} represent the weight of feed in the leaching and the weight of REO obtained, respectively, and $\% \text{REE}_{\text{FEED}}$ and $\% \text{REE}_{\text{REO}}$ represent the percentage of REE values in the feed and the product, respectively.

RESULTS AND DISCUSSION

Material Characterization

The elemental composition of the crushed magnet is shown in Fig. 2a. The feed sample consists of 28% REE values along with 65% Fe. The XRD analysis is shown in Fig. 2a and reveals that the REE values are present in the form of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase. The TGA of the feed shown in Fig. 2b reveals a weight gain of $\sim 35\%$, which is due to the oxidation reaction which corresponds to the formation of Fe_2O_3 and Nd_2O_3 . However, the complete oxidation of $\text{Nd}_2\text{Fe}_{14}\text{B}$ into Fe_2O_3 and Nd_2O_3 requires extended heating (~ 6 h) in a muffle furnace which is expensive and time-consuming.¹⁵ The SEM micrograph of the crushed magnet shown in Fig. 2c reveals a strong solid surface with no porosity. EDS analyses of a certain area are very close to the XRF analysis, indicating compositional homogeneity. Hysteresis loop analysis of the crushed NdFeB magnet revealed saturation magnetization of ~ 120 emu/g and bulk remnant magnetization of ~ 9000 G. In general, NdFeB-based magnets demonstrate a strong hard-magnetic behavior due to bulk remnant

magnetization, and coercivity in the range of 1000–14000 G.²¹ Considering the significant presence of Fe values in the magnet, the potential use of microwaves was investigated. Therefore, the feed sample was exposed to microwave irradiation for a predetermined time to evaluate the effect on REE recovery. It has been widely reported that the $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase decomposes into α -Fe, Fe_2B , and Nd_2O_3 in oxygen according to Eqs. 2–4. The ΔG° variations with temperature (227–1227°C) for the formation of oxide compounds of Nd ($\text{Nd} \rightarrow \text{Nd}_2\text{O}_3$), Dy ($\text{Dy} \rightarrow \text{Dy}_2\text{O}_3$), Fe ($\text{Fe} \rightarrow \text{Fe}_2\text{O}_3$), and NdFeO_3 are shown in Fig. 3.⁷ It can be seen that ΔG° formation of REO is more negative than that of Fe_2O_3 , and therefore the formation of Nd_2O_3 and Fe takes place in the initial stage of heating according to Eq. 2. The metallic iron formed has a tendency to further oxidize according to Eq. 3; however, due to a sufficient presence of Nd_2O_3 , the formation of NdFeO_3 takes place as per reaction (4) due to the much lower value of ΔG° for NdFeO_3 in the entire temperature range.^{7,21–24}

