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Review

Hydrometallurgical Recovery of Rare Earth Elements from NdFeB Permanent Magnet Scrap: A Review

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Abstract: NdFeB permanent magnet scrap is regarded as an important secondary resource which contains rare earth elements (REEs) such as Nd, Pr and Dy. Recovering these valuable REEs from the NdFeB permanent magnet scrap not only increases economic potential, but it also helps to reduce problems relating to disposal and the environment. Hydrometallurgical routes are considered to be the primary choice for recovering the REEs because of higher REEs recovery and its application to all types of magnet compositions. In this paper, the authors firstly reviewed the chemical and physical properties of NdFeB permanent magnet scrap, and then carried out an in-depth discussion on a variety of hydrometallurgical processes for recovering REEs from the NdFeB permanent magnet scrap. The methods mainly included selective leaching or complete leaching processes followed by precipitation, solvent extraction or ionic liquids extraction processes. Particular attention is devoted to the specific technical challenge that emerges in the hydrometallurgical recovery of REEs from NdFeB permanent magnet scrap and to the corresponding potential measures for improving REEs recovery by promoting the processing efficiency. This summarized review will be useful for researchers who are developing processes for recovering REEs from NdFeB permanent magnet scrap.

Keywords: rare earth elements; NdFeB permanent magnet; hydrometallurgical; recovery

1. Introduction

NdFeB magnets are considered as the strongest permanent magnets with the highest energy product BH_{max} (200–440 kJ/m^3) of all permanent magnets [1]. They are widely used in wind turbines, hybrid electric vehicles, hydro-electric turbine generators, etc. [2]. Figure 1 shows the proportion of the different applications around the global NdFeB market.

Depending on the application field of NdFeB magnets, they have different life cycles and weight. The life cycles of NdFeB magnets range from 2–3 years for consumer electronics to 20–30 years in wind turbines. Meanwhile, the weight of NdFeB magnets ranges from less than 1 g for small electronics to 1–2 t for wind turbines [4]. The phase of NdFeB magnets based on (Nd, Pr, Dy)-Fe-B and other trace elements, with REEs contents of 27–32 wt.%, Fe content of 67–73 wt.%, B content of about 1 wt.% [5,6], and other minor metals, are determined by the applications of NdFeB magnets. Obviously, recovering REEs from NdFeB magnet scrap has good economic benefits.

Recyclable materials of NdFeB magnets scrap mainly include: (1) swarf originating from magnet manufacturing; (2) large magnets in wind turbines; (3) small magnets in End-of-Life consumer products. About 20–30 wt.% scrap is generated during the NdFeB magnets cutting and grinding processes, and 95% of those scraps can be recycled [7,8]. The NdFeB magnets used in wind turbines, hybrid vehicles and electric vehicles are easy to directly recycle or re-use [9]. However, it remains a social and technological challenge to collect and recover the magnets from the End-of-Life of small consumer electronics. In view of the potential economic and environmental benefits of utilizing the NdFeB magnet scrap, it is significant to develop appropriate methods for treating the NdFeB magnet scrap. At present, recycling of NdFeB magnet scrap mainly focus on the recovery of REEs. The disclosed methods include direct re-use in current form/shape [10–15], reprocessing of alloys to magnets after hydrogen decrepitation [12,14–18], pyrometallurgical methods [19–28], gas-phase extraction [29,30], and hydrometallurgical methods [31–37]. In Table 1, an overview of different methods for NdFeB magnet scrap recycling is given.

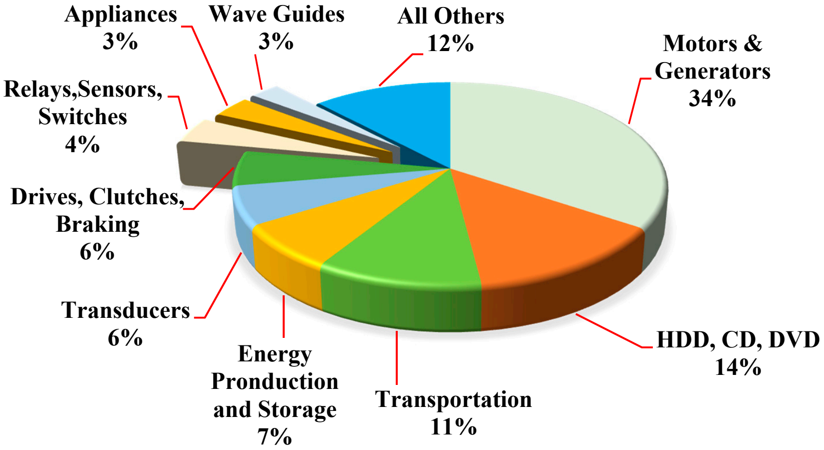


Figure 1. The proportion of different applications around the global NdFeB magnet market, data from [3].

Table 1. Overview of the advantages and disadvantages of different methods for NdFeB magnet scrap recycling, Reproduced with permission from [38]; published by Elsevier, 2013.

Method	Advantages	Disadvantages
Direct re-use in current form/shape	• Most economical way of recycling (low energy input, no consumption of chemicals) • No waste generated	• Only for large, easily accessible magnets (wind turbines, large electric motors and generators in hybrid and electric vehicles) • Not available in large quantities in scrap today
Reprocessing of alloys to magnets after hydrogen decrepitation	• Less energy input required than for hydrometallurgical and pyrometallurgical routes • No waste generated • Especially suited for hard disk drives (little compositional change over the years)	• Not applicable to mixed scrap feed, which contains magnets with large compositional variations • Not applicable to oxidized magnets
Pyrometallurgical methods	• Generally applicable to all types of magnet compositions • No generation of waste water • Fewer processing steps than hydrometallurgical methods • Direct melting allows master alloys to be obtained • Liquid metal extraction allows REEs to be obtained in metallic state	• Larger energy input required • Direct smelting and liquid metal extraction cannot be applied to oxidized magnets • Electroslag refining and the glass slag method generate large amounts of solid waste

Table 1. *Cont.*

Method	Advantages	Disadvantages
Gas-phase extraction	• Generally applicable to all types of magnet compositions • Applicable to non-oxidized and oxidized alloys • No generation of waste water	• Consumption of large amounts of chlorine gas • Aluminum chloride is very corrosive
Hydrometallurgical methods	• Generally applicable to all types of magnet compositions • Applicable to non-oxidized and oxidized alloys • Same processing steps as those for extraction of rare earths from primary ores	• Many process steps required before obtaining new magnets • Consumption of large amounts of chemicals • Generation of large amounts of waste water

Recycling of NdFeB magnet scrap has been researched broadly and various methods have been carried out. Among these methods, the hydrometallurgical methods seem to be the most prominent for recovering REEs from NdFeB magnet scrap because hydrometallurgical methods can be used to treat all types of magnets. More importantly, hydrometallurgical methods can be well connected with the existing REEs production industry. The purpose of the present paper is to provide an overview of REEs recovering from NdFeB magnet scrap by hydrometallurgical processes. The recycling potential of NdFeB permanent magnet scraps is firstly clarified, and then the chemical and physical characteristics of NdFeB permanent magnet scrap are provided. Lastly, hydrometallurgical methods for recovering REEs from NdFeB permanent magnet scrap are reviewed. This paper aims to offer a useful guideline for sustainable recovering REEs from NdFeB permanent magnet scrap.

2. Recycling Potential of NdFeB Permanent Magnet Scrap

According to the United States Geological Survey (USGS), the global annual consumption of rare earth oxides is about 120,000 t [39]. The market share of global consumption of rare earth oxides is shown in Figure 2; approximately 26,400 t of rare earth oxides are used in the permanent magnet market, accounting for a large proportion among all rare earth oxides consumption.

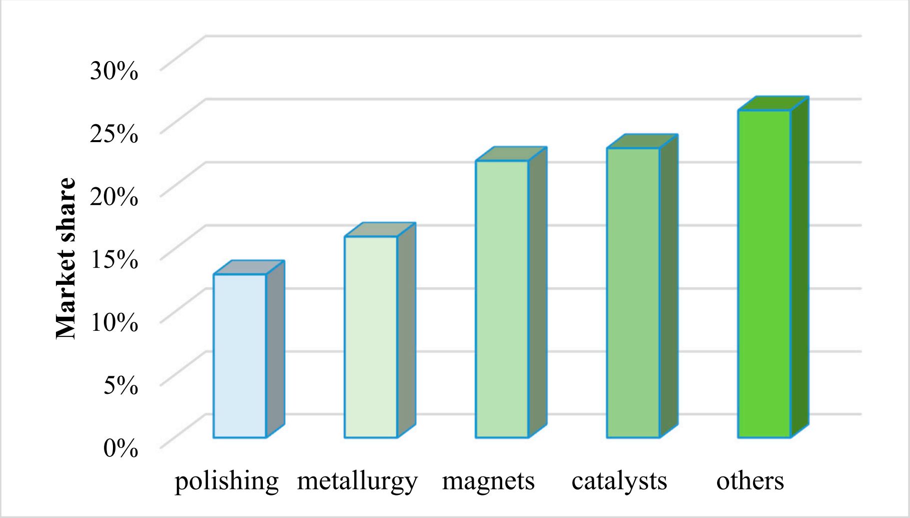


Figure 2. Market share of global consumption of rare earth oxides (based on data from the United States Geological Survey (USGS) [39]).

Alonso et al. [40] estimated the growths of market share of global REEs consumption according to the applications. As seen from Figure 3, the fraction of REEs demand in the magnets increased continuously until 2035. The magnets will become the most in-demand materials of REEs, and the fraction of REEs demand will be close to 50%, because of the rapidly developing technologies for clean energy and transportation (e.g., electric vehicles and wind turbines).

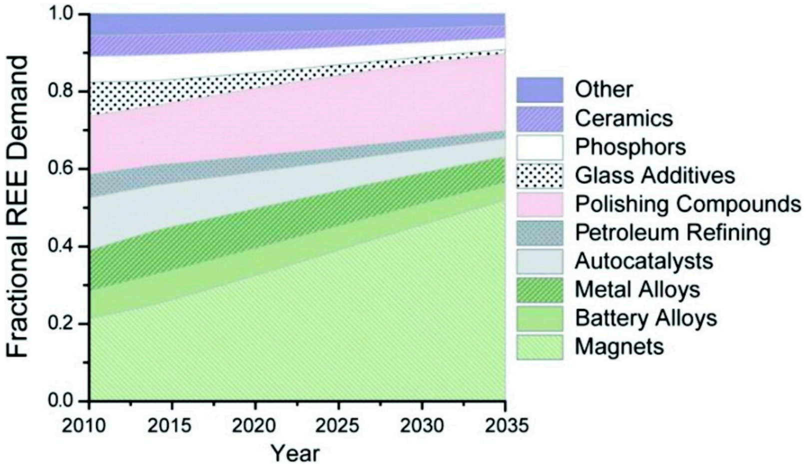


Figure 3. Predicted growths of market share of global rare earth elements (REEs) consumption [40]; published by American Chemical Society, 2012.

Schulze et al. [41] calculated the NdFeB demand for magnets used in different application groups and net availability of secondary NdFeB supply from End-of-Life (EOL) magnets from 2020 to 2030 based on low and high NdFeB demand scenario. As shown in Figure 4, the demand of NdFeB and the net availability of secondary NdFeB supply from EOL magnets both increase gradually. The demand of NdFeBis about 240 kt and 633 kt in 2030 for the low and high NdFeB demand scenario, respectively. Meanwhile, the net availability of secondary NdFeB supply from EOL magnets is about 27 kt and 54 kt in 2030 for the low and high NdFeB demand scenario, respectively. Obviously, the recovery of NdFeB magnets possesses huge potential value.

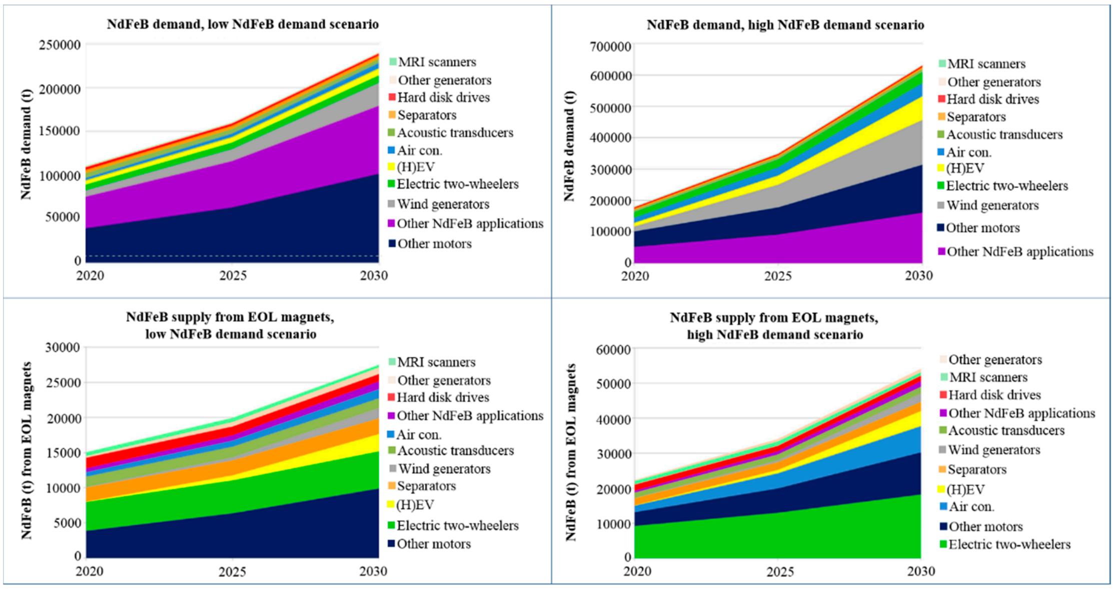


Figure 4. NdFeB demand and net supply from End-of-Life (EOL) magnets (losses during collection and disassembly have been subtracted) [41]; published by Elsevier, 2016.

