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Comparative Study of Manufacturing NdFeB Magnet Wastes Recycling: Oxidative Roasting-Selective Leaching and Whole Leaching Routes

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Abstract: This research investigated recycling of manufacturing NdFeB magnet wastes in as-sintered and powder forms which contained high carbon via pyro-hydro metallurgy process. Effects of oxidative roasting on selective leaching of the magnet wastes were the main focus in comparison to recycling via whole leaching without oxidative roasting. The process started from oxidative roasting at 600 °C, sulfuric leaching, drying, roasting at 750 °C for powder and 800 °C for sintered wastes, water leaching, oxalic acid precipitation and calcination at 1000 °C to obtain neodymium oxides. Oxidative roasting was found to reduce carbon and resulted in neodymium and iron oxide formation with a minimum amount of neodymium iron oxide. This provided effective selective leaching of neodymium. For whole leaching, a significant loss of neodymium into leached residue was observed. Oxidative roasting-selective leaching provided significant recovery in the amount of 75.46% while whole leaching resulted in only 31.62 wt.% in the case of sintered waste. The final composition via oxidative roasting-selective leaching consisted of 68.11 wt.% neodymium, 19.83 wt.% praseodymium and 0.31 wt.% iron, while whole leaching resulted in a higher amount of iron at 1.20 wt.%. Similar results were obtained for powder magnet waste.

Keywords: NdFeB magnet waste; oxidative roasting; selective leaching; precipitation; calcination

1. Introduction

Rare earth magnets are of significance in many applications in such components as personal devices, i.e., mobile phones and gadgets, hard disk drives (HDDs), medical devices, electronic devices, artificial intelligence, electric motors in hybrid/electric vehicles, aviation, air conditioners, and wind power generators [1,2]. Permanent NdFeB magnets, in particular, are increasingly used in electric vehicles and other applications due to high remanence, coercive force and magnetic strength. Device lifetimes are varied, i.e., 5 years for electric two wheelers, 12 years for air conditioners and 6–10 years for HDDs [3]. When becoming wastes, end-of-life (EOL) devices and also manufacturing scraps should be subjected to treatments conforming to permitted regulations. Moreover, it was reported that the current waste flow is small compared to high global demand. Therefore, effective recycling technology and infrastructure should be developed for suitable waste management and to meet the total demands of permanent magnets in the future [4].

Recycling of NdFeB magnets was initially from the Bayan Obo process in China [5] via crushing and grinding, magnetic separation, beneficication, sulfatizing roasting to get rare earth sulfate before going through solvent extraction, precipitation and calcination. Different recycling techniques were developed according to various waste forms and compositions via (i) fractional crystallization, (ii) whole leaching process, (iii) selective roasting-leaching, (iv) selective leaching, (v) hydrothermal method and (vi) solvent extraction and related techniques [5]. For whole leaching, acids such as sulfuric, hydrochloric, nitric and organic acids were used to dissolve rare earths and iron after demagnetization [6–8].
followed by precipitation of neodymium using metal salts such as sodium sulfate, sodium hydroxide or oxalic acid. Iron was separated and converted to hematite. For oxidative roasting of the magnet wastes over 400–800 °C was reported [9–14] to facilitate higher leaching efficiency. It allowed selective separation of rare earths from iron. Roasting at 500 °C [13] gave faster dissolution of neodymium oxide (Nd$_2$O$_3$) and iron oxide (Fe$_2$O$_3$) in 2 M sulfuric acid, compared with results obtained by direct (whole) leaching. However, excessive oxidation led to neodymium iron oxide (NdFeO$_3$) formation, which was not readily leached [14,15]. Roasting at 700 °C resulted in only 70% neodymium recovery when using 4 M sulfuric leaching at controlled pH and temperature [16]. It followed that the key step was to combine suitable roasting condition to leaching selectivity [15]. The optimum oxidative roasting temperature therefore depended on the nature of the magnet wastes; sintered, ground, bonded, coated or EOL wastes.