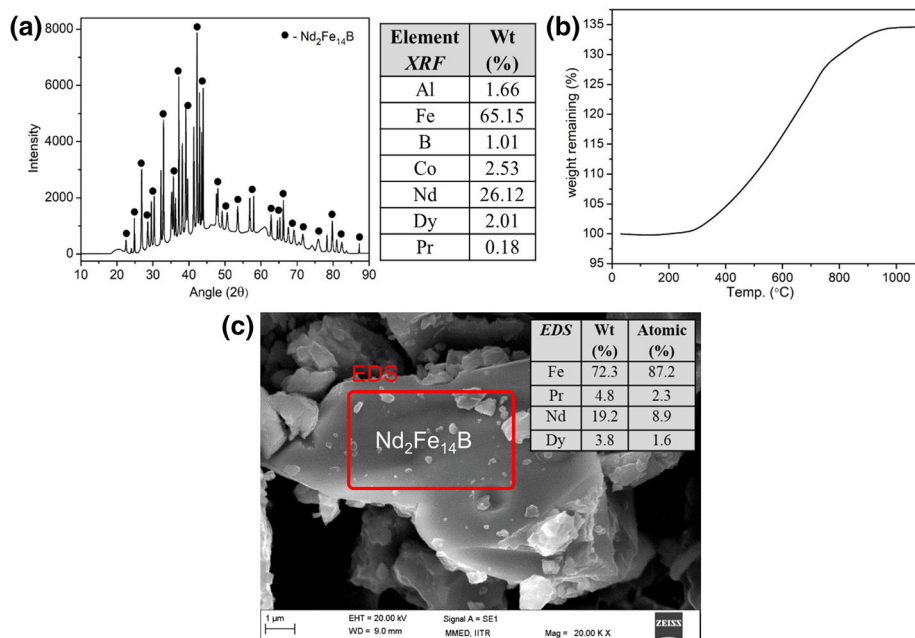
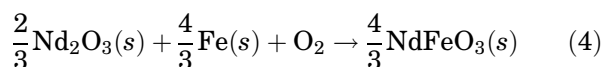
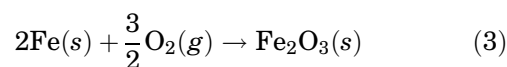
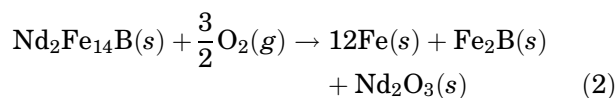


Fig. 2. NdFeB magnet characterization: (a) XRD and XRF, (b) TGA (c) SEM (EDS).

Preliminary Experiments

The crushed NdFeB magnet was heated in a muffle furnace for 6 h, and a weight gain of 34% was observed. The heated mass was further leached in 0.5M HCl for 2 and 6 h followed by precipitation

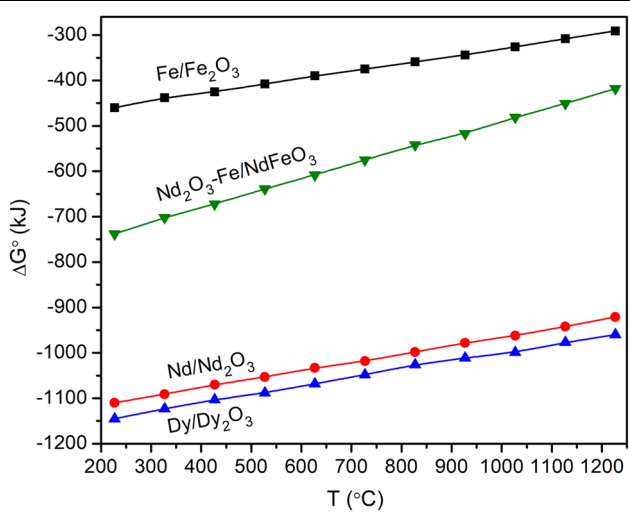


Fig. 3. ΔG° value versus temperature (227–1227°C) for different reactions.

using oxalic acid (0.015 g/ml). REE extraction of 40% and 58% was obtained at 2 and 6 h leaching, respectively. The XRD spectra of REO at 2 and 6 h leaching revealed the presence of Nd/Dy₂O₃ peaks. A similar process has been reported in the literature: with 6–14 h of heat treatment in a muffle furnace at 900–950°C, it is possible to recover more than 90% REE values from NdFeB magnets.^{15,16} These processes involve leaching in 0.5M HCl for 6 h or dissolution based on a carboxyl-functionalized ionic liquid.

