A Comparison of the Hydrometallurgical Methods for Recycling Rare Earths in Permanent NdFeB Magnets

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Abstract

Rare Earth Elements (REEs) are currently very popular in various industrial applications, including electronics, renewable energy technologies, and automotive systems. Given the increasing demand for REEs and the limitations of primary resource extraction, the recycling of NdFeB magnets emerges as a crucial strategy to ensure a sustainable approach. Since hydrometallurgical techniques are the most prominent for recovering REEs from NdFeB magnet scraps, various hydrometallurgical processes from five studies were compared and analyzed according to their efficiency and environmental sustainability. Several leaching methods were evaluated, including leaching with HCl and selective leaching involving oxidation or chlorination roasting. The latter methods showed promise due to their high REE recovery rates and reduced environmental impact compared to strong mineral acids like HCl. For separation techniques, solvent extraction and oxalate precipitation were investigated. While solvent extraction demonstrated high efficiency, concerns about sustainability arose due to the use of mineral acids. In contrast, oxalate precipitation followed by calcination offered a more environmentally friendly approach with impressive REE recovery rates. Moving forward, continued research will be necessary to improve the effectiveness of these techniques and optimize them for implementation on an industrial scale.

Introduction

Rare Earth Elements (REEs) are currently very popular in various industrial applications, including electronics, renewable energy technologies, and automotive systems. Constituted by 17 chemically similar metallic elements, including 15 lanthanoids, scandium, and yttrium, these elements are relevant to us due to their unique properties. These properties include magnetic, conductive, phosphorescent, catalytic, electrochemical, and luminescent characteristics, making them useful when alloyed, or mixed, in small quantities with more common metals (Ramprasad et al., 2022). The demand and dependence on REEs creates pressure on their ongoing extraction from geological primary resources, ores, which does not solely meet the demand. As a result, a sustainable supply approach is required, which can be accomplished through recycling. Nevertheless, less than 1% of the REEs were being recycled in 2011 (Binnemans et al., 2013), and current REE recycling is still minimal, largely due to economic issues (Fujita et al., 2022).

Permanent NdFeB magnets are the most promising materials to be recycled among the principal applications of REEs, which include permanent magnets, nickel metal hydride batteries, and lamp phosphors. In 2020, their manufacturing accounted for about 80% of the economic value of REEs (Fujita et al., 2022). These magnets can be found in several everyday consumer products, such as hybrid and electric vehicles, wind turbines, and hard disk drives. More than an economic benefit, recycling NdFeB magnets is advantageous over other applications due to the specific REEs that can be recovered from this material. NdFeB magnets are based upon neodymium-iron-boron alloys, with a matrix phase of Nd2Fe14B. These magnets are not only surrounded by a neodymium-rich grain boundary phase, but they also include minor admixtures of praseodymium (Pr), gadolinium (Gd), terbium (Tb), and, most notably, dysprosium (Dy). Three of the five critical REEs identified by the U.S. Department of Energy (DOE) in 2011 are present in NdFeB magnets (Nd, Tb, and Dy) (Binnemans et al., 2013). Moreover, Nd and Dy are considered the most important REEs to clean energy, as well as the largest supply risk, implying that these elements require the most care and need for recycling.

The three primary material flows that can be considered for recycling NdFeB magnets are pre-consumer magnet swarfs from manufacturing, end-of-life small magnets, and large magnets used in hybrid, electric vehicles, and wind turbines. Direct recycling and reuse in their current form and shape are only possible for large magnets, making it difficult to recover REEs from the end-of-life small consumer magnets in electronics. In fact, even the first process is difficult to execute because large magnets remain in use for lengthy periods of time and are rarely available as scrap materials. For this reason, other appropriate methods that require pre-processing of magnet alloys are necessary for the recovery of significant concentrations and quantities of REEs, as well as for a cost-effective collection.

Out of several methods that have been researched on a lab scale, hydrometallurgical methods have emerged as the most prominent for recovering REEs from NdFeB magnet scraps because they can be used to treat any type of magnet and follow similar steps as the extraction of REEs processes (Zhang et al., 2020). As a result, this review provides an analysis and comparison between recent hydrometallurgical methods for recycling permanent NdFeB magnets that have been developed during the last 8 years. It considers the methodologies and findings, as well as their respective strengths and weaknesses. Through this examination, this review aims to identify the most effective and sustainable method poised for potential standardization and commercial adoption in future recycling practices.