Most researches focused on EOL magnet wastes recycling where fewer researches studied recycling of manufacturing wastes. In sintering and powder processing, carbon contamination lowered magnet properties. Carbon contamination as free carbon or grain boundary carbides is undesirable for recycling through re-melting cooperated within the manufacturing line. Removal of carbon contamination was feasible via decarburization in air by oxidation [17–19]. Therefore, this current research incorporated the oxidative roasting to the leaching route to benefit selective leaching and carbon reduction. Selected wastes were in the as-sintered and powder forms. Oxidative roasting temperature was pre-determined [20] based on neodymium and iron oxide formation with minimum neodymium iron oxide for the obtained wastes. Effects of oxidative roasting on recovery and purity of the final recycling products via pyro-hydro metallurgical processing were the main focus. Comparison was made between results obtained from oxidative roasting-selective leaching and whole leaching routes based on optimum conditions for particular wastes.

2. Experimental Procedure

2.1. Waste Preparation

The sintered and powder NdFeB magnet manufacturing wastes of different sizes obtained domestically were subjected to mortar crushing to achieve a powder size of lesser than 210 micron (−70 mesh) as shown in Figure 1. This upper limit size was chosen as indicated by [12] to give effective leaching in the later step. Waste chemical composition was analyzed by inductively coupled plasma—optical emission spectrometer (ICP-OES) using a Perkin Elmer, model Optima 8000 by digesting the waste in hydrochloric (37% HCl) and nitric (65% HNO$_3$) solution at 3:1 volume ratio and prepared over alcohol burner until it was completely dissolved. This was followed by diluting at 100, 1000, and 10,000 times for analyzing of iron (Fe), neodymium (Nd), praseodymium (Pr), boron (B) and dysprosium (Dy). The waste composition consisted of 59.81% Fe, 23.97% Nd, 7.124% Pr, 0.261% B, and 0.062% Dy by weight for the sintered waste [20] while that of the powder form gave slightly different amounts, as listed in Table 1. Phase analysis of the original waste was carried out by XRD using Brooker, model D2 Phaser at 2 theta = 10° to 80° as shown in Figure 2. Spectra of NdFeB appeared as the main phase with carbon present as undesirable contamination.

Table 1. Chemical composition of manufacturing NdFeB magnet wastes analyzed by ICP-OES.

| Type          | Fe   | Nd  | Pr  | B   | Dy  | Other |
|---------------|------|-----|-----|-----|-----|-------|
| sintered waste| 59.81| 23.97| 7.124| 0.261| 0.062| balanced |
| powder waste  | 66.33| 21.66| 4.760| -   | 0.056| balanced |
The effects of oxidative roasting and drying to determine the optimum roasting temperature for recycling NdFeB wastes at 600 °C for 1 h, for sintered and powder wastes respectively.

The sintered and powder wastes were subjected to two different recycling routes, namely (i) oxidative roasting—selective leaching and (ii) whole leaching employed in this study in order to investigate effects of oxidative roasting on recovery and purity of neodymium oxide as the final recycling product, as shown in Figure 3. The first route of oxidative roasting—selective leaching—started from oxidative roasting of the crushed NdFeB wastes at 600 °C for 1 h [20]. The powder was subjected to leaching using 2.5 M sulfuric acid at room temperature and 300 rpm stirring speed for 24 h. Sulfuric acid was selected due to its leaching efficiency according to preliminary test of varied acid concentrations over 0.5–2.5 M. The unleached substance was separated by filtering, while the leachate was subjected to drying until a dried powder was obtained. Thermal analysis by TGA/DSC technique using Mettler Toledo over 25–1200 °C was carried out on products after sulfuric leaching and drying to determine the optimum roasting temperature for sintered and powder wastes according to Figure 4. It can be seen that endothermic reaction signifying conversion of iron sulfates to oxides might be completed around 800 °C and 750 °C for sintered and powder wastes, respectively. These temperatures were pre-determined for roasting of the leached product. Parallel work [20] also confirmed desirable phase evolution of the products after leaching and roasting over 700–800 °C by XRD, which were in good agreement with thermal analysis results. The roasted powder was water leached at room temperature using a stirring speed of 300 rpm for 1 h prior to filtering. The water leached
solution contained sulfate compounds of neodymium and other rare earth metals, namely RE solution. Its residual was filtered, dried and subject to WD-XRF analysis using PANalytical, model AXIOS MAX. In the next step, the RE solution was through precipitation using 1 M oxalic acid until achieving neodymium oxalate for calcination at 1000 °C for 2 h to give neodymium oxide as the desired product. The second route began with leaching of crushed NdFeB magnet subjected to similar recycling as route I previously mentioned without oxidative roasting. Products obtained from particular steps were subjected to XRD, WD-XRF and ICP-OES for phase and chemical composition analysis. Morphology and elemental analysis of the final products was investigated via SEM using JEOL, model JSM-6010LV coupled with EDS. Mass balance of each recycling route was proposed such that comparisons of the two recycling routes (i) oxidative roasting—selective leaching and (ii) whole leaching could be made in terms of recovery and purity of neodymium oxide as the final recycling product.