Effect of Microwave Exposure

The final temperature of the sample and the weight gain for different durations of microwave exposure are shown in Fig. 4a. As expected, the temperature of ~ 600°C was attained within 1.2 min of microwave exposure. With the increase in exposure time, the surface of the sample was observed to be hard and it was difficult to insert the thermocouple for temperature monitoring. The weight gain increased to 18% with an increase in exposure time to 15 min. The XRD spectra of the microwaved product at different exposure times are shown in Fig. 4b. The major phase formed during microwave exposure was metallic Fe and Fe₂O₃ along with the release of REE values in form of oxides. Few peaks of feed were present up to 2.5 min of exposure

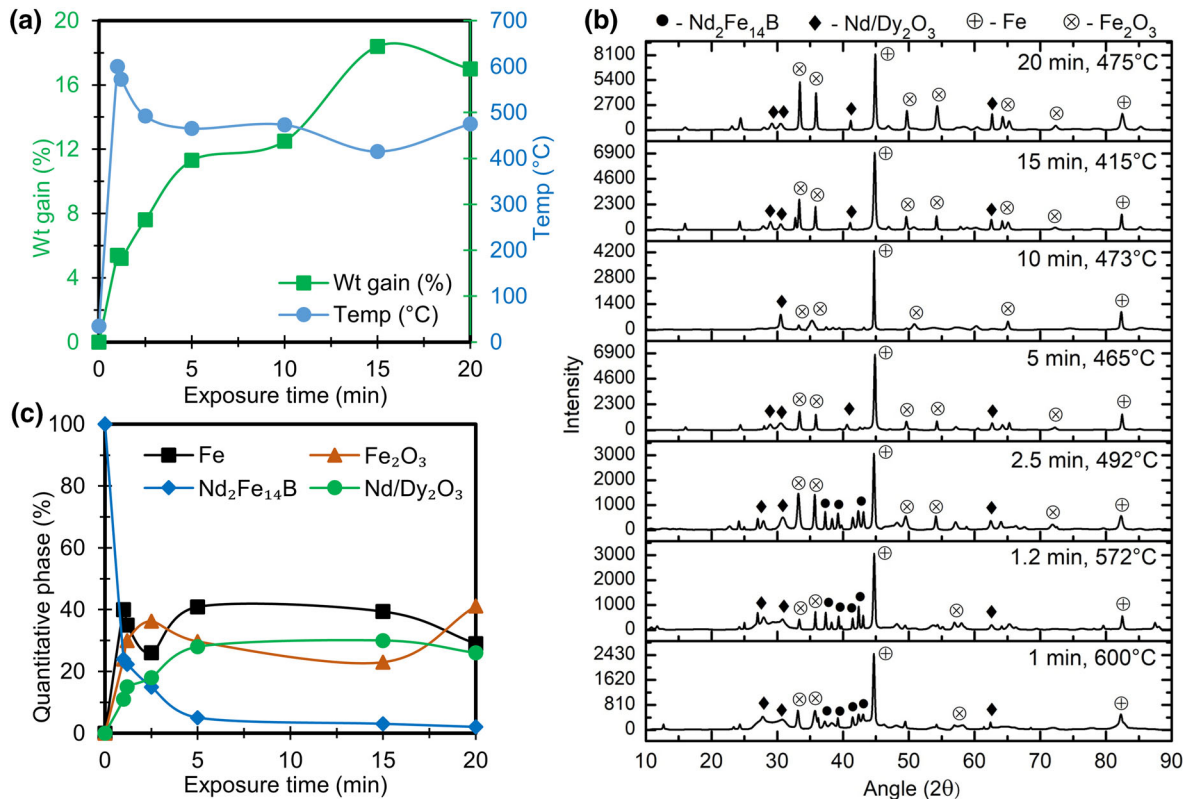


Fig. 4. Microwave product analysis. (a) Weight gain and final temperature attained (b) XRD spectra, (c) XRD quantitative phase analysis.