The historical data (1983–2007) of NdFeB permanent magnets from China, Japan, the United States and Europe were used to estimate the global stock of REEs in NdFeB permanent magnets. The results showed that about 62.6 kt Nd, 15.7 kt Pr, 15.7 kt Dy and 3.1 kt Tb were stocked in NdFeB permanent magnets from 1983 to 2007. If these stocks are effectively recovered, they can serve as a valuable supplement to the geological stocks because they are about four times of the 2007 annual extraction of the individual elements [42]. Guyonnet et al. [43] presented an analysis of flows and stocks of some REEs along the value chain in Europe. The analysis indicated that in 2010, about 580 t Nd and 70 t Dy were wasted. The Sankey diagrams illustrate the serious imbalance of flows of REEs in NdFeB magnets along the value chain, and the Europe mainly depends on the import of finished products. They also indicated that the recirculation flow of Nd in NdFeB magnets is expected to be 170–230 t in 2020.

Schulze and Buchert [44] quantitatively analyzed the global recycling potential of EOL magnets from different application groups and industrial waste by dynamic material flow analysis. The modelled scenario shows that 18–22% of the global Nd and Pr and 20–23% of Dy and Tb used in NdFeB magnet production can be provided by EOL magnets and industrial scrap in 2020, 2025 and 2030. In another study [45], the authors estimated annual waste flows of Nd and Dy from three common permanent magnets. The results indicate that for some time to come, compared to the rapidly growing global REEs demand, the waste stream generated by permanent magnets will remain small, and the global recycling potential for the next few decades is also limited. Due to the small amount of waste, recycling at an economically advantageous scale is impossible. However, in the long term, waste stream generated by permanent magnets will increase dramatically and meet a large portion of the total demand for REEs. Therefore, those authors highlight that the NdFeB magnet is one of the most important secondary resources for the recovery of Nd and Dy. It is also suggested that decision makers should develop recycling technology through pilot projects, which should take about five to ten years to establish recycling practices [41].

There is no denying that recycling is a key technology for metal recycling from various sources. However, at present, recycling of REEs is within 1%, but the current situation demands that we improve the recycling of REEs from REEs-bearing wastes [38]. The NdFeB permanent magnet is an important REEs demanded material, and the NdFeB permanent magnet scrap has huge potential for REEs recovery.

3. Chemical and Physical Characteristics of NdFeB Permanent Magnet Scrap

The chemical and physical properties of NdFeB permanent magnet scrap are the starting point for choosing a suitable recycling process. These characteristics mainly include chemical composition, phase composition, and microstructural morphology.

3.1. Chemical Composition

Table 2 lists typical chemical compositions of NdFeB permanent magnet scraps. In fact, according to the compositions of REEs, NdFeB permanent magnet scraps can be classified into three categories, namely low REEs scraps (the contents of REEs < 20 wt.%), medium REEs scraps (the contents of REEs about 20–30 wt.%), and high REEs scraps (the contents of REEs > 30 wt.%). All types of NdFeB permanent magnet scraps contain Nd, sometimes, Tb, Dy, and Gd are also added to replace some fractions of Nd to increase the operating temperature and intrinsic coercivity of NdFeB permanent magnet [46,47]. Pr, La, and Sm are generally added to replace Nd at a lower production cost [48]. The addition of Co can improve the Curie temperature of the magnet [49]. The addition of Al, Cu, Nb, and Ni is proposed to replace some Fe, to increase the coercivity of NdFeB permanent magnet [50].

Table 2. Typical chemical compositions of NdFeB magnet scrap (wt.%).

Typical	Nd	Fe	B	Pr	Dy	Co	Sm	La	Nb	Gd	Tb	Cu	Al	Ni	Refs.
Low REE sscraps	10.70	79.20	5.75	2.68	0.43	0.79	-	-	-	-	-	0.11	0.19	-	[16]
	14.00	78.00	6.00	-	0.60	-	-	-	0.40	-	-	-	0.70	-	[19]
Medium REEs scraps	26.10	63.50	0.73	0.68	2.68	2.99	-	-	-	0.02	-	-	0.35	-	[51]
	25.38	61.09	1.00	2.62	1.08	1.42	-	-	-	-	-	-	0.95	2.03	[52]
	28.00	68.00	1.00	-	1.00	-	-	-	-	-	-	-		1.00	[53]
	23.70	66.10	0.91	0.12	2.42	3.34	-	-	-	-	-	-		3.00	[13]
	24.43	64.07	0.97	-	-	1.67	-	-	0.37	-	-	0.15	0.20	-	[54]
	21.00	70.60	1.04	-	6.30	0.57	-	-	-	-	-	0.15	-	-	[8]
High REEs scraps	19.40	66.30	0.96	6.43	5.21	-	0.77	-	-	-	-	-	-	0.87	[31]
	30.73	61.60	0.96	4.39	-	-	-	1.58	-	-	-	-	0.83	-	[25]
	18.80	63.90	1.02	5.98	5.93	0.42	-	-	-	1.51	-	-	1.04		[55]
	25.95	58.16	1.00	0.34	4.21	4.22	-	-	-	-	-	-	0.34	0.02	[34]
	25.95	58.16	1.00	0.07	4.21	4.22	-	-	0.83	-	-	-	0.34	0.02	[56]
	22.57	67.15	0.98	7.10	0.79	0.74	-	-	-	-	0.41	-	-	-	[14]

3.2. Phase Composition

The main phase of the NdFeB magnet scrap is $Nd_2Fe_{14}B$ [54,57], which accounts for 96–98%. Herbst et al. indicated the unit cell structure of $Nd_2Fe_{14}B$. The space group is $P4_2/mnm$, and there are four $Nd_2Fe_{14}B$ units (68 atoms) per unit cell. All the Nd and B atoms, but only four of the 56 Fe atoms, reside in the z = 0 and z = 0.5 planes. Between these, the other Fe atoms form puckered, yet fully connected, hexagonal nets [58]. Apart from $Nd_2Fe_{14}B$, NdO, Nd_2O_3, and the minor $NdFe_4B_4$ may appear in the grain boundary [51,55].

3.3. Microstructural Morphology

The coercivity of the NdFeB magnets is closely related to the interface microstructure between main phase ($Nd_2Fe_{14}B$) and the grain boundary phase (Nd-rich) [59]. Figure 5 shows the SEM images of the NdFeB magnet. Grain sizes of the NdFeB magnet are very small (Figure 5 left), and small agglomerates of the Nd-rich phase are also observed. The field emission gun scanning electron microscope image (Figure 5 right) shows a uniform continuous coating of $Nd_2Fe_{14}B$ grains, where the thickness of the Nd-rich grain boundary phase is a few nanometers, separating the individual grains. Scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDS) analysis was carried out to identify the compositional variation in the NdFeB magnets, and the results are listed in Figure 6. The results indicate that the Nd is concentrated in the grain boundaries instead of within the grains, and the Fe is concentrated within the grains.

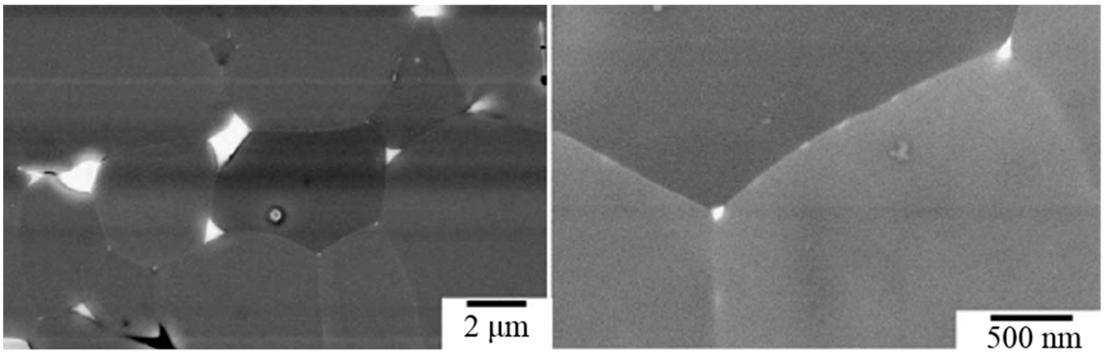
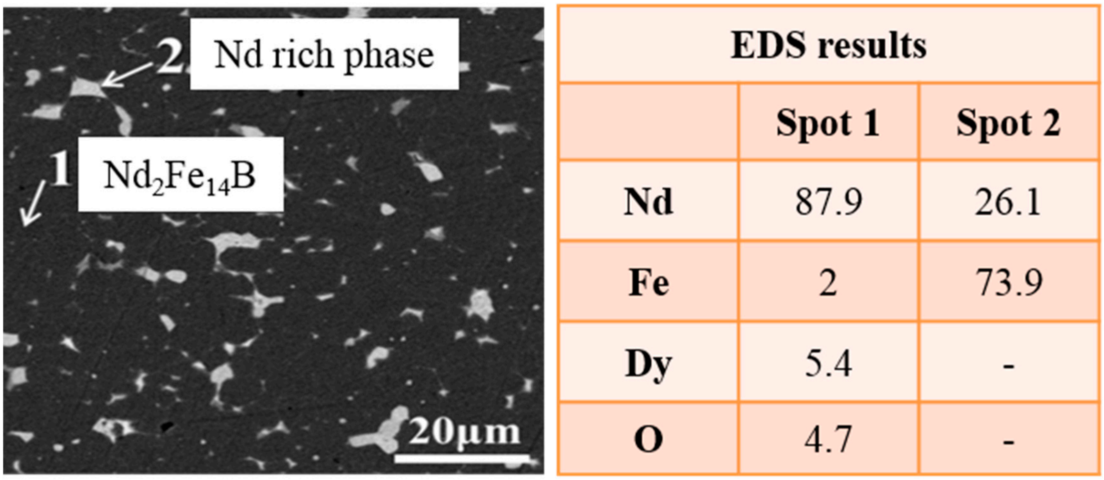


Figure 5. SEM images of NdFeB permanent magnets [59]; published by Elsevier, 2004.



EDS results

	Spot 1	Spot 2
Nd	87.9	26.1
Fe	2	73.9
Dy	5.4	-
O	4.7	-

Figure 6. SEM-EDS analysis of NdFeB permanent magnets [54]; published by Elsevier, 2014.

The distribution of Nd, Dy, C, Al, Si, Fe, Ce, and Pr in the NdFeB magnet scrap was analyzed using energy dispersive X-ray spectroscopy (EDX) mapping. As shown in Figure 7, the Fe is most abundant in the matrix, while Nd and Pr are located in the grains and concentrated on the grain boundaries. Dy and Ce are nearly evenly distributed over the surface [60]. According to Önal et al., the area dominated by Fe indicates the $Nd_2Fe_{14}B$ phase and the area highlighted by Nd and O represent the grain boundary phase. An area with a high B concentration represents the presence of $Nd_1Fe_4B_4$ phase. They also concluded that all target metals are distributed over the entire microstructure of the magnet and the structure needs to be completely destroyed to recover valuable metals from the NdFeB magnet [61].