Figure 3. A schematic of manufacturing NdFeB waste recycling; route I: oxidative roasting—selective leaching, and route II: whole leaching.

Figure 4. The TG/DSC result of leached products, a comparison between sintered and powder wastes.
3. Results and Discussion
3.1. Phase Evolution and Products along the Course of Oxidative Roasting, Acid Leaching, Roasting, Water Leaching, Precipitation and Calcination

3.1.1. Effects of Oxidative Roasting on Phase Evolution

Phase evolution of sintered NdFeB magnet waste from the beginning via the two different recycling routes until receiving the rare earth (RE) solution to proceed precipitation and calcination is addressed here. Initially, the ground magnet waste appeared as dark powder and its color became darker after oxidative roasting as illustrated in Figure 1b,c. Phase changes after oxidative roasting at 600 °C range were detected, as shown in Figure 5. Oxidative roasting at 600 °C resulted in oxide formation, giving hematite (Fe₂O₃) as the main phases, with other minor phases being neodymium iron oxide (NdFeO₃), magnetite (Fe₃O₄) and neodymium oxide (Nd₂O₃). According to previous work [20] on oxidative roasting over 550–800 °C, the optimum temperature was selected at 600 °C to give preferred phases such as iron oxides where both hematite and magnetite co-existed [21], with less neodymium iron oxide (NdFeO₃). However, increasing oxidative roasting temperature above 600 °C offered, however, a greater amount of iron oxides, and the presence of neodymium iron oxide was more pronounced, which made leaching more difficult. In addition, oxidative roasting appeared to give noticeably smaller carbon spectra in the XRD result in comparison to the carbon peaks previously present as a contaminant in the as-received wastes.

Figure 5. An XRD analysis after oxidative roasting of NdFeB waste in sintered and powder forms.

3.1.2. Acid Leaching and Drying

For sintered NdFeB waste, leaching by using 2.5 M H₂SO₄ for 24 h condition was selected for both route I and route II recycling, which aimed to obtain neodymium sulfate (Nd₂(SO₄)₃) as referred to in Equations (1) [22] and (2) for route I and route II, respectively. Route I: oxidative roasting—selective-leaching

\[
\text{Nd}_2\text{O}_3(s) + 3\text{H}_2\text{SO}_4(l) \rightarrow \text{Nd}_2(\text{SO}_4)_3(l) + 3\text{H}_2\text{O}(l)
\]

Route II: whole leaching

\[
2\text{Nd}(s) + 3\text{H}_2\text{SO}_4(l) \rightarrow \text{Nd}_2(\text{SO}_4)_3(l) + 3\text{H}_2(g)
\]