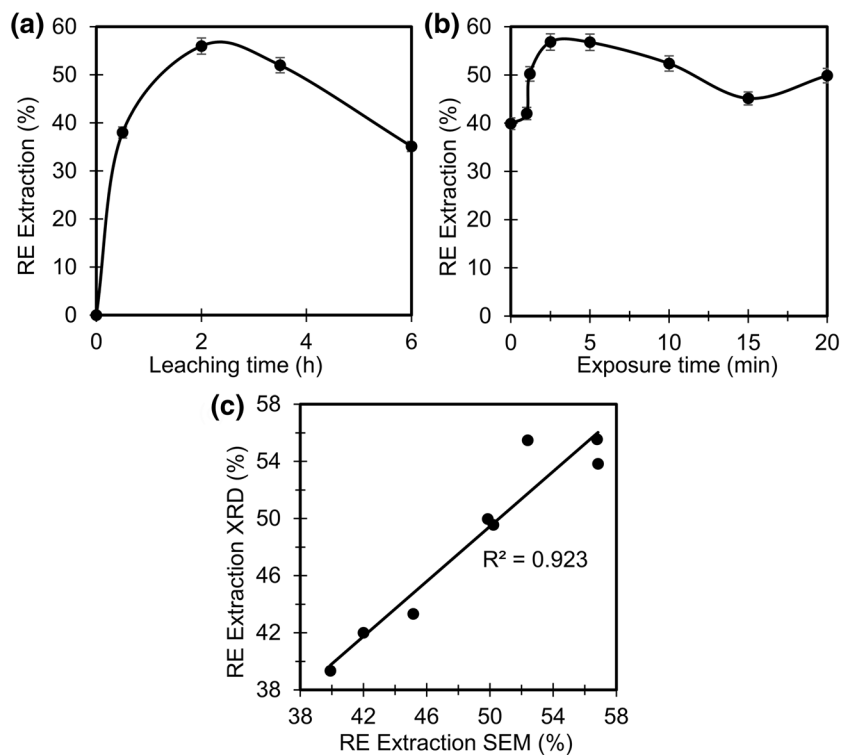


Fig. 5. Rare earth extraction: (a) different leaching time (5 min microwave exposure), (b) variable exposure time (leaching: 0.5M HCl, 2 h), (c) regression plot.

indicating incomplete conversion or oxidation. It can be observed that ferrite (metallic iron) and hematite peaks were observed for all the exposure times. Post-2.5 min, feed peaks were not observed; however, the presence of REO was evident. XRD quantitative phase analysis was also carried out, as shown in Fig. 3c. With microwave exposure of ~ 5 min, 40% Fe, 29% Fe_2O_3 , and 26% Nd/Dy $_2\text{O}_3$ phases were formed. It should be noted that higher exposure times lead to increased weight gain; however, it does not ensure the formation of pure Nd/Dy $_2\text{O}_3$, and rather it leads to the formation of NdFeO $_3$ as revealed by XRD, which is in agreement with theoretical findings. On average, with an increase in exposure time, Fe and the REO phase increase and saturate. It can be seen that the feed phase dissociates almost 80% within 1.2 min of microwave exposure. The SEM micrograph of the final product at 5 min of exposure depicts the porous nature of the magnet, indicating diffusion of oxygen into the bulk sample during the microwave exposure.

REE Extraction and Characterization

The recovery of REEs from the microwaved product was carried out by leaching in 0.5M HCl followed by precipitation using oxalic acid (0.015 g/ml). The proton destabilized the REO crystal lattice by attacking the oxygen to form water. The corresponding anion acts as a complexing ligand and

forms a Nd/DyCl $_3$ complex with the destabilized REE cation according to Eqs. 5 and 6. The pH of the solution was observed to increase from ~ 1 to ~ 5 after leaching. The reaction can proceed forward or backward depending on the concentration and solubility of the REE remaining in the residue.²⁶

Oxalic acid is an important reagent in REE chemistry because hydrated lanthanide oxalates form readily in an acidic solution in a densely crystalline and easily filtered form.²⁷ Each mole of REE oxalate formed six moles of H $^+$ ions which decrease the pH, and the corresponding reaction is shown in Eqs. 7 and 8. A pH value of ~ 1 was maintained during the precipitation process and the dosage of oxalic acid was kept to more than the stoichiometric amount due to the presence of other non-REE species, such as Fe $^{3+}$. Thermal decomposition of these oxalates yields oxides and is the most common form of these elements.