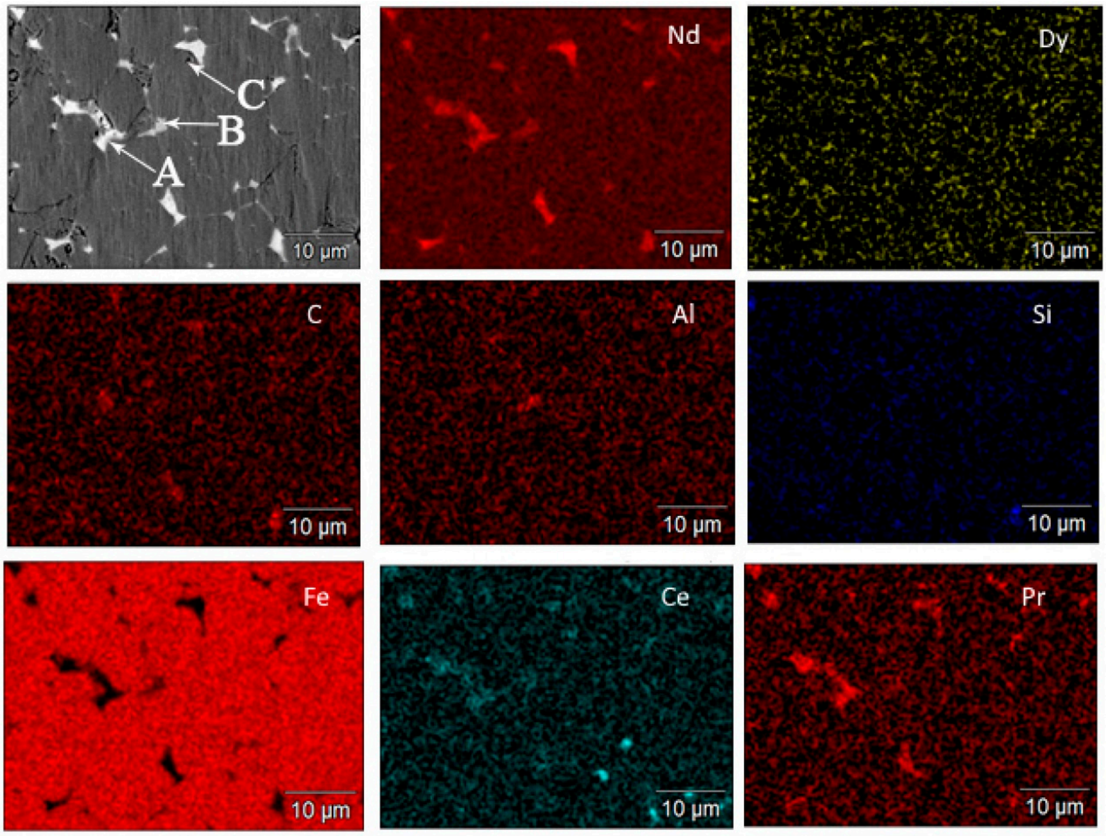


Figure 7. High-resolution EDX mapping of the NdFeB magnet scrap [60]; published by Elsevier, 2020.

4. Hydrometallurgical Processes for Recovering REEs from the NdFeB Magnet Scrap

For the treatment of NdFeB permanent magnet scrap, many hydrometallurgical processes have been developed or are under development. A brief schematic diagram of these hydrometallurgical processes is shown in Figure 8. The principle processes employed during hydrometallurgical treatment of REEs resources mainly include leaching, and REEs separation process [62–64]. In the present study, leaching technologies used for NdFeB permanent magnet scrap include selective leaching process and complete leaching process, which are followed by REEs separation technologies consisting of precipitation process, solvent extraction process and ionic liquids extraction process.

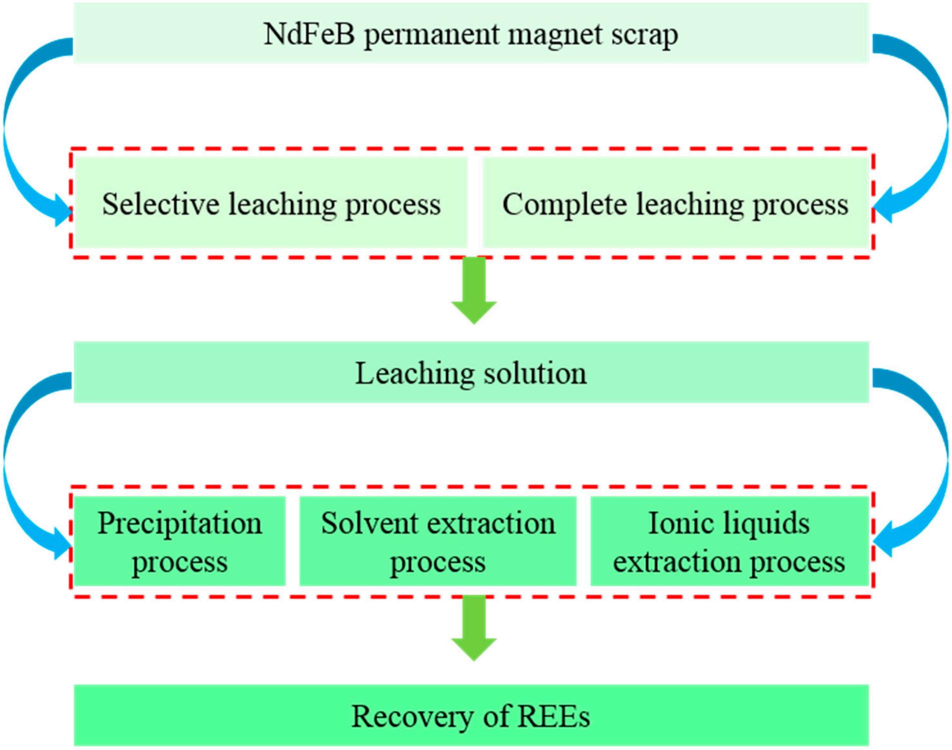


Figure 8. Schematic diagram of hydrometallurgical processes.

4.1. Leaching Technologies Used for NdFeB Permanent Magnet Scraps

Leaching is always the first step to dissolve the REEs in the magnet scraps [65,66]. According to the complexity level, different dissolution methods are used. Dissolution of the magnet scrap can be performed in two different ways: (1) selective leaching of NdFeB permanent magnet scrap depending on the solubility of metal at different conditions, (2) complete leaching of the NdFeB permanent magnet scrap.

4.1.1. Selective Leaching Process

The selective leaching process depends on the solubility between REEs and Fe. In order to improve the selectivity and efficiency, many pretreatment processes (e.g., roasting) have been carried out.

Thermal oxidation is often used to improve the selectivity before leaching [63,64]. During the thermal oxidation process, the relatively easily soluble Nd_2O_3 and insoluble Fe_2O_3 were formed to hinder the leaching of Fe in acidic solution. It was reported that, after oxidative roasting at 900 °C for 360 min, the roasted sample was leached by 0.02 mol/L HCl at 180 °C for 120 min, and the recovery of REEs and iron were 99% and 5%, respectively [67,68]. Similar research [59] reported that, under conditions of oxidative roasting at 900 °C for 480 min and subsequent dissolution with 37 wt.% HCl at 80 °C for 900 min, the leaching percentages of Nd and Dy were both above 90%. According to Kumari et al., the roasting of the magnet enhances the selectivity as well as the leaching efficiency. 98% of the REEs were selectively leached and iron oxide was left in the leaching residue under the conditions of roasting temperature of 850 °C, roasting time of 360 min, HCl concentration of 0.5 mol/L, leaching temperature of 95 °C, and leaching time of 300 min. At leaching temperature of 75–95 °C, the leaching of REEs follows the mixed controlled kinetic model with Ea of 30.1 kJ/mol [69]. An identical leaching process with HNO_3 as leaching agent was carried out and very similar results were obtained. Leaching with HCl and HNO_3 in the presence of a concentrated chloride or nitrate matrix (3.75 mol/L of $CaCl_2$ or 7.5 mol/L of NH_4NO_3) was also tested to prove that the leachate could be used directly into a cheap solvent extraction systems to further extract and purify the REEs [70,71]. However, during the oxidation roasting process, the inevitable formation of neodymium-iron mixed oxide ($NdFeO_3$) will hinder the leaching of Nd. To avoid the formation of $NdFeO_3$, Martina et al. [72], roasting the NdFeB scrap in Ar atmosphere at $PO_2 \leqq$ 10–20 atm with 5 wt.% C at 1400 °C for 120 min. The results showed that the roasting sample included a metallic Fe phase and B-Dy-Nd phase. After the recovery of metallic iron by mechanical treatment, the REEs in the NdFeB scrap can be completely dissolved in the water-containing ionic liquid [Hbet][Tf_2N] in 20 min.

Rabatho et al. described a process for recovering Nd and Dy from a NdFeB manufacturing process via selective leaching process. The leaching agents were 1 mol/L HNO_3+0.3 mol/L H_2O_2. The leaching of Nd and Dy was up to 98% and 81%, respectively, and the leaching of Fe was below 15% [73]. Another research reported that the pretreatment of the corrosion process increased the selectivity between Nd and Fe at room temperature, and nearly 100% of Nd was recovered from NdFeB magnet scrap [74].

An alkaline treatment of NdFeB magnet at various NaOH concentration was carried out. When the equivalents of NaOH was 10, the leaching of Nd and Dy was 91.6% and 94.6%, respectively, and the leaching of Fe of 24.2%, resulting in the highest selective leaching efficiency [60]. Using a sample prepared under the grinding and alkaline roasting treatments, 94.2%, 93.1%, 1.0% of Nd, Dy, Fe can be selectively leached at 90 °C in 1 mol/cm^3 acetic acid solution with 1% pulp density [75].

Itoh et al. proposed a new recovery process for REEs by selective chlorination roasting of the NdFeB magnet and leaching of the roasted sample in distilled water, the leaching of REEs reached 87% when chlorinating at 300 °C for 3 h, with a nearly negligible content of Fe in the solution [30]. Önal et al. developed a sulfation selective roasting followed by water leaching process. A suitable selective roasting and water leaching treatment showed that 95–100% Nd, Dy, Pr, Gd, Tb, and Eu were leached, while Fe remained in the leaching residue to form a marketable Fe_2O_3-based by-product [60]. This process offers a simple and controllable processing alternative that is completely compatible with the existing REEs production process [76]. It also faces some disadvantages; one disadvantage was that the sulfation roasting required relatively high temperature (750–800 °C). The other disadvantage was related to the low solubility limit of REE sulfate, which may have negative impact on process capability. More seriously, these solubility limitations can also cause problems in subsequent downstream processes, where organic/inorganic solvents are introduced into the leachate at higher temperatures (e.g., 60–80 °C) [34]. In order to avoid those disadvantages, they replaced sulfuric acid with nitric acid. Similar to sulfation roasting, the REEs nitrates are expected to remain soluble, and the solubility limit of the REEs nitrates is higher than that of its sulfate counterparts [55].

Venkatesan et al. reported an electrochemical route to selectively leach REEs from the NdFeB magnet scrap. At first, part of the magnet scrap was leached by HCl. A portion of the leachate was collected with the undissolved magnet scrap on the anolyte side of the two-chamber reactor (Figure 9), which was separated by an anion exchange membrane, and the catholyte was composed of NaCl solution. The Fe(II) in the leachate was oxidized and precipitated as $Fe(OH)_3$, and more than 95% of the REEs were dissolved in the solution [77]. In addition, when the NdFeB magnet scrap was completely leached with HCl, the Fe(II) in the leachate can be selectively oxidized to Fe(III) [78]. In another research, a route for recovering REEs from NdFeB magnet scrap based on electrochemical leaching was also verified (Figure 10). NdFeB magnet scrap was taken as an anode along with an inert anode in an electrochemical reactor (NH_4Cl was used as the electrolyte) to ensure the elements in the magnet scrap into the respective hydroxides, then leaching with HCl. The leaching of REEs and Co exceed 97% with Fe was left in the leaching residue [79].

The selective leaching process is considered to be a relatively commercial process for recovering REEs from NdFeB permanent magnet scrap in spite of several disadvantages [80–83]. The major shortcoming of this process is insufficient separation efficiency, and it is hard to avoid the unwanted elements going into a solution.

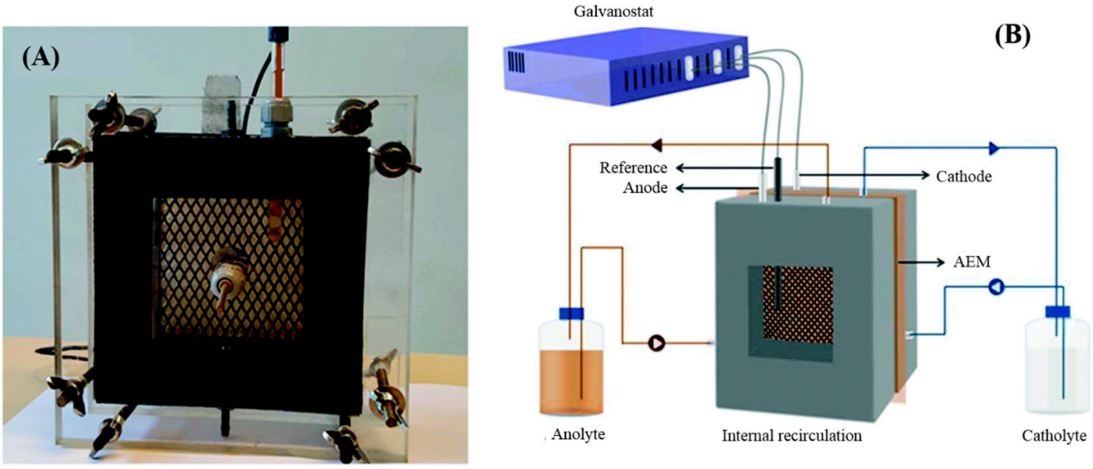


Figure 9. (**A**) Photo and (**B**) schematic illustration of the membrane electrochemical reactor [77]; published by Royal Society of Chemistry, 2018.