The leachates of sintered waste appearing as reddish dark brown solution were filtered and dried to give powders obtained from route I and route II as shown in Figures 6 and 7. It is noted that one obtained from route I: oxidative roasting and selective leaching appeared as light purple powder while that from route II: whole leaching gave light grey powder.
XRD analysis confirmed the presences of \( \text{Nd}_2(\text{SO}_4)_3 \) spectra along with those of ferric sulfate \( \text{Fe}_2(\text{SO}_4)_3 \) as the main phases while \( \text{Fe}_2\text{O}_3 \) and \( \text{Fe}_3\text{O}_4 \) were detected as minor phases for powder obtained from route I, as shown in Figure 8a). Its chemical composition by XRF denoted as OR, LC, as listed in Table 2, signified key elements as 68.42% iron, 10.37% neodymium, 3.31% praseodymium, and 4.65% cobalt. Comparatively, chemical composition of that obtained from route II: whole leaching, denoted as LC, possessed 71.49% iron, 7.65% neodymium, 2.40% praseodymium and 4.33% cobalt by weight. It should be noted that there was a significant amount of residue left in the leached solution via route II: whole leaching, and its composition comprised a notable content of 67.12 wt.% neodymium with 0.92 wt.% iron analyzed by XRF as listed in Table 2 (denoted as LC residue). On the other hand, complete leaching was achieved via route I: oxidative roasting—selective leaching route with very few residues having only 1.72 wt.% neodymium with the key element being iron of 94.93 wt.%. It thereby indicated that the rare earth elements could be leached more effectively via oxidative roasting—selective leaching. This will be further discussed according to mass balance and recovery for the two recycling routes. In the case of powder NdFeB waste, the leachate appeared transparent green, indicating the main specie being \( \text{FeSO}_4 \) rather than \( \text{Fe}_2(\text{SO}_4)_3 \) as in the case of sintered NdFeB waste, as compared in Figure 6. It is plausible that the powder NdFeB waste form was subject to powder processing without sintering.

| Route I: oxidative roasting – selective leaching | Route II: whole leaching |
|-----------------------------------------------|------------------------|
| ![Leachate (sintered waste)](image) | ![Leachate (powder waste)](image) |
| ![Leachate (sintered waste)](image) | ![Leachate (powder waste)](image) |

**Figure 6.** Leachates via route I and route II recycling, for sintered and powder NdFeB wastes.

| Route I: oxidative roasting – selective leaching | Route II: whole leaching |
|-----------------------------------------------|------------------------|
| ![leached and dried](image) | ![roasted at 800 °C/2 h](image) |
| ![roasted at 800 °C/2 h](image) | ![leached and dried](image) |
| ![precipitated](image) | ![calcined at 1000 °C/2 h](image) |
| ![calcined at 1000 °C/2 h](image) | ![precipitated](image) |

**Figure 7.** Products obtained via route I and route II recycling of sintered wastes, (a,b) after leaching, drying and roasting at 800 °C/2 h, (c,d) after precipitation and calcination.
Figure 8. An XRD analyses of the products from route 1 oxidative roasting—selective leaching and route 2 whole leaching, (a) after leaching and drying, and (b) after roasting. Note: OR: oxidative roasting, LC: leaching and R: roasting.
Table 2. The chemical composition of products in various steps of recycling analyzed by XRF.

| Recycling Step | Fe (wt.%) | Nd (wt.%) | Pr (wt.%) | Co (wt.%) | O (wt.%) | S (wt.%) | Other |
|----------------|-----------|-----------|-----------|-----------|----------|---------|--------|
| Crushed magnet | 67.50     | 18.705    | 6.29      | 3.85      | 0.63     | 0.02    | balanced |

**Route I: Oxidative roasting—selective leaching**

| OR             | 74.75     | 14.80     | 4.66      | 3.39      | 0.85     | 0.02    | balanced |
| OR, LC         | 68.42     | 10.37     | 3.31      | 4.65      | 1.34     | 11.17   | balanced |
| OR, LC residue | 94.93     | 1.72      | 0.58      | 0.74      | 0.33     | 1.01    | balanced |
| OR, LC, R      | 77.07     | 11.28     | 3.68      | 5.45      | 0.79     | 1.40    | balanced |
| OR, LC, R, WL residue | 92.15 | 0.41     | 0.11     | 6.31     | 0.61     | 0.17 | balanced |
| OR, LC, R, WL, PP | 0.50 | 71.89     | 22.63     | -         | 3.19     | 0.18    | balanced |
| OR, LC, R, WL, PP, C | 0.31 | 73.81     | 23.80     | -         | 0.83     | 0.07    | balanced |

