# Recycling of Sintered NdFeB Magnet Waste via Oxidative Roasting and Selective Leaching

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Abstract-Neodymium-iron-boron (NdFeB) magnets classified as high-power magnets are widely used in various applications such as automotive, electrical and medical devices. Because significant amounts of rare earth metals will be subjected to shortages in the future, therefore domestic NdFeB magnet waste recycling should therefore be developed in order to reduce social and environmental impacts towards a circular economy. Each type of wastes has different characteristics and compositions. As a result, these directly affect recycling efficiency as well as types and purity of the recyclable products. This research, therefore, focused on the recycling of manufacturing NdFeB magnet waste obtained from the sintering stage of magnet production and the waste contained 23.6% Nd, 60.3% Fe and 0.261% B in order to recover high purity neodymium oxide (Nd<sub>2</sub>O<sub>3</sub>) using hybrid metallurgical process via oxidative roasting and selective leaching techniques. The sintered NdFeB waste was first ground to under 70 mesh prior to oxidative roasting at 550-800 °C to enable selective leaching of neodymium in the subsequent leaching step using H<sub>2</sub>SO<sub>4</sub> at 2.5 M over 24 h. The leachate was then subjected to drying and roasting at 700-800 °C prior to precipitation by oxalic acid and calcination to obtain Nd2O3 as the recycling product. According to XRD analyses, it was found that increasing oxidative roasting temperature led to an increasing amount of hematite (Fe<sub>2</sub>O<sub>3</sub>) as the main composition with a smaller amount of magnetite (Fe<sub>3</sub>O<sub>4</sub>) found. Peaks of Nd<sub>2</sub>O<sub>3</sub> were also observed in a lesser amount. Furthermore, neodymium iron oxide (NdFeO3) was present and its XRD peaks were pronounced at higher oxidative roasting temperatures. When proceeded to acid leaching and drying, iron sulfate and neodymium sulfate were mainly obtained. After the roasting step prior to water leaching, iron sulfate was converted to form Fe<sub>2</sub>O<sub>3</sub> as the main compound, while neodymium sulfate remained in the ingredient. However, a small amount of Fe<sub>3</sub>O<sub>4</sub> was still detected by XRD. The higher roasting temperature at 800 °C resulted in a greater Fe<sub>2</sub>O<sub>3</sub> to Nd<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> ratio, indicating a more effective roasting temperature. Iron oxides were subsequently water leached and filtered out while the solution contained mainly neodymium sulfate. Therefore, low oxidative roasting temperature not exceeding 600 °C followed by acid leaching and roasting at 800 °C gave the optimum condition for further steps of precipitation and calcination to finally achieve Nd<sub>2</sub>O<sub>3</sub>.

*Keywords*—NdFeB magnet waste, oxidative roasting, recycling, selective leaching.

## I. INTRODUCTION

**R**ARE earth elements are currently on increasing demands and also being predicted to be scarce in the future. Specifically, rare earth element magnets are responsible for 21% of all rare element use in terms of volume [1]. Further, among four types of permanent magnets; ferrite, NdFeB, Alnico and SmCo magnets, NdFeB magnet is commercially used in automotive, electronics, and medical industries, accounting for 13.5% of the magnet production based on weight [2]. Its hard magnetic field offers one of the most efficient permanent magnet types. The typical composition is of around 29-32% Nd, 64.2-68.5% Fe and 1-1.2% B [3]. Because the magnets contain rare earth elements such as neodymium and also praseodymium which are expensive and unexpendable, disposal of such magnet wastes is uneconomical and environmentally harmful. Recycling of NdFeB magnet wastes is therefore in necessity towards circular economy.

There are two types of NdFeB magnet wastes; i) one generated from manufacturing process such as in magnet powder manufacturing, after sintering process, in assembly line, etc., and ii) one obtained after uses or end of life (EOL) products. In manufacturing process particularly in the sintering step, 30% of sintered NdFeB magnets turn into wastes in the powder and solid forms [2]. This might be due to contamination such as high carbon content, undesirable shapes and sizes, fractured or cracked parts, etc. Reusing these sintered wastes back in the process might cause contamination that reduce the magnetic strength and so on. This research therefore focused on recycling of this sintered NdFeB manufacturing waste via pyrohydro metallurgical process in order to recover neodymium in the form of oxide.