The 5-min microwave-treated product was leached in 0.5M HCl for the different durations and corresponding extractions, as shown in Fig. 5a. Almost 56% REE extraction was achieved after 2 h of leaching. Fe_2O_3 being insoluble in acid stays in the leach residue whereas some part of Fe dissolves during leaching and, with an increase in leaching duration, Fe also leaches out, which restricts the precipitation process. The REE extraction at 2 h of leaching in 0.5M HCl is shown in Fig. 5b. The extraction reached $\sim 55\%$ after 2.5 min of exposure

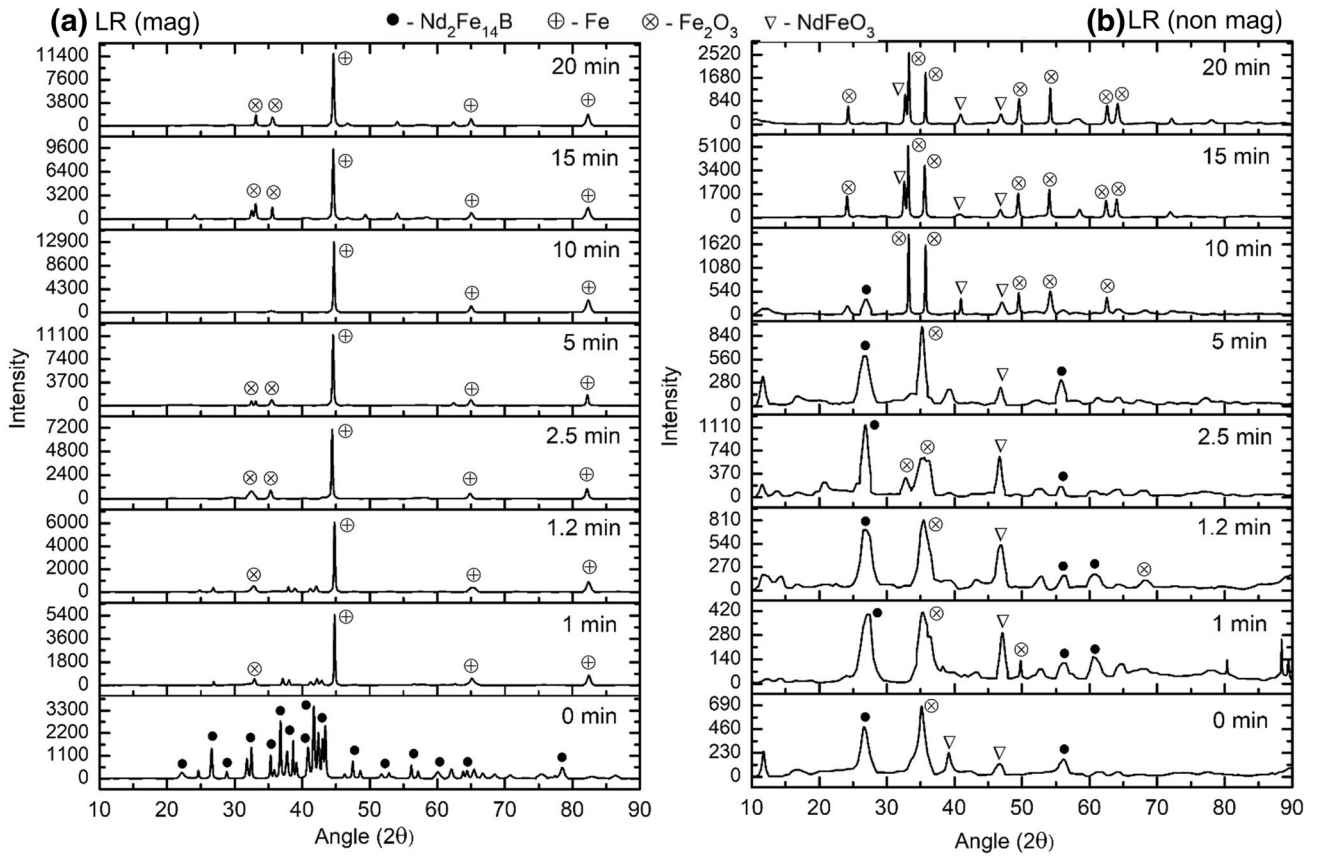


Fig. 6. XRD spectra of leach residue: (a) magnetic fraction, (b) non-magnetic fraction.



Fig. 7. Sample specimen photographs at different stages of treatment.

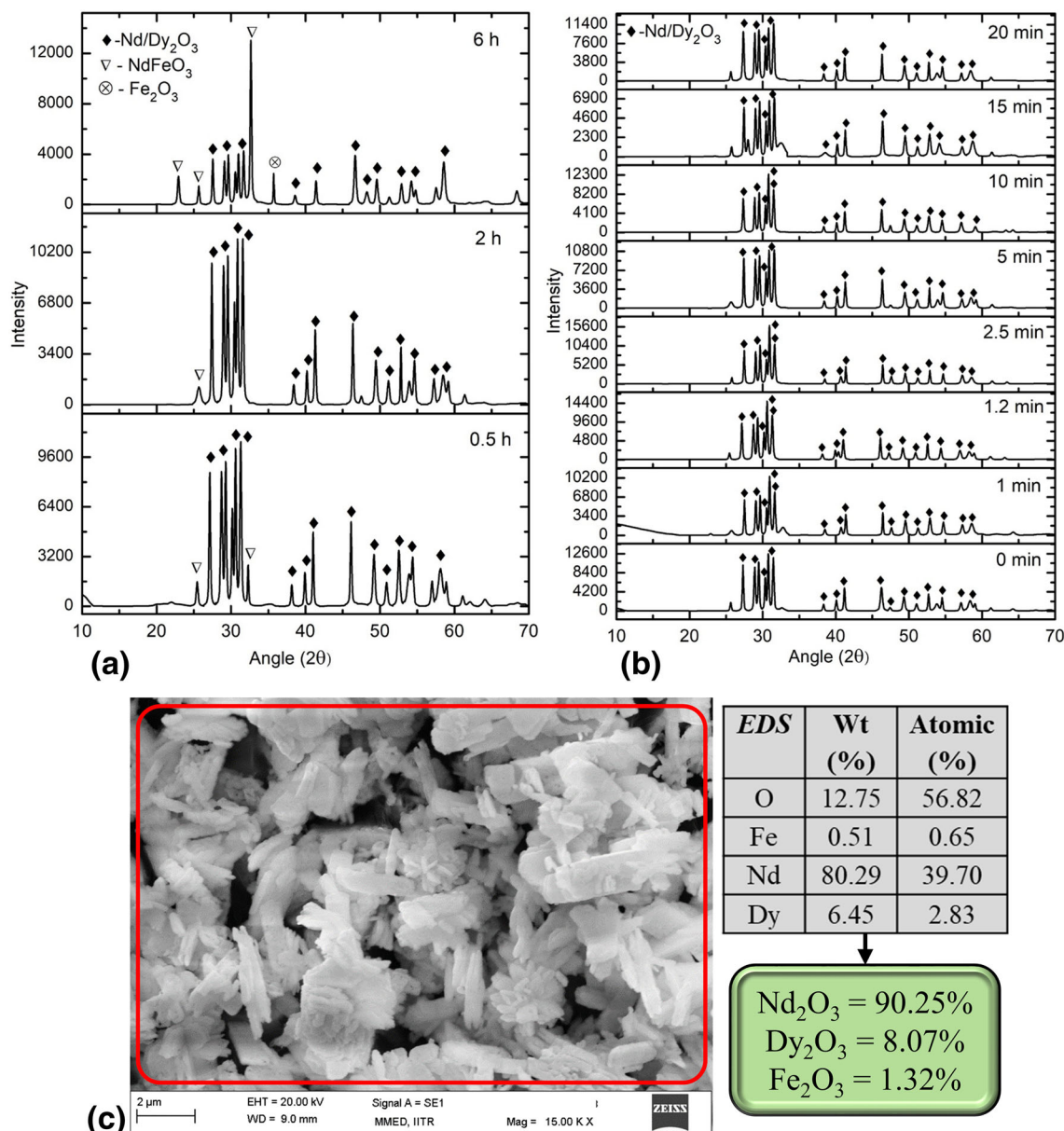
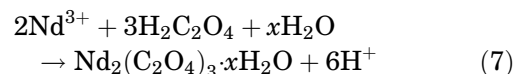
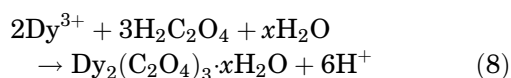