**Route II: Whole leaching**

| LC             | 71.49     | 7.65      | 2.40      | 4.33      | 0.69     | 13.06   | balanced |
| LC residue     | 0.92      | 67.12     | 20.29     | -         | 0.87     | 8.70    | balanced |
| LC, R          | 83.81     | 7.40      | 2.45      | 5.03      | -        | 1.06    | balanced |
| LC, R, WL residue | 93.14 | 0.71     | 0.21     | 5.42     | 0.26     | 0.07 | balanced |
| LC, R, WL, PP  | 0.45      | 73.80     | 24.47     | -         | 0.56     | 0.12    | balanced |
| LC, R, WL, PP, C | 1.20 | 72.59     | 23.22     | -         | 1.45     | 0.13    | balanced |

Note: OR—oxidative roasting at 600 °C, LC—leaching, R—roasting at 800 °C, WL—water leaching, PP—precipitation, C—calcination.

3.1.3. Roasting and Water Leaching

After roasting at 800 °C for 2 h, the powder turned dark red since ferric sulfate has transformed into iron oxides. At such a roasting temperature, neodymium sulfate remained according to XRD pattern, as shown in Figure 8b for both route I and route II recycling. Very small peaks of iron sulfate were present. This signified that a longer roasting time might be required. Next, the roasted powder was subjected to water leaching and filtering in order to separate out iron oxide (Fe$_2$O$_3$) from the solution as residue, leaving the soluble neodymium sulfate (Nd$_2$(SO$_4$)$_3$) in the RE solution. For this step, the RE solution was purified, containing neodymium as the key element and other minor elements such as praseodymium and cobalt. The dried residue appeared as a reddish brown powder, containing iron oxide as the main phase. XRF analysis showed 92.15 wt.% Fe and 6.31 wt.% Co that could be possibly used as a raw material in the pigment and ceramic industries.

3.1.4. Precipitation of Neodymium Oxalate

According to ICP-OES results, the RE solution via oxidative roasting—selective leaching comprised 2.74 g/L of neodymium, while that obtained via whole leaching consisted of a slightly lower neodymium amount of 2.17 g/L. By gradually adding 1 M oxalic acid (C$_2$H$_2$O$_4$), neodymium oxalate (Nd$_2$(C$_2$O$_4$)$_3$) was precipitated as a white powder, as shown in Figure 7.

For route I recycling of the sintered NdFeB waste, neodymium in the RE solution reduced rapidly from 2.74 g/L to 0.175 g/L after adding oxalic acid for the amount of 3–9 mL, as shown in Figure 9a). When adding more oxalic acid, the curve leveled off, giving us the minimum neodymium value of only 0.006 g/L in the solution. Praseodymium content was found to be reduced while the amounts of cobalt and dysprosium remained apparently unchanged. Precipitation of neodymium oxalate reached almost 100% as n(oxalic)/n(Nd) approached 2.86 as illustrated in Figure 10. Though the n(oxalic)/n(Nd) value should have reached the value of 3.0 based on Equation (3), it might be that under this investigation, the reaction could not reach 100% precipitation with continual oxalic acid addition. This might be due to oxalate precipitation of other rare earth such as praseodymium and dysprosium. Comparatively, with a lower amount of neodymium in the RE solution at 2.17 g/L obtained from route II, steady state precipitation was reached at 2.41 n(oxalic)/n(Nd) ratio, having 0.003 g/L neodymium left in the solution. XRD
analysis, as shown in Figure 11 also confirmed that precipitate contained neodymium oxalate hydrate (Nd$_2$(C$_2$O$_4$)$_3$.10H$_2$O) as the main phase. Praseodymium was found to precipitate as an oxalate, while its spectra coincided with that of neodymium oxalate with less intensity of peaks. Minor spectra of Fe(C$_2$O$_4$)$_2$H$_2$O were also present. The greater amount of neodymium in the RE solution from route I led to greater amount of neodymium oxalate precipitate.