Recycling of neodymium stemmed from the extraction of rare earth (Nd) from Bayan Obo, China based on a mixed bastnaesite and monazite raw ores [3]. The process can be simplified as crushing & grinding, magnetic separation, sulfatizing roasting, prior to hydrometallurgy process consisting solvent extraction and precipitation, along with calcination to obtain Nd<sub>2</sub>O<sub>3</sub>. The oxide will then be subjected to electrolysis to finally achieve neodymium metal for reuse or resale back in the market. Önal et al. [4] investigated recycling of NdFeB magnet waste using sulfation using 14.5 M H<sub>2</sub>SO<sub>4</sub>, selective roasting at 750 °C and water leaching, leachate of about 98% REM (Nd, Dy, Pr, Gd, Tb and Eu) purity while Fe remained as marketable Fe<sub>2</sub>O<sub>3</sub>. Rabatho et al. [5] recovered Nd and Dy from manufacturing rare earth magnet waste sludge by hydrometallurgy process using 1 M HNO<sub>3</sub> plus H<sub>2</sub>O<sub>2</sub> as an oxidant, followed by Fe precipitation using NaOH at pH 3 to get rid of iron prior to precipitation by oxalic acid and calcination at 800 °C to obtain Nd<sub>2</sub>O<sub>3</sub> of 68% purity, with 69.7% recovery of Nd and 51% recovery of Dy. Investigation

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on calcination of neodymium oxalate using TGA-DSC under argon by [6] also confirmed the calcination temperature to obtain Nd<sub>2</sub>O<sub>3</sub> is up to 850 °C. The oxidative roasting - selective leaching was also studied by [7] and [8]. The magnet waste made into the powder form is first oxidative roasting to convert iron into iron oxides. This will later aid the selective leaching of neodymium in before going through further step of precipitation and calcination. The oxidative roasting temperature was found effective in the range of 700-800 °C [8] prior to leaching using HCl, while [9] showed that at oxidative temperature higher than 800°C results in NdFeO3 which is difficult to leach. Therefore, this research applied the oxidative roasting - selective leaching using H<sub>2</sub>SO<sub>4</sub>, followed by roasting, water leaching, oxalic acid precipitation and calcination to recover Nd<sub>2</sub>O<sub>3</sub> as the final product from the sintered NdFeB manufacturing waste with high carbon. The effects of oxidative roasting temperature and roasting temperature on Nd<sub>2</sub>O<sub>3</sub> purity were studied.

#### II. EXPERIMENTAL

#### A. Materials

The sintered NdFeB waste was obtained from manufacturing process in a bulk form. Its composition analyzed by Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) consisted of 59.81 wt.% Fe and 23.97 wt.% Nd as shown in Table I and its X-Ray Diffraction (XRD) pattern indicating Nd<sub>2</sub>Fe<sub>14</sub>B as the main phase, as demonstrated in Fig. 1. Carbon was also detected as contaminant.



Fig. 1 XRD pattern of the sintered NdFeB waste.

TABLE I								
	CHEMICAL COMPOSITION OF NDFEB MAGNETS WASTE BY ICP-OES							
	Element	Fe	Nd	Pr	В	Dy	Other	
	wt.%	59.81	23.97	7.124	0.261	0.062	balance	

## **B.** Recycling Process

Oxidative roasting and selective leaching techniques were selected as the key recycling route for the obtained NdFeB waste as illustrated in Fig. 2. In the primary step of waste preparation, the bulk NdFeB magnet was crushed to under 70 mesh (212  $\mu$ m) prior to oxidative roasting in a muffle furnace at 550, 600, 700 and 800 °C for 1 h. After oxidative roasting, water rinsing was carried out to remove iron oxide before leaching with 2.5 M sulfuric acid (solid/liquid ratio of 1:10 g.ml<sup>-1</sup>) at room temperature for 24 h. The leached solution was

filtered and left to dry on a hot plate at 110 °C. In the secondary step, roasting was done at 700 and 800 °C for 2 h prior to water leaching to remove iron oxide. The obtained RE solution was subjected to precipitation using oxalic acid. Finally, calcination at 800, 900, 1000 and 1100 °C was carried out to obtain  $Nd_2O_3$  as the recycling product.



Fig. 2 NdFeB magnets waste recycling process flow chart

### C. Characterization

Chemical composition of the sintered NdFeB waste was characterized by ICP-OES model optima 8000. XRD analysis was operated using model D2 Phaser to confirm the products obtained from each step.







Fig. 3 XRD pattern of oxidative roasting at various temperatures.

Result on XRD after oxidative roasting at 550, 600, 700, and 800 °C is illustrated in Fig. 3. The intensity of  $Fe_2O_3$  and  $Fe_3O_4$  peaks increases as the temperature rises. NdFeO<sub>3</sub> peaks are also

enhanced by increasing temperature, but in a lesser extent. However, the presence of NdFeO<sub>3</sub> could result in a reduction in leaching efficiency in the later step. Nd<sub>2</sub>O<sub>3</sub> peaks are also detected and with the remained carbon in relatively small amount.