Experimental Section

Hydrometallurgical methods are characterized by aqueous-based processes, allowing for the dissolution, separation, and recovery of Rare Earth Elements (REEs) from NdFeB magnet scraps. REE processing has two main steps: leaching and separation (Fujita et al., 2022). Out of the five studies being reviewed, all developed their own hydrometallurgical processes based on these two steps with the objective of not only finding the optimal conditions to achieve the best percentage recovery of REEs, but also developing environment-favorable alternatives. Each study will be described and compared methodologically, including experimental conditions, reagents, and mechanisms, so that its results can be understood and explored further.

Leaching

The leaching process is characterized by the dissolution of Rare Earth Elements (REEs) in the NdFeB magnet scraps into the aqueous phase. This dissolution method can be performed in two different ways: complete leaching and selective leaching. Parhi et al. 2016 was the only study being reviewed that used the complete leaching approach. The process consisted of completely dissolving a scrap permanent magnet sample using 0.2 M HCl, a strong mineral acid, at 90ºC for 2 hours. Equation 1 shows a simplified mechanism for this reaction, illustrating how the HCl acid, represented as dissociated hydrogen cations (H^+), leached the REEs, including Nd and Pr. Beyond REEs, the final leach liquor which also contained Fe and B, was filtered, diluted, and analyzed to determine the four element concentrations.

$$2\mathrm{REE}\ (s) + 6\mathrm{H}^+\ (aq) \rightarrow 2\mathrm{REE}^{3+}\ (aq) + 6\mathrm{H}_2\ (g)$$

(Eq. 1)

The other four studies utilized a selective leaching approach, taking advantage of the solubility between REEs and Fe. Different types of roasting were carried out as pretreatment processes in the studies of Gergoric et al. 2018 and Kumari et al. 2021 to improve selectivity and efficiency in the leaching method. Gergoric et al. 2018 carried out a pretreatment heating by oxidation roasting NdFeB magnet powder at 400ºC for 1.5 hours. During this thermal oxidation process, the readily soluble REE_2O_3 (REE = Nd, Pr) and insoluble Fe_2O_3 were formed to prevent the leaching of Fe in acidic solution. The leaching process was then performed using organic acids (harmless lixiviants compared to mineral acids like HCl) such as maleic, glycolic, and L-ascorbic acids, following the simplified mechanism shown in Equation 2.

$$\mathrm{REE}_2\mathrm{O}_3\ (aq) + 6\mathrm{H}^+\ (aq) \rightarrow 2\mathrm{REE}^{3+}\ (aq) + 3\mathrm{H}_2\mathrm{O}\ (l)$$

(Eq. 2)

After the optimum leaching conditions were found for each organic acid, maleic acid was the most efficient lixiviant (Gergoric et al., 2018). Therefore, the REE recovery of NdFeB magnets was found for 1 M maleic acid at room temperature (25ºC) and 1/80 g/ml solid/liquid ratio.

Aiming to avoid the use of acids throughout the leaching process, Kumari et al. 2021 carried out a chlorination roasting of NdFeB magnet powder from a wind turbine with ammonium chloride (NH_4Cl) at 300ºC for 3 hours. Throughout this process, it was found through thermodynamic investigation that when the NdFeB magnet is roasted with 3 times the stoichiometric requirement of NH_4Cl, rare earths (REE = Nd, Pr, Dy) are selectively converted to $REECl_3$ (Equation 3) and Fe is oxidated to form Fe_2O_3 (Equation 4).

$$\mathbf{REE\ (s) + 3NH_4Cl\ (s) + 0.75O_2\ (g) \rightarrow REECl_3\ (s) + 3NH_3\ (g) + 1.5\ H_2O(g)}$$

(Eq. 3)

$$\mathbf{Fe\ (s) + 0.75O_2\ (g) \rightarrow 0.5Fe_2O_3\ (s)}$$

(Eq. 4)

$REECl_3$ was readily soluble in water, but Fe_2O_3 was insoluble, hence water leaching was performed at 95ºC for 1 hour and the leach liquor was separated from the leach residue by filtration (Kumari et al., 2021).

Like Kumari et al. 2021, another acid-free selective leaching process was carried out in the studies of Prodius et al. 2019 and Prodius et al. 2020. However, this time, preprocessing through roasting was not required. Both studies performed selective leaching of NdFeB magnets through redox-dissolution with copper(II) salts, as described in Equation 5. During this process, Fe^{2+} was also oxidized to Fe^{3+} (Equation 6), so that it could be further easily precipitated as a Fe(III) hydroxide in the separation step.

$$\mathbf{2REE_2Fe_{14}B\ (s) + 34Cu^{2+}\ (aq) + 10.5O_2\ (g) \rightarrow 4\ REE^{3+}\ (aq) + 28Fe^{2+}\ (aq) + Cu(BO_3)_2\ (s) + 15Cu_2O\ (s) + Cu\ (s)}$$

(Eq. 5)

$$\mathbf{12Fe^{2+}\ (aq) + 6H_2O\ (l) \rightarrow 4Fe(OH)_3\ (s) + 8Fe^{3+}\ (aq)}$$

(Eq. 6)

The comparison between REE recovery from NdFeB magnets via the proposed acid-free leaching process and the general acid-based leaching process (Gergoric et al., 2018) is represented in Figure 1.