\[
\text{Nd}_2(\text{SO}_4)_3 (l) + 3 \text{H}_2\text{C}_2\text{O}_4 (l) \rightarrow \text{Nd}_2(\text{C}_2\text{O}_4)_3 (s) + 3 \text{H}_2\text{SO}_4 (l)
\]  

(3)

\[
3\text{Nd}_2(\text{SO}_4)_3 (l) + 3 \text{H}_2\text{C}_2\text{O}_4 (l) \rightarrow 3\text{Nd}_2(\text{C}_2\text{O}_4)_3.10\text{H}_2\text{O}(s) + 3 \text{H}_2\text{SO}_4 (l)
\]  

(4)

Figure 9. Metal concentration in the rare earth (RE) solution of as-sintered waste after precipitation using oxalic acid for (a) route I and (b) route II.

Figure 10. The dependence of Nd precipitation on n(oxalic)/n(Nd), route I: oxidative roasting and selective-leaching, and route II: whole leaching for sintered NdFeB waste.

Figure 11. The XRD analyses of neodymium oxalates obtained from route I: oxidative roasting and selective-leaching, and route II: whole leaching. Note: OR: oxidative roasting, LC: leaching, R: roasting and P: precipitation.
3.1.5. Calcination

Finally, neodymium oxalate was subjected to calcination at 1000 °C for 2 h to obtain neodymium oxide following the reactions as summarized in Equation (5) [23]. Carbon dioxide was released through different steps of phase evolution up to 1000 °C. Neodymium oxalate (Nd₂(C₂O₄)₃) was first transformed into neodymium (III) carbonate (Nd₂(CO₃)₃), and then neodymium oxide carbonate (Nd₂O₂CO₃) before obtaining neodymium oxide (Nd₂O₃).

\[
\text{Nd}_2(C_2O_4)_3 \rightarrow \text{Nd}_2(CO_3)_3 \rightarrow \text{Nd}_2O_2CO_3 \rightarrow \text{Nd}_2O_3 \quad (5)
\]

However, neodymium oxide is rather hydrophilic, and it should be kept away from moisture. Otherwise, the final product becomes undesirable neodymium hydroxide (Nd(OH)₃). Calcination at moderate temperature of >650 °C can be applied to convert neodymium hydroxide to neodymium oxide [24]. XRD analysis also confirmed the existence of neodymium oxide achieved from route I: oxidative roasting—selective leaching and route II: whole leaching as displayed in Figure 12. Though, neodymium hydroxide spectra were observed, but to a minor extent, which might be due to storage. The carbon peaks were absent. This indicated that the carbon impurity present in the origin NdFeB waste was removed. Table 3 summarized final composition of recycling products by ICP-OES analysis. For sintered waste, the final composition of the recycling products for route I contained 65.09% neodymium, 19.83% praseodymium, and 0.31% iron by weight, while products from route II contained 63.16% neodymium, 21.32% praseodymium and 0.30% iron by weight. For powder waste, the final composition of the recycling product from route I contained 68.11 wt.% neodymium, 14.93 wt.% praseodymium, and 0.51 wt.% iron, while product from route II contained 61.23 wt.% neodymium, 13.83 wt.% praseodymium and 0.31% iron. It can be seen that oxidative roasting provided slightly higher neodymium contents for recycling of both sintered and powder waste forms. Moreover, lesser amounts of iron were also beneficial.