Fig. 4 EDS mapping of NdFeB after oxidative roasting at 600 °C



Fig. 5 XRD patterns after leaching process of oxidative roasted powder at 550-800 °C



Fig. 6 XRD patterns after selective leaching showing effects of water rinsing following oxidative roasting at 600 °C

SEM and EDS analyses of NdFeB after oxidative roasting at 600 °C are shown in Fig. 4. Large and fine particles are

generally iron, neodymium, and oxygen concentrations, corresponding to the XRD results previously stated in Fig. 2.

#### B. Selective Leaching

The effect of oxidative roasting temperature on the leaching efficiency by using 2.5 M H<sub>2</sub>SO<sub>4</sub> for 24 h is shown in XRD analysis in Fig. 5. H<sub>2</sub>SO<sub>4</sub> leaching gave Nd<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> and Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> as the main phases when oxidative roasting was carried out at 600-800 °C. Lower oxidative roasting at 550 °C however seemed to give lesser amounts of Nd<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> and Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> while the Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub> are evident. It is noted that the presence of NdFeO<sub>3</sub> still remained and it is known not to be readily leached by H<sub>2</sub>SO<sub>4</sub>. This phase appeared more apparent when oxidative roasting was applied at high temperatures of 700 and 800 °C. Therefore, 600 °C oxidative roasting temperature is preferred. Furthermore, effect of water rinsing after oxidative roasting at 600 °C on selective leaching was also studied. Greater intensity of Nd<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> peaks were detected when water rinsing was applied after oxidative roasting in comparison to that without water rinsing as depicted in XRD patterns in Fig. 6. Without water rinsing, there are NdFeO3 peaks together with Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub> peaks detected. If water rinsing was applied after oxidative roasting, the Fe<sub>3</sub>O<sub>4</sub> could be rinsed off as it is water soluble. Therefore, no Fe<sub>3</sub>O<sub>4</sub> peak was observed from XRD obtained from the leached sample when water rinsing was applied after oxidative roasting. It is then implied that the water rinsing step is important to get rid of some of the iron oxides. Minor phases such as sulfates of praseodymium and cobalt are difficult to detect at this step and also in the subsequent step of roasting.

### C. Roasting and Water Leaching

Since the selected oxidative roasting was at 600 °C, the XRD results after leaching and roasting at 700 and 800 °C are depicted in Fig. 7. The roasting step aimed for converting Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> into iron oxides (Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub>) that will later be get rid of after proceeding to water leaching. It is seen that Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub> peaks were increasingly observed when the roasting temperature raised from 700 to 800 °C. XRD patterns also confirmed the remaining Nd<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> as the desirable phase at both roasting temperatures. It is noted that  $Fe_2(SO_4)_3$  still remained after roasting at 700 °C while roasting at 800°C did not give Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>. After water leaching (WL) using S/L ratio at 5 g/100 ml of DI water plus stirring for 1 h, the RE sulfates dissolved back to the solution while the residue containing iron oxides were filtered and dried. XRD patterns of dried residue showed particularly Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub> phases, which means that WL can remove iron oxides after the roasting process and leave the solution containing rare earth (RE) for the next step of precipitation. Therefore, roasting at 800 °C is preferred because  $Fe_2(SO_4)_3$  has been converted to iron oxides and then removed by WL.

### D.Precipitation

After precipitation by using 1 M oxalic acid at 20 ml/100 ml RE solution till the pH reaching ~ 0.9, white oxalate precipitate was obtained. XRD patterns confirm neodymium oxalate hydrate  $(Nd_2(C_2O_4)_3 \cdot 10H_2O)$  and iron oxalate hydrate

 $(Fe(C_2O_4).2H_2O)$  peaks as the main phases as shown in Fig. 8.



Fig. 7 XRD patterns of residues after roasting at i) 700 °C, ii) 800 °C, and iii) roasting at 800 °C plus WL



Fig. 8 XRD patterns of precipitate obtained by using oxalic acid

It is noted that there are still  $Nd_2(SO_4)_3$  peaks found in smaller intensities. Therefore, the amount of oxalic acid added might not be adequate. Furthermore, the XRD results also indicated the effects of roasting temperature on phase evolution of the precipitates where the existence of  $Fe(C_2O_4).2H_2O$ seemed to be quite lower when roasting was at 800 °C in comparison to that obtained when roasting was at 700 °C. It is worth to note that up to this point, peaks of carbon still remained in the precipitates, but have been much reduced since oxidative roasting in comparison to that of the waste originally obtained. It should be noted that praseodymium oxalate hydrate was also detected where its XRD peaks co-existed where those of neodymium oxalate hydrate are.