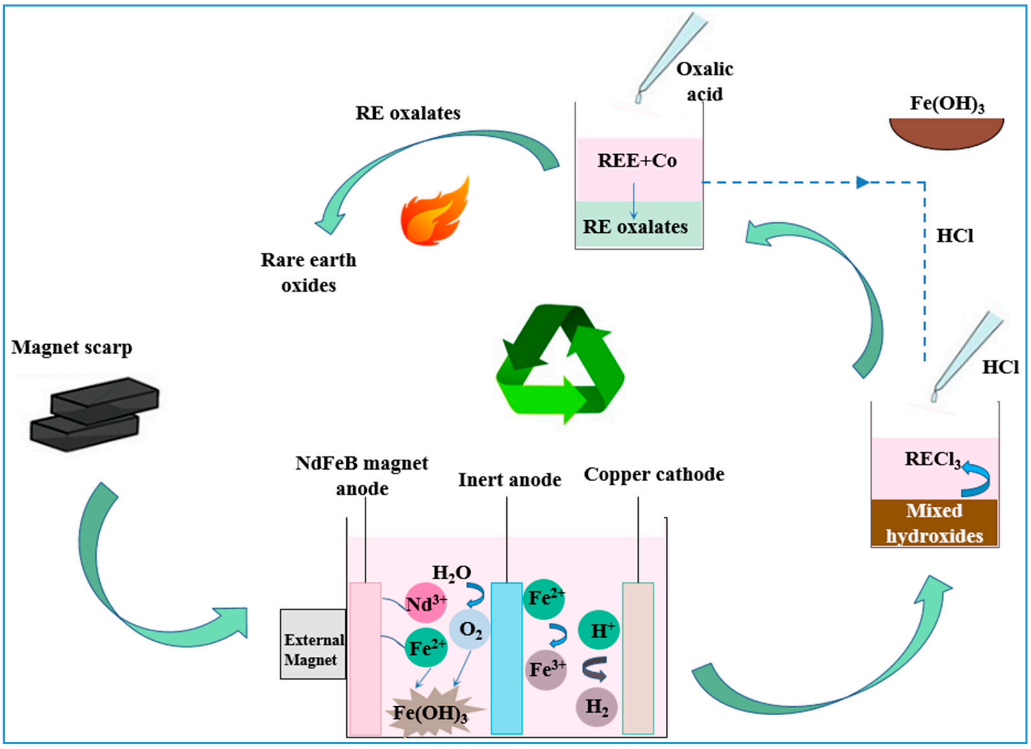


Figure 10. Process flowsheet for the proposed recycling scheme [79]; published by American Chemical Society, 2018.

4.1.2. Complete Leaching Process

The aim of complete leaching process is to dissolve the magnet completely. According to Itakura et al., a commercially available Ni-coated NdFeB sintered magnet was leached by 3 mol/L HCl and 0.2 mol/L $H_2C_2O_4$ at 110 °C for 6 h [53]. The NdFeB magnet went into a solution and Nd was formed a precipitate of neodymium oxalate and more than 99% of Nd was recovered. By addition of $Ca(OH)_2$, the B can be recovered from the highly acidic waste water by formation of $CaB_2O_5{\cdot}H_2O$ [84,85]. Abrahami et al. indicated the feasibility of directly leaching of NdFeB magnet scrap by H_2SO_4, although the composition of the scrap was complex, the combination of different steps still achieved a high recovery with a relatively pure rare earth double salt product (98.4%). Many impurities (mainly iron) were also dissolved in sulfuric acid, and these impurities can be removed after precipitation of

REEs [86]. A decomposition and leaching process of NdFeB permanent magnet scrap by oxidation roasting and sulfuric acid leaching were examined by Yoon et al. [87]. Under the conditions of roasting temperature of 500 °C for sintered scrap and of 700 °C for bonded scrap followed by H_2SO_4 (2 mol/L) leaching at 50 °C for 120 min, the leaching of Nd was over 99.4%, but 95.7% of Fe was also dissolved into the solution, which was similar to the results obtained by Layman and Palmer [88]. HCl and HNO_3 could also be used to completely leach magnet scrap [89]. The feasibility of organic acids for leaching REEs was verified by Gergoric et al. the results showed that after leaching with 1 mol/L acetic acid or citric acid at 25 °C for 24 h, the leaching of REEs exceeded 95% [90].

Electrochemical leaching was investigated to leach Fe and REEs from NdFeB magnet scrap with H_2SO_4 and $H_2C_2O_4$ by Makarova et al. [60]. The scanning Kelvin probe force microscopy results showed that the Local Volta potential difference between $Nd_2Fe_{14}B$ ϕ-phase and the Nd-rich anodic phases exceeded 500 mV, which indicated preferential selective leaching of the Nd-rich phase. A 3D printed Ti basket (Figure 11) was used to leach metals from the magnet scrap, the experimental results found that the acid concentration and current density strongly affected the leaching of REEs, and the addition of oxalic acid reduced the energy consumption and improved the recovery of REEs. The mechanism of dissolution was shown in Figure 12, fast and preferential leaching occurs in the less noble Nd-rich phases located around the Fe-rich $Nd_2Fe_{14}B$ grains (ϕ-phase), then whole grains of the ϕ-phase eventually falls off from the surface.

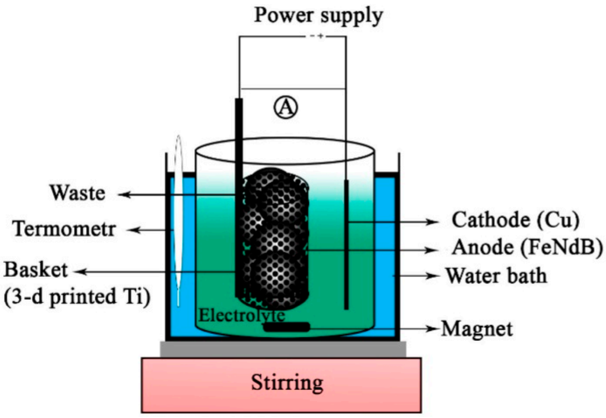


Figure 11. Schematic picture of electro-leaching in a Ti basket [60]; published by Elsevier, 2020.

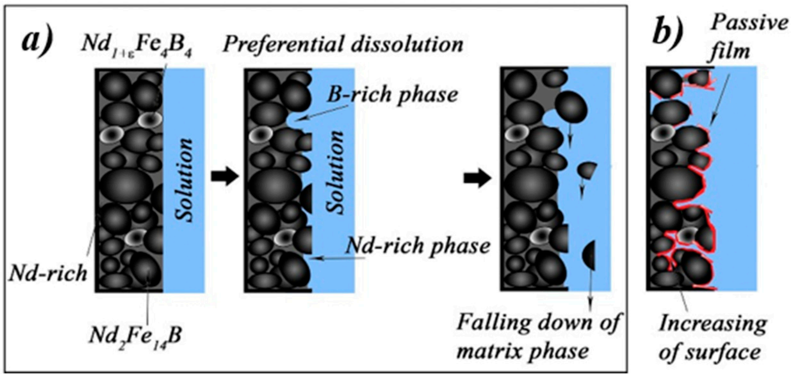


Figure 12. Schematic illustration of leaching process on the surface of NdFeB magnet scrap in (**a**) H_2SO_4, (**b**) mixture of H_2SO_4 and $H_2C_2O_4$ [60]; published by Elsevier, 2020.

Auerbach et al. [82] suggested recovering REEs from NdFeB magnet scrap by means of bioleaching with various bacteria. The *Acidithiobacillus ferrooxidans* and *Leptospirillum ferrooxidans* was confirmed to have highest leaching efficiencies with the leaching of Dy, Nd, and Pr of 86%, 91%, and 100%, respectively. However, due to the non-selective leaching of bacteria, further separation and purification processes should be carried out. Precipitation with concentrated $H_2C_2O_4$ and a two-step extraction process with the ionic liquid Cyphos IL 101 and subsequent treatment with DEHPA are considered to be the most effective methods. Extraction rates up to 100% with a purity of 98% were achieved.

The complete leaching process features a simple and easy operation, but the main shortcomings of this process include relatively high consumption of leaching agent and subsequent difficulties in removing impurities.

4.2. REEs Separation Technologies Used for NdFeB Permanent Magnet Scrap

Leaching liquor obtained through various leaching processes should be treated by different separation techniques such as precipitation, solvent extraction, and ionic liquids extraction to selectively separate REEs from the liquor [83,90]. Note that precipitation and solvent extraction can also use a combination of these. A brief comparison of these separation technologies is shown in Table 3.

Table 3. Comparison of different REEs separation technologies for NdFeB permanent magnet scraps.

Methods.	**Advantages**	**Disadvantages**
Precipitation	Low cost The process is simple	Low recovery Product is impurity Hard to obtain single REE
Solvent extraction	High recovery Can obtain high purity single REE	High cost The process is complicate Generation of large amount of waste
Ionic liquids extraction	High recovery Can obtain high purity single REE Efficient Environmentally friendly	High cost It is difficult to prepare ionic liquids system

4.2.1. Precipitation Process

The precipitation methods could be classified into two categories, namely selective precipitation and co-precipitation. According to the leaching process, the principle flowsheets of the precipitation processes are shown in Figure 13.

The resulting leaching solution is treated by a precipitation method with pH changes to separate Nd. Nd can usually be precipitated by direct methods such as fluoride method with HF and oxalate method with $H_2C_2O_4$ [83,91]. It has been found that strongly acidic solvents are suitable for the dissolution of NdFeB magnet scrap. However, these solvents cannot produce precipitation of the Nd compound. Therefore, some precipitating agents for Nd is needed. NaCl, ethanol and $H_2C_2O_4$ were used as precipitating agents by Itakura et al. It was indicated that these precipitating agents led to the formation of insoluble Nd compounds. However, Fe was contained in the precipitate when H_2SO_4/NaCl or H_2SO_4/ethanol were used as precipitating agents. But in a mixed aqueous solvent of 3.0 mol/L HCl and 0.2 mol/L $H_2C_2O_4$ via hydrothermal treatment at 110 °C for 360 min. About 99% of Nd contained in the magnet scrap was recovered as $Nd_2(C_2O_4)_3 \cdot xH_2O$ with a purity of 99.8% [56]. Mechano-chemical treatment with a mixed aqueous solution of HCl and $(COOH)_2$ has been proved to be an efficient method that can selectively recover REEs as oxalate from NdFeB magnet scrap without external heating. The optimal concentrations of HCl and $(COOH)_2$ were found to be 0.2 mol/L and 0.25 mol/L, respectively. The recovery and purity of REEs were 95.3% and 95.0%, respectively [92]. Over 99% of Nd can be recovered from a Fe-Nd solution by using H_3PO_4 and ascorbic acid via selective precipitation process [31]. Nd also can be recovered as Mn_2O_3-type Nd_2O_3, with the recovery of Nd of 97% via oxalic acid precipitation from NdFeB magnet scrap [74].

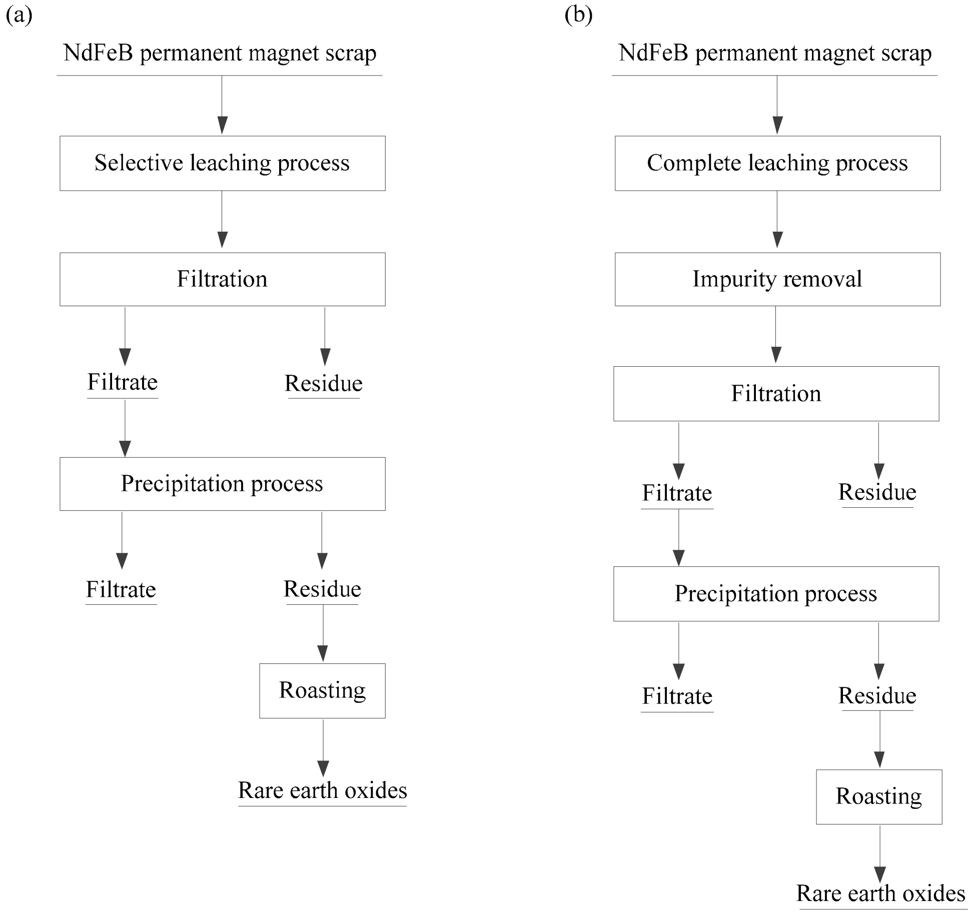


Figure 13. Principle flow of precipitation processes. (**a**) selective precipitation (**b**) co-precipitation.