![Figure 12. The XRD analyses of neodymium oxide obtained from route I: oxidative roasting and selective -leaching and route II: whole leaching. Note: OR: oxidative roasting, LC: leaching, R: roasting, P: precipitation and C: calcination.](image)

Table 3. The chemical composition of recycling products analyzed by ICP-OES.

| Waste     | Route | Composition, wt.% | % Recovery |
|-----------|-------|-------------------|-----------|
|           |       | Nd    | Pr   | Fe  | Others|            |
| Sintered  | I     | 65.09 | 19.83| 0.31| balanced| 76.03       |
|           | II    | 63.16 | 21.32| 1.20| balanced| 31.62       |
| Powder    | I     | 68.11 | 14.93| 0.30| balanced| 75.46       |
|           | II    | 61.23 | 13.83| 0.51| balanced| 59.36       |
An investigation under SEM revealed that the calcined products were fine agglomerate-shaped, as shown in Figure 13e–h. As the examined products were glued to silver paste and lightly gold sputtered for enhanced electrical conduction, their analyzed percentages were excluded. The key elements were neodymium, praseodymium and oxygen, in which carbon could be from free carbon and oxalates. In the last step of calcination, the carbon content has been significantly reduced in relation to that obtained from the oxalate precipitate, as shown in Figure 13a–d by EDS point analysis. Route I: oxidative roasting notably gave the calcined product with less carbon of 1.42 wt.% than 5.22 wt.% obtained from route II: whole leaching. Therefore, carbon formerly presented as the contaminant in the as-received sintered waste could be significantly reduced through the proposed recycling. However, work by K. Asabe et al., [17–19] indicated that both free carbon and grain boundary carbides could be removed down to 0.001% via decarburization in air by oxidation at 1000 °C, plus oxygen reduction. In this current work, though the carbon contamination could not be completely eradicated, but it has been reduced in a significant amount via oxidative roasting at 600 °C for 1 h applied at the first step. Further, the applied process could also be extended not only to other manufacturing scraps but also to the EOL scraps in the aspect of various waste stream recycling in order to offer both demagnetization and oxidative roasting effect in the single waste treatment step prior to succeeding step of selective leaching. This therefore requires further investigation, and in more detail.

Figure 13. SEM and EDS analyses of (a–d) neodymium (RE) oxalates and (e–h) neodymium (RE) oxides obtained from route I: oxidative roasting and selective leaching, and route II: whole leaching.
3.2. Recovery and Purity of Neodymium Oxide

In terms of recovery, mass flow and material balance were studied in order to obtain recovery of neodymium according to expression in Equation (5) where contents of neodymium in the original NdFeB waste and in the final product as neodymium oxide were obtained by using ICP-OES result.

\[
\text{% Recovery} = \left( \frac{\text{Nd}_{\text{waste}}}{\text{Nd}_{\text{product}}} \right) \times 100
\]

(6)

Firstly, in the case of sintered NdFeB magnet waste, recovery of neodymium achieved from route I: oxidative roasting and selective leaching is 76.03% while that obtained from route II: whole leaching was significantly lower at 31.62%. Figure 14 schematically shows material flow of route I, starting from oxidative roasting, selective leaching, drying, roasting, precipitation and finally calcination. To begin with 1 kg of manufacturing NdFeB waste, the attained neodymium (RE) oxides is 0.28 kg. Comparatively, without oxidative roasting, route II: whole leaching yielded less neodymium (RE) oxides of only 0.12 kg as shown in Figure 15. A summary of recycling products, its compositions, phases and recovery for sintered and powder NdFeB magnet wastes under route I: oxidative roasting-selective leaching and route II: whole leaching are shown in Figure 16. Under route I: oxidative roasting and selective leaching, greater recovery has been achieved at 76.03% and 75.46% for sintered and powder NdFeB magnet wastes respectively. A significantly lower recovery has been at only 31.62% and 59.36% for sintered and powder NdFeB magnet wastes, respectively, via route II: whole leaching. Along the course of recycling steps of route II: whole leaching, a significant loss of neodymium yield was in the step of leaching, where neodymium went through residue (67.12 wt.% neodymium). In order to investigate the effect of bulk and crushed forms of NdFeB magnet wastes, parallel investigation has been performed using a similar leaching condition, which indicated identical results. It is therefore suggested here that oxidative roasting played an important role on selective leaching of neodymium and gave the leached residue having only 1.72 wt.% neodymium. In terms of recycling product purity, lower iron contents in the products via route I recycling is considered beneficial. It is suggested that longer roasting time might be needed and required future work to completely convert iron sulfate into iron oxides.