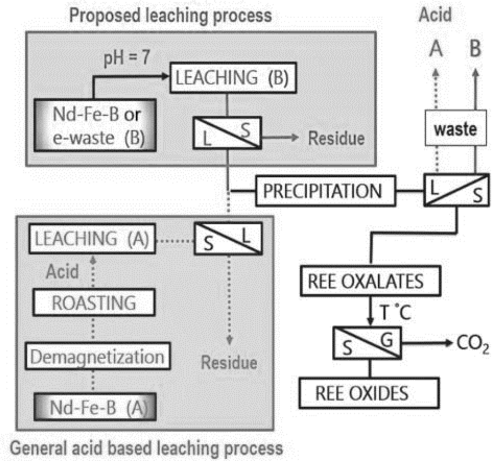

Figure 1
(Prodius et al., 2019).

While the feedstock material used for Prodius et al. 2019 was NdFeB magnet swarfs, decrepitated magnets from HDDs, and magnets from electronic waste, Prodius et al. 2020 focused only on NdFeB magnets from electronic waste. For this specific study, copper(II) chloride dehydrate was used to dissolve the magnet at room temperature (25ºC) for 24 hours.

Separation

Once the Rare Earth Elements (REEs) and other co-solubilized constituents have been extracted into the aqueous phase as a leaching liquor, the liquid should be treated using separation techniques to separate REEs from non-REEs, followed by further separation of individual REEs. Solvent extraction (SX) and precipitation were the main separation methods used in the studies being reviewed.

Parhi et al. 2016 and Gergoric et al. 2018 carried out a solvent extraction method for the selective separation and extraction of Nd and Pr with a water-immiscible organic reagent. Since Fe had already been removed from the leaching liquor in Gergoric et al. 2018, only Parhi et al. 2016 required Fe removal by precipitation using lime water (Ca(OH)2) prior to SX. Both studies used D2EHPA (di-(2-ethylhexyl)phosphoric acid) as an acidic extractant for the extraction of REEs, which followed the ion exchange mechanism shown in Equation 7, with HR representing D2EHPA.

$$\textbf{REE+3 (aq) + 3(HR)2 (org)} \leftrightarrow \textbf{REER33HR (org) + 3H+ (aq)}$$

(Eq. 7)

To form the organic phase, also known as the solvent, the extracting agent needed to be dissolved by a diluent. While Parhi et al. 2016 used H2SO4/NaOH as a diluent, Gergoric et al. 2018 tested several to find the most efficient, including alcohols (1-octanol), ketones (cyclohexanone), and alkanes (pentane, hexane, dodecane, and solvent 70 - hydrocarbons C11– C14, < aromatics). The final optimal conditions found for the solvent extraction process in Parhi et al. 2016 was using 0.8 M D2EHPA 30% neutralized by H2SO4/NaOH at pH 4.0. For Gergoric et al. 2018, solvent extraction was performed using 1.0 M D2EHPA dissolved in pentane.

Separation by precipitation was carried out in the studies by both Kumari et al. 2021 and Prodius et al. 2019. After chlorination roasting and water leaching, Kumari et al. 2021 treated the leaching solution with oxalic acid (H2C2O4) at pH 2 to produce hydrated rare earth oxalate precipitates (REE2(C2O4)3·10H2O) leaving other impurities like Al, B, Co, and Fe in solution. Prodius et al. 2019 performed a similar oxalate precipitation process, but due to its leaching solution being composed of both REE and Fe cations, precipitation of Fe(III) and REE(III) hydroxides had to be performed prior, using an aqueous ammonia solution (28%) (NH4OH) at 60ºC for 2 hours (Equation 8). For the oxalate precipitation to occur, excess of solid crystalline oxalic acid (H2C2O4·2H2O) was added at 80ºC until insoluble REE oxalate precipitated and highly soluble double salt of iron-ammonium oxalate formed (Equation 9).