Rabatho et al. tried to recover REEs from NdFeB magnetic waste sludge via selective precipitation process. Fe impurity in solution was first removed as $Fe(OH)_3$ with losses of Nd and Dy of 22.50% and 23.65%, respectively, by addition of NaOH solution to control the solution pH of 3, then Nd and Dy were precipitated by addition of $H_2C_2O_4$. 91.5% of Nd and 81.8% of Dy were recovered from the solution. After roasting the Nd and Dy containing precipitate at 800 °C, an Nd_2O_3 product with purity of 68% could be obtained, and the final recovery of Nd and Dy of 69.7% and 51% achieved, respectively [73]. Similarly, Kikuchi et al. researched precipitation of Fe^{3+} from NdFeB magnet scrap HNO_3 leaching solution by adjusting pH to 4.3 with the addition of NaOH [93]. As shown in Figure 14, the REEs were selectively dissolved from a crushed and roasted NdFeB magnet by acid, then purified by solvent extraction and precipitated as pure REE oxalate salt [56].

Although these methods can effectively separate Nd from other metals, due to the difficulty of filtering NdF_3 (because of the addition of HF), the production cost of Nd oxalate is high and non-selective, so it is not preferred. Double salt precipitation ($Nd_2(SO_4)_3$, $Na_2SO_4 \cdot 6H_2O$) may be an option for the precipitation of Nd with NaOH, and the REEs can be separated from Fe inexpensively without filtration problems. Nd was successfully separated from the optimized H_2SO_4 leaching solution and Nd was separated in the form of heavy salt precipitation with a heavy salt content of 75.41% [89]. Although the composition of NdFeB magnet scrap is complex, the combination of different steps makes it possible to obtain a relatively pure rare earth double salt product (98.4%) with a high recovery by using the precipitation method [82,94].

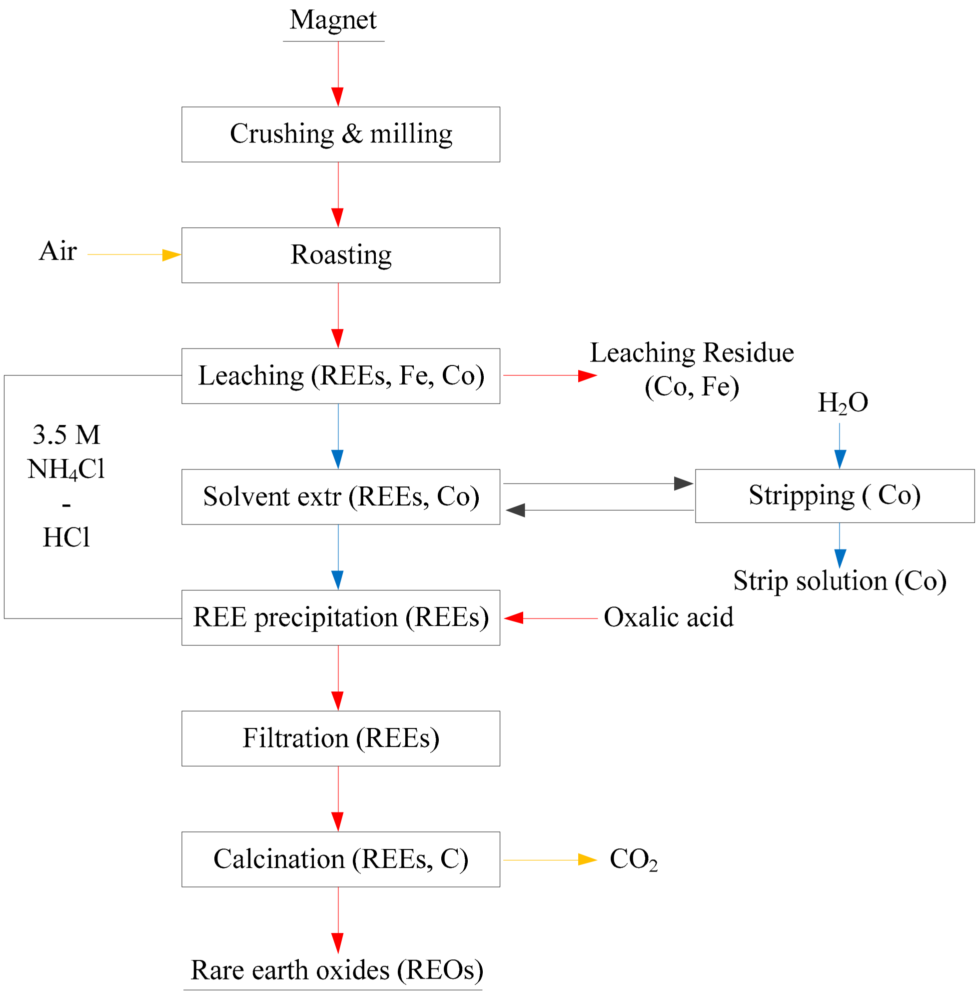


Figure 14. Flow chart of the recycling scheme. Yellow arrows: gas steams, blue arrows: aqueous streams, black arrows: ionic liquid steam, and red arrows: solid streams [56]; published by Royal Society of Chemistry, 2014.

Compared with the selective precipitation method, the co-precipitation method can simultaneously recover the valuable elements in the NdFeB magnet leaching solution [37,95,96]. Using this method, a composite powder containing REEs, Fe and Co can be obtained. The powder can be directly used as raw material for the preparation of all types of NdFeB magnetic powder with controlling to add desirable elements. Based on the thermodynamic simulation and calculation of MATLAB in the $H_2C_2O_4$-NH_3 co-precipitation system, an effective co-precipitation route (see Figure 15) was carried out to obtain a composite powder containing more than 99.4% of valuable elements, such as Fe_2O_3, $Fe_2O_3{\cdot}Nd_2O_3$, and Pr_2CoO_4. These valuable elements can be directly used as raw materials for the preparation of recycled NdFeB magnetic powder [37].

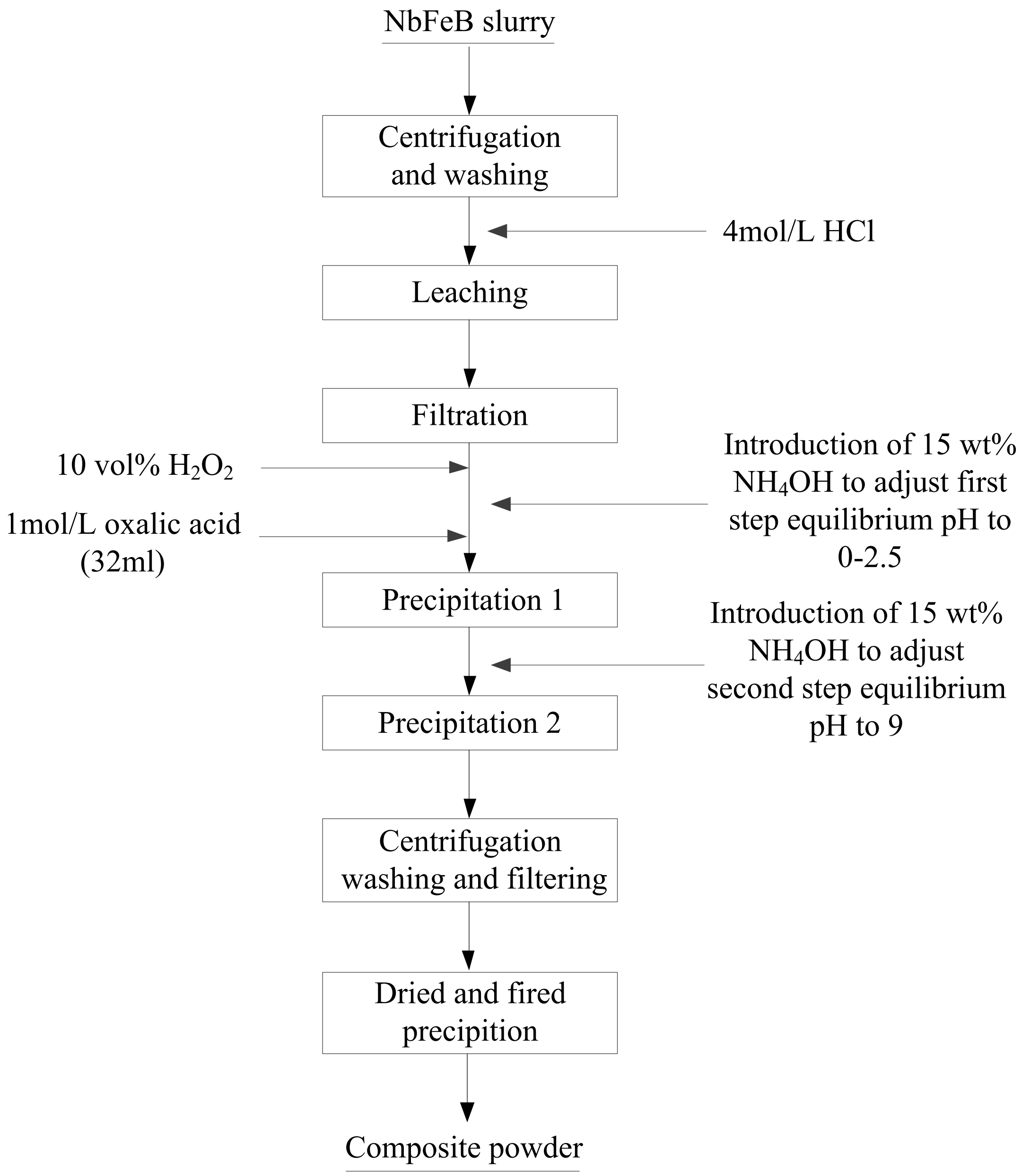
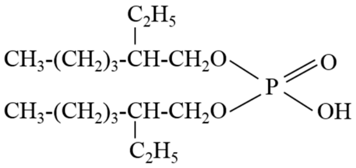
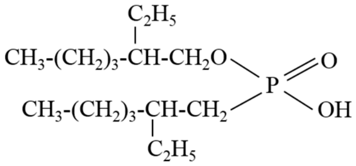
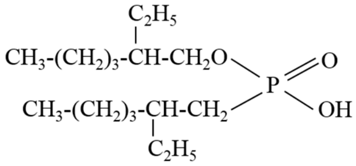
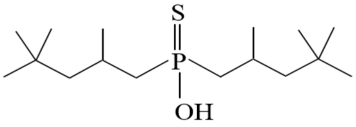
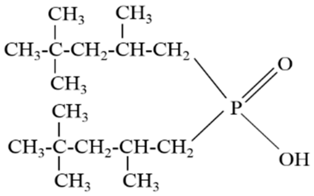
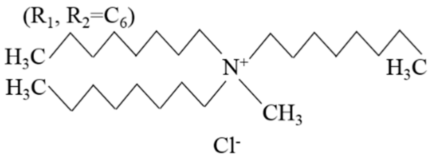
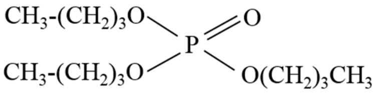
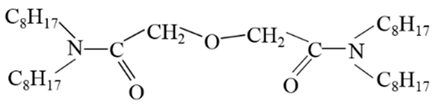


Figure 15. Scheme for the synthesis of a composite powder from NdFeB magnet scrap leaching solution using a co-precipitation method [37]; published by Elsevier, 2014.

4.2.2. Solvent Extraction Process

Because of the chemical similarity of REEs, separation of each other from different sources is one of the greatest challenges in the recycling of REEs [97,98]. Among various separation techniques, solvent extraction can be an effective method for separating and extracting individual metal or obtaining mixed solutions and compounds. Solvent extraction is a process for the selective extraction of a target component from an aqueous solution with one or more water immiscible organic reagents. To develop feasible and eco-friendly processes, extensive studies have been carried out for the extraction of various REEs by solvent extraction process using different organic extractants. Corresponding salient features of extractants are presented in Table 4. According to the solvent extraction mechanism, the solvent extraction process could be classified into four categories, including acidic solvent extraction (cationic solvent extraction), ion-pair solvent extraction (anion solvent extraction), neutral solvent extraction, and synergetic solvent extraction [99]. The properties of their extraction and separation, the formation of complex, separation factor, etc., have been highlighted as given below.