**Figure 14.** The material balance of sintered NdFeB recycling under route I: oxidative roasting and selective leaching.
Comparatively, route I: oxidative roasting—selective leaching has been shown to be more effective than route II: whole leaching in terms of recovery and purity of neodymium (RE) oxides. The key step was the oxidative roasting at 600 °C leading to iron oxide formation, while keeping neodymium iron oxide at minimum. Higher oxidative roasting temperature up to 800 °C led to more neodymium iron oxide, which was not readily leached [11–13]. The oxidative roasting temperature was thus selected at 600 °C to obtain iron oxides and to avoid neodymium iron oxide formation. In the leaching step, neodymium sulfate was obtained with some iron sulfates being present. After roasting, neodymium remained in the sulfate form, allowing it to be dissolved back into the solution via water leaching. Therefore, the RE solution now possessed neodymium sulfate as the prime resource to be precipitated using oxalic acid. Conversion of iron sulfates to oxides allowed it to be removed during water leaching. In this step, a small content percentage of cobalt in the original waste was lost through residue, along with iron oxides. Praseodymium and dysprosium until remained in the RE solution and precipitated as RE oxalates but in smaller amounts, especially dysprosium. Lastly, calcination at 1000 °C for 2 h turned neodymium (RE) oxalates into neodymium (RE) oxides as the recycling product.
In general, neodymium oxide appears in light purple powder. The calcined powders obtained however were rather light greyish, which was possibly due to the presence of praseodymium oxide. Though neodymium oxide could not be achieved in its pure form, it is recommended that molten fluoride electrolysis of both neodymium and praseodymium oxides could give a successful co-deposition of neodymium and praseodymium for the complete recycling [25,26].

4. Conclusions

Manufacturing NdFeB magnet wastes in the as-sintered and powder forms can be recovered as neodymium (RE) oxides via pyro-hydro metallurgical process. Carbon contamination in as-received wastes was greatly reduced. For this study, the optimum condition for sintered waste was oxidative roasting at 600 °C for 1 h, followed by 2.5 M H2SO4 leaching for 24 h, roasting at 800 °C for 2 h, water leaching, precipitation using 1 M oxalic acid at n(oxalic)/n(Nd) = 2.86 and finally calcination at 1000 °C for 2 h. For powder magnet wastes, the optimum condition followed the sintered waste apart from requiring lower roasting temperature at 750 °C to give optimum iron oxide formation with minimum amount of neodymium iron oxide. Comparatively, oxidative roasting—selective leaching route yielded significantly higher recovery at 75–76% for both wastes while whole leaching gave reduced recovery at 31–60% due to neodymium loss into leached residue. Oxidative roasting also benefited the purity of neodymium (RE) oxide product in that slightly higher neodymium and a lower amount of iron were obtained.

Author Contributions: Funding acquisition, S.K. and T.P.; conceptualization, S.K. and T.P.; investigation, T.P. and W.K.; methodology, T.P. and W.K.; experimental, W.K.; formal analysis, T.P. and W.K.; writing—original draft; T.P.; writing—review & editing; T.P. and W.K. All authors have read and agreed to the published version of the manuscript.

Funding: This research is supported by Innovative Production and Recycling of Metals Research Center (IPRMRRC), Suranaree University of Technology on analysis of waste and recycling products. Student research grant no. 32/2563 is by Suranaree University of Technology. Waste provision is by Magnequench (Korat) Co., Ltd. (Ratchasima, Thailand).

Acknowledgments: Authors would like to acknowledge Innovative Processing and Recycling of Metals Research Center (IPRMRRC) for waste and recycling product analysis fee supports, and Suranaree University of Technology for student research grant. Department of Primary Industries and Mines (DPIM), Ministry of Industry, Thailand is thankful for collaborative work and advise. Thanks are also due to Magnequench (Korat) Co., Ltd. for waste provision and technical supports.

Conflicts of Interest: The authors declare no conflict of interest.

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