Fig. 8. REO characterization. (a) XRD spectra at variable leaching time (5 min microwave), (b) XRD spectra at variable microwave exposure (2 h leaching), (c) SEM (EDS) analysis (2.5 min exposure, 2 h leaching).

and was found to be constant up to 5 min, and then further decreased with increasing time duration. The REE extraction was also calculated from quantitative XRD phase analysis of the REO product, and the corresponding correlation plot between the extraction % obtained from EDS and XRD is shown in Fig. 5c. The regression coefficient value (R^2) of 0.923 reflects that the extraction % obtained from EDS is almost consistent with XRD analysis. As shown in Fig. 6, the magnetic leach residue consists of Fe as the major phase and the non-magnetic leach residue showed an amorphous character up to 5 min of exposure. NdFeO₃ was observed in the non-magnetic leach residue of higher exposure times

(> 10 min exposure) which hinders the REE release during leaching. With increasing exposure time, the formation of NdFeO₃ was found to be dominant which encapsulates the Nd values. The sample specimen photographs at different stages of the treatment are shown in Fig. 7.





The XRD spectra of the final REO product at variable leaching times are shown in Fig. 8a. At 6 h of leaching, Fe dissolution was enhanced and iron oxalate was formed during precipitation. Also, the precipitates were yellow in color indicating the presence of iron oxalate. The XRD spectra at different microwave exposure times (1 min, 1.2 min, 2.5 min, 5 min, 10 min, 15 min, and 20 min), and 2 h of leaching, shown in Fig. 8b, reveals the presence of Nd/Dy₂O₃ peaks. The SEM (EDS) analysis of REO at 2.5 min exposure and 2 h of leaching is shown in Fig. 8c, and the product consists of a mixed oxide of neodymium and dysprosium with > 98% purity.

CONCLUSION

The crushed hard disc drive magnets used in this study consist of 28% Nd and Dy values along with 65% Fe in the form of the Nd₂Fe₁₄B phase. During microwave exposure, a temperature of ~ 600°C was attained within 1.2 min. The recovery of REE from the microwaved product through the leaching–precipitation route (0.5M HCl for 2 h, 0.015 g/ml oxalic acid) yielded approximately 56% REO. The formation of the NdFeO₃ phase was dominant at higher microwave exposure times leading to the partial release of REE values. The present process of microwave exposure, leaching and precipitation is short (~ 2.5 min exposure), and can be employed to recover REE oxides with a purity of more than 98% along with the recovery of iron. Compared to oxidation in a conventional muffle furnace (900°C for 6 h) where approximately 58% REE values were recovered after 6 h leaching in 0.5M HCl, the microwave process adopted in this study is less time-consuming and a high temperature (600°C) is achieved in the very short interval of 1.2 min.

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