4Fe2+ (aq) + Fe3+ (aq) + REE3+ (aq) + 14NH4OH (aq) + 2H2O (l) + O2 (g) →
5Fe(OH)3 (s) +
+ REE(OH)3 (s) + 14NH4+ (aq)
(Eq. 8)

10Fe(OH)3 (s) + 2 REE(OH)3 (s) + 30NH4OH (aq) + 33H2C2O4 (s) →
10(NH4)3[Fe(C2O4)3]
(aq) + REE2(C2O4) 3·10H2O (s) + 56H2O (l)
(Eq. 9)

To obtain a final mixture of recovered rare earth oxides (oxide of Nd, Pr, and Dy), Kumari et al. 2021 and Prodius et al. 2019 lastly carried out a calcination of the mixed REE oxalates in air at 800ºC (Equation 10). This process consisted mainly of heating the inorganic material under a controlled temperature and environment so that volatile components could be removed.

2REE2(C2O4) 3·10H2O (s) + O2 (g) → 2REE2O3 + 20H2O (g) + 12CO2(g)
(Eq. 10)

Following the same leaching treatment as in Prodius et al. 2019, Prodius et al. 2020 developed a new separation method aiming for a more environmentally friendly and cost-effective approach. The method is known as CSEREOX, which stands for "chemical separation of rare-earth element oxalates". It involves the selective reaction of water-insoluble rare earth oxalates with an aqueous mixture of oxalic acid and organic base, separating light and heavy rare earths due to different solubilities. The lighter elements (LREEs) which include La-Sm are much less soluble than the heavy elements (HREEs) which include Gd-Lu, meaning they can precipitate first. Equation 11 shows how the CSEREOX extraction method was performed for the separation of Nd and Pr (both LREEs) from Dy (HREE), by adding oxalic acid, 1-methylimidazole as a base, and water as a solvent to the rare-earth(III) oxalates obtained from the oxalate precipitation for 15 minutes.

xREE2(C2O4)3·10H2O + H2C2O4·2H2O + 2C4H6N2 → [H3O]m(C4H6N2-H+)a [REE(C2O4)b](H2O)c
(Eq. 11)

Where x = 0.01/1.6 ; m = 0 or 1 ; a = 1, 3, 4, 5, 8 ; b = 2, 3, 4, 7 ; c = 1,1.5, 2 and 10.

Results and Discussion

All five studies showed reasonable results regarding the leaching and separation of Rare Earth Elements (REEs) from NdFeB magnets. More than just effective, several methods encountered environmentally friendly alternatives which are feasible to be further performed for industrial scale recycling. The complete leaching using HCl (Parhi et al., 2016), the selective leaching involving oxidation roasting and usage of maleic acid as a lixiviant (Gergoric et al., 2018), and the selective leaching involving chlorination roasting and water as a lixiviant (Kumari et al., 2021) were the most effective leaching methods for the recovery of REEs in leaching aqueous solution (>90 %). Even though HCl leaching had the highest REE recovery (99.99 %), this process had some significant drawbacks regarding sustainability compared to the others. The usage of strong inorganic acids like HCl lead to poisonous gas evolution during leaching (H2) which can be challenging during handling and has adverse impacts on the environment due to the consumption and discharge of large amounts of acid (Gergoric et al., 2018). It is estimated that treating 1000 kg of NdFeB magnet requires 1622 kg of HCl (over 1.6 times the mass of the magnet) (Kumari et al., 2021).

Due to this environmental issue, both studies of Gergoric et al. 2018 and Kumari et al. 2021 performed a more environmentally friendly approach aiming to potentially decrease and replace the usage of strong mineral acids in the hydrometallurgical recovery of REEs. Kumari et al. 2021 showed a slightly higher recovery of REEs (99%) than Gergoric et al. 2018 (96%). Moreover, the chlorination roasting using NH4Cl prior to leaching (Kumari et al., 2021) was found to be a more energy-efficient process than oxidation roasting (Gergoric et al., 2018) because it was performed at a much lower temperature and over a shorter time. For this reason, the selective leaching of REEs involving chlorination roasting and water leaching seems to be the selective method with the most effective and sustainable characteristics for the recycling of REEs from NdFeB magnets. The acid-free selective method performed in Prodius et al. 2019 and Prodius et al. 2020 looked promising due to its environmentally-friendly approach, but no explicit data of the REEs recovery in leach solution was presented in either study.

Regarding the separation methods, the solvent extraction with D2EHPA as the acidic extractor and H2SO4/NaOH as the diluent (Parhi et al., 2016) and the oxalate precipitation using oxalic acid followed by calcination (Kumari et al., 2021) were the most effective methods for the extraction of REEs from the leach liquor (>95 %). Despite the high efficacy of 99% recovery of a Nd and Pr mixture in the solvent extraction performed in Parhi et al. 2016, like its complete leaching method, environmental issues associated with the usage of mineral acids (H2SO4) and the generation of large amounts of waste limit this procedure feasibility in an industrial scale. Moreover, this process was unable to extract Dy, an important critical rare earth component of NdFeB magnets.