Table 4. Different organic solvents used for the extraction of REEs.

Reagents Class	Extractants	Chemical Name	Structure
Acidic extractant	D2EHPA	Di-2-ethylhexyl phosphoric acid	
	EHEHPA	2-ethylhexylphosphonic acid mono-2-ethylhexyl ester	
	PC88A	2-Ethylhexyl phosphonic acid mono 2-ethylhexyl ester	
	Cyanex 302	Bis(2,4,4-trimethylpentyl) monothiophosphinic acid	
	Cyanex 272	Di-2,4,4,-trimethylpentyl phosphinic acid	
Anion extractant	Aliquat 336	Tri-octyl methylammonium chloride	
Neutral extractant	TBP	Tri-n-butyl phosphate	
	TODGA	Tetraoctyldigylcol amide	

Acidic Solvent Extraction

Acidic solvent extraction uses weak organic acid as the extractants. Acidic extractants are used to extract and separate REEs because they form cationic species in aqueous solution. The general extraction mechanism shows as the following equation [99]:

$$\mathrm{M^{n+} + nHA = MA_{n(org)} + nH^{+}{}_{(aq)}} \tag{1}$$

Various acidic organophosphorous extractants have been used in REEs extraction processes. D2EHPA, di-(2-ethylhexyl) phosphoric acid (HDEHP), PC88A and EHEHPA are the most widely used solvents [100,101]. HCl, H_2SO_4 and HNO_3 were utilized as extraction media for the extraction of Nd, Eu and Tm using D2EHPA as an extractant. The results indicated that the equilibrium constants increased as the order: Nd < Eu < Tm [102,103]. Proximate researches confirmed that the extraction results of lanthanides with D2EHPA from HNO_3 were poorer than those from HCl and H_2SO_4 solutions [97]. The selectivity sequence for extracting REEs from 0.5 mol/L HCl solution with 0.75 mol/L D2EHPA in toluene was Lu > Yb > Tm > Tb > Eu > Pm > Pr > Ce > La, and the average separation factor of two adjacent REEs was 2.5 [104]. Although the REEs extraction efficiency of D2EHPA is very high, however, the difficulty of stripping the loaded extractant limits its utilization, especially for the extraction of heavy REEs. Lately, PC88A has attracted considerable attention to replace D2EHPA in the separation of REEs because of its higher separation factor for REEs (Table 5) [105]. Mohammadi et al. compared the separation of Nd, Dy and Y by D2EHPA and EPEHPA, the calculated separation factors at equilibrium pH = 1 indicated that D2EHPA was the most effective for separating Nd from Y and Dy, and the EHEHPA showed the highest separation factor for Y and Dy [106].

Table 5. Separation factors for extraction of rare earths by DEHPA and PC88A.

Rare Earths Pair	DEHPA	PC88A
Ce/La	2.98	6.83
Pr/Ce	2.05	2.03
Nd/Pr	1.38	1.55
Sm/Nd	6.58	10.60
Eu/Sm	1.90	2.30
Gd/Eu	1.43	1.50
Tb/Gd	0.93	5.80
Dy/Tb	2.40	2.82
Ho/Dy	1.90	2.00
Er/Ho	2.25	2.73
Er/Y	1.37	1.43
Tm/Er	2.90	3.34
Yb/Tm	3.09	3.56
Lu/Yb	1.86	1.78

The PC88A in kerosene exists in the form of dimer, and the extraction of Nd with PC88A can be expressed as the Equation (2) [107]. According to Lee et al., the extraction reaction of Nd with PC88A in chloride solution was identified by the graphical method as shown in Equation (3). They also observed that the distribution coefficients of Nd increased linearly with the equilibrium pH range of 0.62–1.01 [108].

$$\mathrm{Nd}^{3+} + \frac{3+x}{2} H_2A_{2,org} = NdA_3xHA_{org} + 3H^{+} \tag{2}$$

$$Nd^{3+} + 1.5H_2A_{2,org} = NdA_3HA_{org} + 3H_{aq}{}^{+} \tag{3}$$

where H_2A_2 and org represents the PC88A dimer and the organic phase, respectively.

The acidic extractants saponified with NaOH was researched to overcome the adversely affects caused by acid liberated during the acidic extraction process [106,109–111]. Moreover, partial saponification was preferred to avoid gel formation and the solution of the saponified extractant in the aqueous phase. Compared with Nd distribution coefficients of PC88A, the use of 40% saponified PC88A significantly improved the extraction of Nd [108]. A comparative study between Cyanex 302, PC88A and Cyanex 272, NaCyanex 302, NaPC88A and NaCyanex 272 for extracting Nd from a chloride solution has been conducted by Padhan et al. [33]. It was found that Cyanex 272 had the highest extraction rate and Cyanex 302 showed the lowest extraction rate. It is reported that the synthesized Primene 81R·Cyanex 572 ionic liquids can overcome the shortcomings of Cyanex 272 and Cyanex 572 of the sensitivity to pH value. 99.99% of Nd can be extracted from Nd/Tb/Dy containing aqueous by two stages counter-current extraction process with 0.30 mol/L Primene 81R·Cyanex 572 ionic liquid, and without pH adjusting [112]. Because saponified Cyanex 302 was an effective commercial reagent for extracting Nd, Padhan et al. [111] used it as the extractant to separate Nd and Dy. A maximum separation factor (D_{Dy}/D_{Nd}) of 53.65 was observed at pH = 1.2. Extraction of Dy was 98% with co-extraction of Nd only 7.22% after two stages of counter current extraction in 0.125 mol/L NaCyanex 302 at A:O = 1:1. Then, 99.79% of Nd can be recovered with 0.2 mol/L NaCyanex 302 in two counter current extraction stages at A:O = 1:1.

Ion-Pair Solvent Extraction

Ion-pair solvent extraction is effective in the presence of strong anionic ligands because of ion-pair solvent extraction metal ions as anionic complexes. Ion-pair solvent extract mainly nitrogen and oxygen containing organic compounds, such as tri-alkyl methylamine (Primene JMT) and tri-octylmethylammonium nitrate (Aliquat 336).

According to early work, separation factors for adjacent REEs with primary or tertiary amines were higher in sulfate media than in chloride media, so that sulfate media was more promising for ion-pair solvent extraction [113,114]. El-Yamani and Shabana indicated that the extraction of La from sulfate solutions with Primene JMT was extracted according to the following Reactions (4) and (5) [115]. The extraction reaction of quaternary ammonium salts could be also simply represented as Reaction (6) [116,117] where RNH_2 denotes the Primene JMT in the organic phase, Ln denotes the rare earth ion and $R_4N^+NO_3{}^-$ the quaternary ammonium nitrate salt.

$$2\overline{RNH_2} + H_2SO_4 = \overline{(RNH_3)_2SO_4} \tag{4}$$

$$2\mathrm{La}(SO_4)_2{}^{3-} + \overline{3(RNH_3)_2SO_4} = \overline{2(RNH_3)_3La(SO_4)}_3 + 3SO_4{}^{2-} \tag{5}$$

$$Ln^{3+} + 3NO_3{}^- + x\overline{(R_4N^+NO_3{}^-}_n = \overline{Ln(NO_3)_3\ xnR_4N^+NO_3{}^-} \tag{6}$$

Amines is mainly used for the separation of Pr, Nd, Y and heavy lanthanoids [117]. Lu et al. [118] obtained a high purity (>99%) of Nd with recovery of 95% from didymium nitrate solution by Aliquat 336 in a 45-stage tube-type mixer-settler. Another study described a solvent-extraction process for the recovery of magnet-grade Nd_2O_3 from a light rare earth nitrate liquor used a 0.50 mol/L Aliquat 336 nitrate in Shellsol AB in 8 extraction and 6 scrubbing stages [119].

Neutral Solvent Extraction

Various neutral extractants have been used for REEs separations, and it has been confirmed that TODGA is a promising extractant [120] and could be used for the extraction of REEs from the NdFeB magnet scrap leaching solution. TODGA forms a strong tridentate complex with metal ions, and, compared with other ions in aqueous solution, it has previously exhibited particularly good extraction performance for lanthanides and action elements in terms of the selectivity [121].

The effect of the diluent on the extraction and the selectivity of the TODGA was researched by Gergoric et al. [52]. The efficiency of the diluents decreases in the following order: hexane < cyclohexanone < Solvent 70 < toluene < 1-octanol. With the exception of cyclohexanone, the distribution ratio of extractable substances decreases with the polarity of the diluent [122]. It was also found that, in all diluents, the distribution ratio of REEs increased with TODGA concentration increased. A supported liquid membrane processes for extracting REEs from NdFeB magnets with TODGA or Cyanex 923 as extractants were evaluated to define the distribution coefficient and selectivity of Nd and Dy, respectively. It was found that TODGA has superior selectivity in REEs recovery than Cyanex 923. REEs solution in HNO_3 showed higher distribution coefficients and selectivity than in HCl. Lower molar concentration of HNO_3 in the strip resulted in higher recovery of Nd [123].

Synergetic Solvent Extraction

The phenomenon that the distribution coefficient of some extracted substances is greater than the sum of the partition coefficients when two or more extractants are used alone under the same conditions is called the synergistic effects. Many types of synergistic solvent extraction systems for extracting and separating REEs have been reported, including mixtures of acidic extractants, mixtures of neutral extractants, and combinations thereof [124–127].

In the past ten years, the use of different mixtures of acidic organophosphorous extractants to improve the extraction efficiency and selectivity of REEs has attracted attention. Extraction of REEs with a mixture of D2EHPA and EHEHPA was reported to be a promising method, which could not only decrease the acidity required for stripping the loaded D2EHPA but also increase the extraction efficiency of EHEHPA [128,129]. Higher selectivity and extraction efficiency of REEs can be achieved by using mixtures of D2EHPA and EHEHPA. The extraction reaction of REE with cationic extractants D2EHPA and EHEHPA, represented as Reaction (7) [130,131].

$$\mathrm{REE^{3+} + mH_2A_2 = REEA_3(HA)_{2m-3} + 3H^+} \quad (7)$$

where H_2A_2 represents the dimeric form of the extractant.

It was suggested that the improvement of the extraction capacity of the mixed system may be attributed to the breakage of the dimers of D2EHPA and EHEHPA [132,133]. As the HCl concentration increases, with the exception of the cationic exchange reaction in Reaction (7), a solvating reaction has been proposed, as shown in Reaction (8) [131].

$$\mathrm{REE^{3+} + 3Cl^- + mH_2A_2 = REECl_3(HA)_{2m},} \quad (8)$$

Extraction of Nd, Dy, and Y from HCl solution by using D2EHPA, EHEHPA and their mixtures were investigated by Mohammadi et al. [105], the extraction order in general was found to be Y > Dy > Nd. The extraction efficiency of Y, Dy, and Nd increased with the extractant concentration increased and the acidity decreased. Mixture of EHEHPA and D2EHPA improves the extraction of Nd when extractants concentration of 0.15 mol/L and equilibrium pH = 1. Separation factors calculated for an equilibrium pH of 1 show that at low concentration of extractant (0.06 mol/L and 0.09 mol/L) the mixture of EHEHPA and D2EHPA beneficial to separate Dy and Y. The REE distribution ratios and EHEHPA/D2EHPA ratios of the two extractants and their mixtures at different extractant concentrations indicate that the stoichiometrically different complexes of Dy, Nd and Y depend on the concentration of REEs and D2EHPA concentration.

The synergistic extraction of Nd from HNO_3 medium using the mixture of Cyanex 272 and Cyanex 921/Cyanex 923 (B) has been studied by Panda et al. [134]. The extraction of Nd from 0.001 mol/L HNO_3 using 0.6 mol/L Cyanex 272 in kerosene was 95.5%. It was found that the calculated synergy coefficient for the extraction of Nd using a mixture of 0.1 mol/L Cyanex 272 and Cyanex 923 was higher than that for the extraction of a mixture of 0.1 mol/L Cyanex 272 and Cyanex 921 in 0.001 mol/L HNO_3 solution.

To increase the extraction of Pr and Nd by Cyanex 272, the mixture of Cyanex 272 with Alamine 336, TOA or TEHA have been employed from chloride solution [135]. Among those mixture systems, the Cyanex 272 and Alamine 336 mixture performed the highest synergism enhancement factors for Pr (14.2) and Nd (10.1). The extraction reaction of Pr and Nd with the mixture of Cyanex 272 and Alamine 336 progresses gradually. At first, the REEs were extracted by Cyanex 272 with a cationic exchange mechanism (Equation (9)). Secondly, during the extraction process, the protons released by Cyanex 272 were simultaneously extracted into organic matter through Alamine336. The overall extraction reaction of Pr and Nd with the mixture of Cyanex 272 and Alamine 336 could be written as Equation (10).

$$RE^{3+} + Cl^- + 2H_2A_2 = REClA_2{\cdot}2HA + 2H^+ \text{ (RE = Pr, Nd)} \tag{9}$$

$$RE^{3+} + (x+1)Cl^- + 2H_2A_2 + xNR_3 = RECl(HA_2)_2 + xR_3NHCl + (2-x)H^+ \text{(RE = Pr, Nd)} \tag{10}$$

where the value of x ($0 \le x \le 2$) is dependent on the concentration ratio of Alamine 336 to the chloride ion.