#### E. Calcination

The final step to convert neodymium oxalate to Nd<sub>2</sub>O<sub>3</sub> is via calcination at 1000 °C for 2 h. The XRD results showed that Nd<sub>2</sub>O<sub>3</sub> was obtained as the main phase illustrated in Fig. 9. Effect of roasting temperature prior to precipitation and calcination can also be obviously seen. Roasting at 800 °C gave the calcined product with higher intensity of Nd<sub>2</sub>O<sub>3</sub> peaks in comparison to that obtained by roasting at 700 °C. Nevertheless, fairly small peaks of Nd(OH)<sub>3</sub> were detected, due to its

hydrophilic nature. Although Nd(OH)<sub>3</sub> is not the desirable phase, it can be converted to Nd<sub>2</sub>O<sub>3</sub> after calcination at temperature higher than 650 °C.



Fig. 9 XRD pattern after calcination at 1000 °C

Investigation after calcination at 1000 °C (roasting at 800 °C) under SEM showed irregular shaped Nd<sub>2</sub>O<sub>3</sub> powder of approximately finer than 5  $\mu$ m, as demonstrated in Fig. 10 (a). EDS analysis revealed Nd, Pr and O elements to be 61.65%, 16.96% and 21.39% respectively, as listed in Fig. 10 (b). When

roasting was at 700 °C, as shown in Figs. 10 (c) and (d), Fe element was observed in very small content of 0.43 wt.%, that is consistent with XRD result shown in Fig. 9 where iron oxides

still remained. Therefore, this is to confirm that calcination at 1000 °C following roasting at 800 °C is preferable.



Fig. 10 SEM - EDS results after calcination at 1000 °C with prior step of roasting at a) and b) 800 °C, c) and d) roasting at 700 °C

According to the NdFeB magnet recycling route investigated starting from 550-800 °C oxidative roasting, followed by H<sub>2</sub>SO<sub>4</sub> selective leaching, 700-800 °C roasting, then water leaching, precipitation and 1000 °C calcination, the related reactions can be further discussed at this point. After oxidative roasting when iron was converted to iron oxides then the following step of selective leaching involves related reactions as shown in (1):

$$2Nd(s)+3H_2SO_4(l) \rightarrow Nd_2(SO_4)_3(l)+3H_2(g)$$
 (1)

Iron sulfate in the form of  $Fe_2(SO_4)_3$  was also obtained at this step and was transformed into iron oxides in the form of  $Fe_2O_3$ and  $Fe_3O_4$  and be rid of in the WL process. Then oxalic acid precipitation turned neodymium sulfate into neodymium oxalate hydrate as shown in (2):

$$3Nd_2(SO_4)_3 + 3H_2C_2O_4 \rightarrow 3Nd_2(C_2O_4)_3 \cdot 10H_2O + 3H_2SO_4$$
 (2)

Finally, in the calcination step this neodymium oxalate hydrate has gone through dehydration and oxidation at higher temperature to achieve Nd<sub>2</sub>O<sub>3</sub> [6] in (3):

$$Nd_2(C_2O_4)_3 \rightarrow Nd_2(CO_3)_3 \rightarrow Nd_2O_2CO_3 \rightarrow Nd_2O_3$$
(3)

The products obtained through various reactions such as neodymium sulfate, oxalate and oxide are noted to be rather hydrophilic, then the storage is quite critical. The carbon previously present as contaminant has been much reduced. The obtained  $Nd_2O_3$  was analyzed to have around 61.65% Nd,

16.96% Pr and 21.39% O.

## IV. CONCLUSION

In summary, the sintered NdFeB waste can be recycled though oxidative roasting – selective leaching hybrid metallurgical process as follows:

- The preferred recycling route was via 600 °C/1 h oxidative roasting of under 70 mesh crushed sintered magnet wastes, followed by 2.5 M H<sub>2</sub>SO<sub>4</sub> leaching over 24 h, 800 °C/ 2 h roasting prior to precipitation by 1 M oxalic acid and 1000 °C/2 h calcination to finally obtain Nd<sub>2</sub>O<sub>3</sub> as the recycling product.
- 2) Oxidative roasting at 600 °C was effective to convert iron to iron oxides prior to selective leaching of neodymium.
- 3) Roasting at 800 °C was more effective than roasting at 700 °C in that iron sulfate is completely converted to iron oxides to be separated out in the WL step. This also led to better results in the later steps of precipitation and calcination at 1000 °C where Nd<sub>2</sub>O<sub>3</sub> of higher purity was obtained.

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