The separation method performed in Kumari et al. 2021 allowed for the extraction of 96% Nd, 98% Pr, and 98% Dy from the leach liquor as a mixture of REE oxides. Not only was the recovery of Nd and Pr high, but the process also permitted the high recovery of Dy. The only drawback of this process was the high temperature in which the calcination needed to occur, a high-energy process. The CSEREOX route performed in Prodius et al. 2020 was able to extract Dy with a lower efficiency of 68%, but still developed an energy-efficient approach, with water as the only extraction media, contributing to less hazardous chemical synthesis. This is a promising sustainable approach for the separation and extraction of REEs from NdFeB magnets, but further studies need to be done in order to improve the efficacy of this new technique. Therefore, based on efficacy and lower environmental issues, the oxalate precipitation followed by calcination performed in Kumari et al. 2021 seems to be the best approach for the separation and extraction of REEs. The complete process for the recovery of mixed rare earth oxides from 100g of NdFeB magnet followed by Kumari et al. 2021 can be seen in Figure 2.

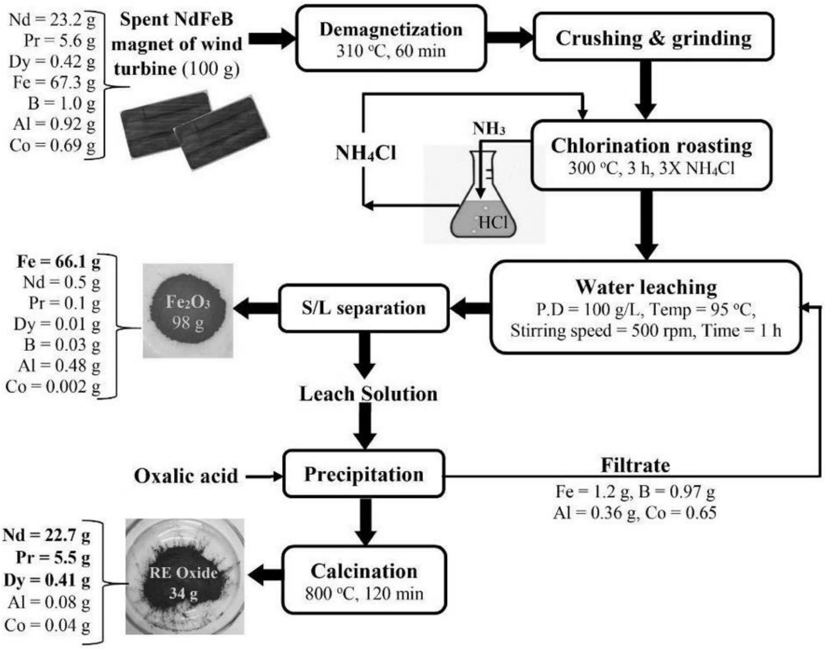

Figure 2

(Kumari et al., 2021).

Conclusion

In conclusion, the comparison of hydrometallurgical methods for recycling rare earth elements (REEs) from permanent NdFeB magnets reveals significant progress and potential developments toward sustainable recovery. With the rising demand for REEs in various industrial applications, recycling NdFeB magnets emerges as a crucial strategy to mitigate supply constraints and reduce environmental impacts.

The reviewed studies showcase diverse approaches to leaching and separation processes, each with its advantages and limitations. Complete leaching using HCl demonstrates exceptional REE recovery but raises concerns about sustainability and environmental impact due to the use of strong mineral acids. On the other hand, selective leaching methods, particularly chlorination roasting followed by water leaching, offer promising results with high REE recovery rates and a reduced environmental footprint. In terms of separation techniques, solvent extraction and oxalate precipitation emerge as effective methods for extracting REEs from leach liquors. While solvent extraction exhibits high efficiency, concerns regarding environmental sustainability persist due to the use of mineral acids. In contrast, oxalate precipitation, followed by calcination, offers a more environmentally friendly approach with impressive REE recovery rates. The adoption of acid-free selective leaching methods and environmentally friendly separation techniques underscores a growing emphasis on sustainability in REE recycling. However, further research is needed to improve the effectiveness of these techniques and optimize them for implementation on an industrial scale.

Moving forward, continued innovation and collaboration will be essential to address the challenges and maximize the potential of REE recycling from NdFeB magnets. By prioritizing sustainability and efficacy, these methods can contribute to a more environmentally responsible and resilient supply chain for REEs.

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