Hence, it can be concluded that the chloride ion concentration in the aqueous phase is significantly affecting the extraction of Nd and Pr in the mixture of Cyanex 272 and Alamine 336.

A similar experiment was performed on the extraction of Nd with a mixture of Cyanex 302 (HB) and Alamine 308 by Kumar et al. The mixture showed a significant synergistic effect with a synergistic factor of 44.1. Raction for extracting Nd with this mixture is shows in Equation (11) [136].

$$Nd^{3+} + Cl^- + (HB)_2 + 2R_3N = NdClB_2{\cdot}2R_3N + 2H^+ \tag{11}$$

Because of the extractants used in synergistic systems are generally consist of a mixture of acidic and neutral extractant, the acids released during the extraction of REEs with these acidic extractants can adversely affect extraction. Thus, a present work was directed to study the extraction behavior of La and Nd from HNO_3 solution using a mixture of TOPO and TRPO neutral extractants in kerosene to keep the best conditions to recover and separate REEs. Extraction of Y from HNO_3 medium with a mixture of neutral organophosphorus reagents gave synergistic behavior and forming a neutral complex of the form of $\overline{M(NO_3)_3(TOPO)(TRPO)}$, and the reaction in case of synergism could be written as Equation (12) [137]. The extraction order for the REEs studied was Nd > Y > La.

$$M^{3+} + 3NO_3{}^- + \overline{TOPO} + \overline{TRPO} = \overline{M(NO_3)_3(TOPO)(TRPO)} \tag{12}$$

4.2.3. Ionic Liquids Extraction Process

Ionic liquids (ILs) have the ability to solvate many compounds [138]. Meanwhile, ILs was considered to be environment friendly solvents with the potential to replace traditional organic solvent [139]. Recently, emphasis has been placed on such solvents in cleaner production processes [140,141].

Non-Functional Ionic Liquids

ILs made with imidazolium salts, which are denoted as $[C_nmim]$, were the first potential ILs to be used for extracting REEs. $[C_8mim][PF_6]$ was first tested for separating Ce (IV) from HNO_3 solutions containing La (III) and Th (IV) [142]. It was found that the distribution ratios of Ce (IV) and Th (IV) using pure $[C_8mim][PF_6]$ as the extract phase was similar to that using HDEHP or DEHPA in n-heptane, which indicated that $[C_8mim][PF_6]$ is possible to act as both extractant and diluent.

In traditional organic solvents, metal ions are always extracted with a neutral extractant together with their counter anions, which is called the neutral mechanism. However, the cation exchange mechanism, an anion exchange mechanism, or neutral mechanism can appear in the IL system.

A general equation of the cation exchange mechanism can be written as in Equation (13) or demonstrated as in Figure 16a, where L is the extractant, M is the REE, and C is the cation of IL.

$$M^{m+} + mL + mC_{IL}{}^{+} = ML_{m,IL}{}^{m+} + mC^{+} \quad (13)$$

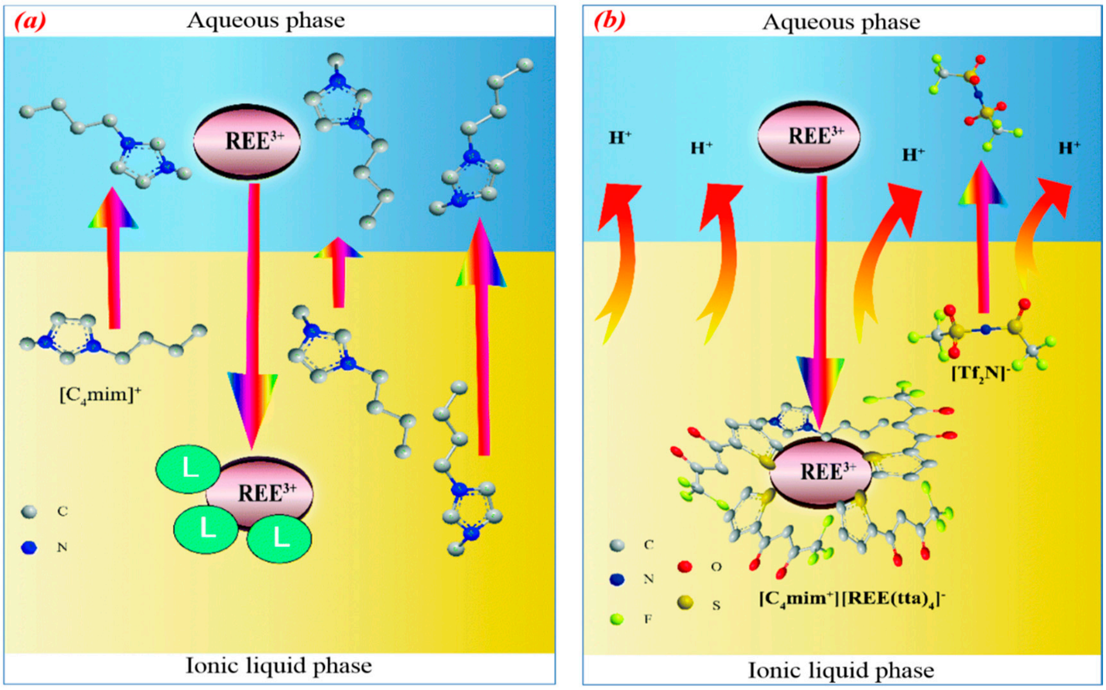


Figure 16. (**a**) Cation exchange in an ionic liquids (IL) system, (**b**) Anion exchange in IL system [143]; published by Royal Society of Chemistry, 2017.

The cation exchange mechanism largely depends on the hydrophobic character of ILs, Nd^{3+} extraction with Cyanex 923 in five ILs with the same anion but different cations showed that the extraction efficiency of Nd^{3+} in ILs with a small hydrophilic cation such as $[C_4mim][Tf_2N]$ and $[N_{1444}][Tf_2N]$ was higher than that in ILs with a hydrophobic cation such as $[C_{10}mim][Tf_2N]$, $[P_{66614}][Tf_2N]$, or $[N_{1888}][Tf_2N]$ [144]. In other words, hydrophilic cations promote cation exchange, while hydrophobic cations inhibit cation exchange.

Anion exchange was observed in the biphasic aqueous/IL system by Jensen et al. $[C_4mim][Tf_2N]$ functioned via liquid anion exchange mechanisms accelerates the formation of $REE(tta)_4{}^-$ in the IL phase, while $REE(tta)_3$ were generally formed in organic solvents or cationic complexes, $REE(tta)_2{}^+$, as observed in previously reported IL systems. $[Tf_2N]^-$ was transferred to the aqueous phase to keep the charge neutrality, and $[C_4mim^+][REE(tta)_4{}^-]$ be part of the IL phase without greatly changing the general structure of the IL [145]. The full equilibrium could be described as in Equation (14), and the details of an anion exchange mechanism in an IL, as shown in Figure 16b.

$$REE^{3+} + 4Htta + [C_4mim][Tf_2N]_{IL} = [C_4mim+][REE(tta)_4{}^-]_{IL} + 4H^+ + [Tf_2N]^- \quad (14)$$

Part of the ionic liquid components in the anion exchange system will still be transferred to the water phase, which will contaminate the water phase and consume IL. Therefore, the neutral mechanism opposite to the conventional organic solvent mechanism can also be used in the IL system. According to Kubota et al. [146] the mechanism in $[C_nmim][Tf_2N]$/DODGAA is the same as that in n-dodecane, that is, protons exchange in the reaction between DODGAA and REEs. The extraction equation of REE^{3+} ions with DODGAA (HL) is given in Equation (15) and Figure 17.

$$M^{3+} + 3HL_{IL} = ML_{3,\,IL} + 3H^{+} \quad (15)$$

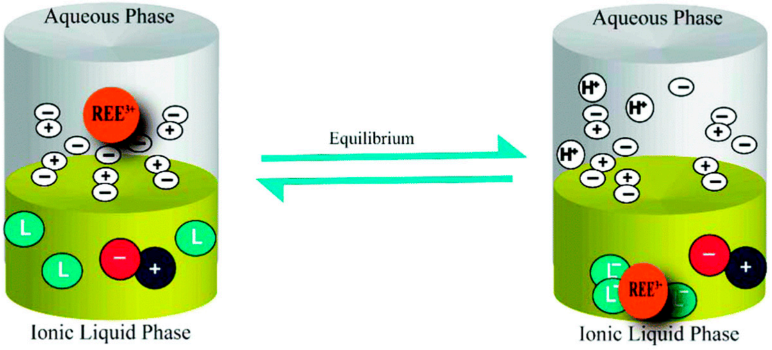


Figure 17. Neutral mechanism in non-functional IL-based extraction system [143]; published by Royal Society of Chemistry, 2017.

The same group used mainly $[C_8mim][Tf_2N]$ with DODGAA as the extractant for extraction of a series of REEs, the results showed that all the REEs can be extracted at low pH from a H_2SO_4 solution. The ILs were confirmed to be applicable for the separation of REEs from a variety of resources [147]. Finally, they used $[C_4mim][Tf_2N]$/DODGAA to recover REEs from waste fluorescent lamps, the $[C_4mim][Tf_2N]$/DODGAA showed a high affinity for REEs in liquid-liquid extraction [148]. $[C_4mim][Tf_2N]$/DODGAA showed to be a promising system for recovering REEs from fluorescent lamps or NdFeB magnets containing large amounts of Zn and Fe.

Functional Ionic Liquids

Since one of the most important characteristics of IL is to improve its chemical and physical properties by combining appropriate anion/cation pairs, functional groups can be introduced into anionic or cationic compositions. IL with functional groups is called functional IL, and due to its unique chemical and physical properties, it has attracted much attention in the metal recycling process [149–152].

The ionic liquids $[C_6mim][DEHP]$, $[C_6mpyr][DEHP]$ and $[N_{4444}][DEHP]$ with bis(2-ethylhexyl)phosphate anions were prepared and the extraction behavior of Nd with the ILs extraction in HNO_3 medium were studied. Compared with the quaternary ammonium analog $[N_{4444}][DEHP]$, except the extraction properties of Nd in the ionic liquids $[C_6mim][DEHP]$ and $[C_6mpyr][DEHP]$ were significantly different, the extraction efficiency of Nd can exceed 99%, and the extraction process can be selected by the ionic liquid cation [148]. In another research, because the functional phosphate moiety of DEHPA, Nd^{3+} was extracted by $[C_6mim][Tf_2N]$/DEHPA and $[C_6mpyr][Tf_2N]$/DEHPA systems, the Equation (16) can be proposed for the extraction mechanism of Nd by DEHPA in $[C_6mim][NTf_2]$ and $[C_6mpyr][NTf_2]$ [153]. These non-functional ILs only acted as dilutants and were not included in the extraction mechanism, as shown in Figure 18. When the functional IL $[C_6mim][DEHP]$ was used to extract Nd^{3+}, both the anion and cation were involved in the extraction so that neither cation nor anion was lost to the aqueous phase.

$$\mathrm{Nd}^{3+} + \overline{3DEHPA} = \overline{\mathrm{Nd}(DEHP)_3} + 3H^{+} \quad (16)$$

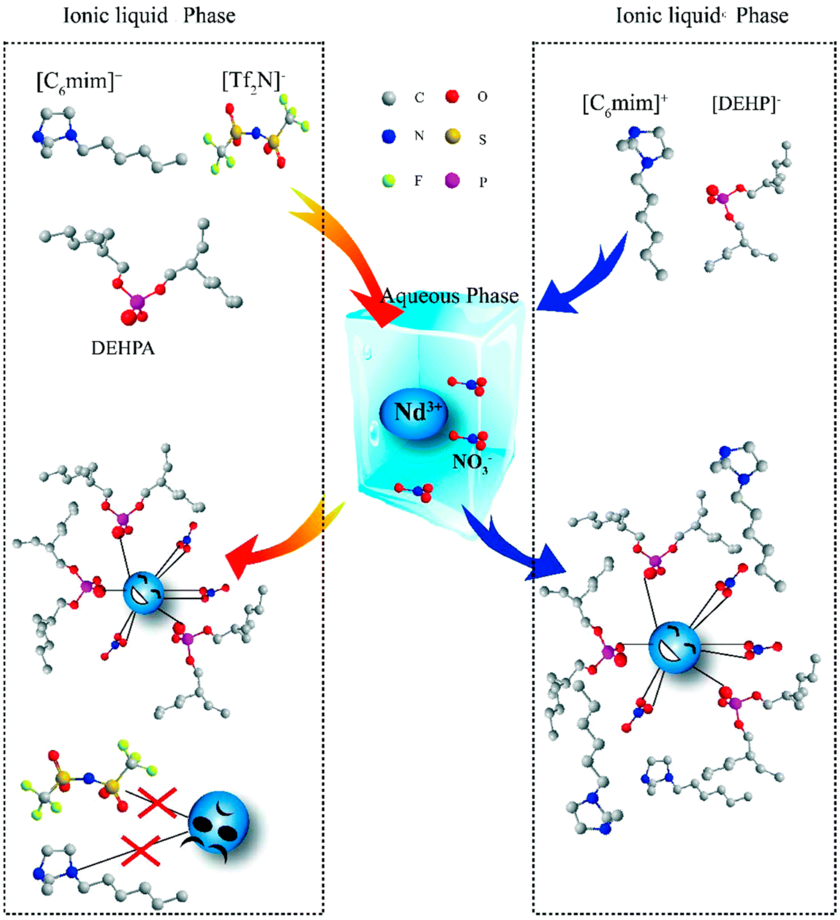


Figure 18. Different Nd^{3+} extraction behaviors in [C_6mpyr][Tf_2N]/DEHPA and [C_6mim][DEHP] systems [143]; published by Royal Society of Chemistry, 2017.

The use of these type of functionalized ionic liquids for separating REEs indicated that the light REEs La and Ce are poorly extracted, however, Nd and Yb are strongly extracted by the [C_6mim][DEHP]/[C_6mim][NTf_2] and [C_6mpyr][DEHP]/[C_6mpyr][NTf_2] ionic liquid extraction systems. A separation factor of 340 is obtained for Nd over La in the [C_6mim][DEHP]. Pr is weakly extracted by the [C_6mpyr][DEHP]/[C_6mpyr][NTf_2] system, but rather strongly by the [C_6mim][DEHP]/[C_6mim][NTf_2] system. Overall, these DEHPA-based ILs were suitable for recovering Nd from NdFeB magnet scrap.

A new recycling process for NdFeB magnets was carried out by Dupont and Binnemans, based on the carboxyl-functionalized ionic liquid: betainium bis(trifluoromethylsulfonyl)imide, [Hbet][Tf_2N], a combined leaching/extraction step was proposed, and the detailed recycling process as shown in Figure 19 [36]. First, roasting of NdFeB magnets convert all elements in the magnets to their respective oxides, because these oxides are more easily dissolved in [Hbet][Tf_2N]-H_2O systems. The leaching of the roasted NdFeB was tested using a 1:1 wt/wt [Hbet][Tf_2N]-H_2O at 80 °C to form a homogeneous phase. After that, the solution was cooled to 25 °C, the mixture could be separated into a valuable REEs/Co-rich aqueous phase and an iron-rich ionic liquid phase. The two separated phases were stripped with $H_2C_2O_4$ to remove the Fe and produce a REEs/Co oxalate. Then, aqueous ammonia was added to separate REEs and Co. The obtained REEs oxalate with a purity higher than 99.9% and can be calcined to obtain Nd_2O_3 and Dy_2O_3 mixture, which is the precursors of NdFeB magnets. The stripping step can automatically regenerate the ionic liquid, and the ionic liquid recovery was also considered. Therefore, the proposed closed-loop system only generates little waste and offers selectivity, which makes this a promising green method for recovering NdFeB magnets [149].

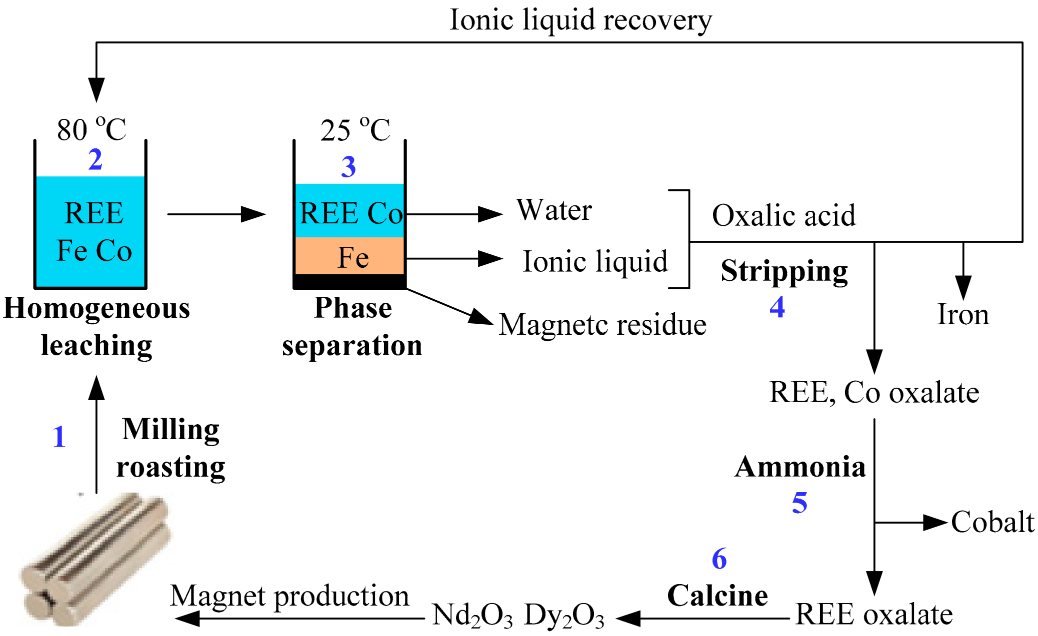


Figure 19. Overview of the proposed recycling process for roasted NdFeB magnets [36]; published by Royal Society of Chemistry, 2015.

Bi-Functional Ionic Liquids

Ionic liquid extractants prepared from ammoniumand phosphonium are considered to be bi-functional IL extractants (Bif-ILs) because the cations and anions of ILs are involved in the extraction [150].

Rout et al. [148] synthesized two ionic liquids derived from Aliquat 336: trioctylmethylammonium bis(2-ethylhexyl)phosphate, [A336][DEHP], and trioctylmethylammonium bis(2-ethylhexyl)diglycolamate, [A336][DGA]. These ionic liquids were applied to the separation of Eu from Am. The extraction of Eu in these Bif-ILs showed a strong dependence on the properties of molecular diluent used. In their further researcher [151], [A336][DGA] combined with [A336][NO_3] to extract Nd from La ions, and the Nd extraction behavior of [A336][DGA] in [A336][NO_3] was compared with that of [A336][DGA] in the Cl-containing ionic liquid diluent [A336][Cl]. The results shown that extraction of Nd can reach nearly 100%, and the nitrate media was found to be more suitable for extracting Nd than in chloride media. The extraction mechanism in a system with the ionic liquid diluent [A336][NO_3] is significant different from that of extraction systems with molecular diluents. A rational mechanism for extracting Nd by [A336][DGA] in [A336][NO_3] at pH 2–5 with 0.1 M salting-out agent in the feed phase is shown as Equation (17).

$$Nd^{3+} + 3NO_3^{\,-} + \overline{[A336][DGA]} = \overline{Nd(NO_3)_3 \bullet [A336][DGA]} \tag{17}$$

A comparative study was carried out between Bi-ILs [A336][CA-12] (tricaprylmethylammonium secoctylphenoxy acetic acid)/[A336][CA-100] (tricaprylmethylammonium secnonylphenoxy acetic acid), organic carboxylic acids CA-12/CA-100 and neutral organophosphorus extractants TBP/P350 for extracting REEs in HNO_3 medium [148]. The efficiency of different extractants for metal extraction follows the order: [A336][CA-12]/[A336][CA-100] > CA-12/CA-100 > TBP/P350. Extraction and separation for REEs from chloride medium used [A336][CA-12] and [A336][CA-100] as extractants have also researched by Wang et al. [152] The results showed that at the same conditions, the extraction capacity of [A336][CA-12] and [A336][CA-100] was higher than that of CA-12, CA-100, TBP, and P350. [A336][CA-12] and [A336][CA-100] in the present of NaCl, can efficiently extraction of REEs at low acidity, avoiding the harm that the conventional acidity and neutral extractants produced in the extraction.

The inner synergistic effect of Bi-ILs extractants using [A336][P204] as an extractant for solvent extraction of Eu was reported. The distribution coefficients of Eu in [A336][P204], [A336][P507], [A336][CA-12], [A336][CA-100], [A336][Cyanex272] and corresponding mixtures of their precursors were carried out to explore whether there are similar inner synergistic effects in some other Bi-ILs [153]. As shown in Table 6, obviously, the distribution coefficients of the Bi-ILs are all higher than their mixed precursors, showing good inner synergistic effect of these Bi-ILs [154]. HDEHP and HEH [EHP] have been developed into 6 types acid-base coupling bifunctionalized ionic liquids (ABC-BILs) extractants. As with the mixture of HDEHP and HEH[EHP], the combined [DEHP]2 type ABC-BILs and [EHEHP]2 type ABC-BILs revealed synergistic extraction effects for REEs in 7 different ABC-BILs combinations. The synergy coefficients of REEs also confirmed the synergistic extraction effects from combined ABC-BILs [155].

Table 6. Comparison of the distribution ratios obtained using mixed extractants and Bi-ILs in hydrochloric acid and nitric acid media [154]; published by Elsevier, 2010.

Extractant	Hydrochloric Acid Media		Nitric Acid Media	
	D	D_{IL}/D_{mix}	D	D_{IL}/D_{mix}
A336 + P204	0.071	27.86	0.912	23.79
[A336][P204]	1.97	-	21.7	-
A336 + P507	0.192	13.28	0.269	70.63
[A336][P507]	2.55	-	19	-
A336 + CA-12	0.169	3.04	0.067	19.79
[A336][CA-12]	0.513	-	1.33	-
A336 + CA-100	0.054	8.28	0.055	15.57
[A336][CA-100]	0.445	-	0.855	-
A336 + Cyanex272	0.928	2.55	0.912	3.44
[A336][Cyanex272]	2.37	-	3.14	-

It was indicated that the IL consisting the mixture of Aliquat 336 and Cyanex 272 showed good selectivity and extractability for REEs, therefore, a detailed study has been researched to extract Nd and Pr using Aliquat 336 based ionic liquid from the NdBFe magnet scrap leach liquor. A comparative study showed that the extraction efficiency of Bi-ILs trioctylmethylammoniumbis (2,4,4-trimethylpentyl)phosphate (R_4NCy) and trioctylmethylammonium di(2-ethylhexyl)phosphate (R_4ND) was higher than the conventional extractants Aliquat 336, Cyanex 272 and D2EHPA under the same conditions. The extraction efficiency of different extractants for Nd and Pr is: R_4NCy > R_4ND > Cyanex 272 > D2EHPA > Aliquat 336, with a maximum extraction of Nd and Pr of 98.97%, 99.02%, respectively.

5. Conclusions

NdFeB permanent magnet scrap is an important secondary resource that contains a number of valuable REEs. Recovery of REEs from this scrap via appropriate methods such as hydrometallurgical processes has both remarkable economic and environmental benefits. The authors reviewed the chemical, physical characteristics of NdFeB permanent magnet scrap and the main hydrometallurgical processes for recovering REEs from the magnet scrap, from the leaching process to the separation process. A variety of leaching technologies have been developed for REEs recovery depending upon their mineralogy, REEs occurrence and engineering feasibility. Both selective leaching and complete leaching are interactively used for leaching REEs from the magnet scrap, among which complete leaching treatment was found to be acceptable from industrial point of view. Although electrochemical selectively leaching seems to be a promising method, more systematic research is still needed. The REEs separation process mainly include precipitation process, solvent extraction process and ionic liquids extraction process. The precipitation process is a simple and easy separation process for REEs by different precipitating reagents; however, the problem of incomplete separation needs to be addressed. The leaching liquor generated is put to solvent extraction studies using different process such as acidic solvent extraction, ion-pair solvent extraction, neutral solvent extraction and synergetic solvent extraction. D2EHPA and PC88A have been considered feasible for recovering REEs from the leaching liquors. The physical properties of ionic liquids make them potentially valuable replacements for traditional organic solvents used in liquid-liquid separation processes. However, the extraction mechanisms of ionic liquids extraction are still indefinite, and the high price of most types of ionic liquids hinders its widespread use. Future research focus should be on the understanding of extraction mechanisms, which is very important for the better design of extraction systems from laboratory curiosities to industrial processes. Technically, for further optimization of treatment of the magnet scrap, hydrometallurgical recovery of REEs from the magnet scrap has to confront the challenges of many process steps required before obtaining REEs, consumption of large amount of chemicals, generation of large amount waste water and effluents. To resolve these issues, it is necessary to use high selective leaching agents, recycle the leaching agents and establish a closed-loop system. This review is expected to serve as a useful guideline for promoting treatment of NdFeB permanent magnet scrap by a hydrometallurgical processes.

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