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 $\text{BH}_{\text{max}}$ (200–440 kJ/m³) 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.

**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                  | • Consumption of large amounts of chlorine gas                                 |
|                         | • Applicable to non-oxidized and oxidized alloys                            | • Aluminum chloride is very corrosive                                          |
|                         | • No generation of waste water                                              |                                                                               |
| Hydrometallurgical      | • Generally applicable to all types of magnet compositions                  | • Many process steps required before obtaining new magnets                    |
| methods                 | • Applicable to non-oxidized and oxidized alloys                            | • Consumption of large amounts of chemicals                                    |
|                         | • Same processing steps as those for extraction of rare earths from primary ores | • 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]).](image-url)
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.](image)

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 NdFeB is 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.](image)
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 scraps   | 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| -   | -   | 0.11| 0.70| -    | [19]  |
| Medium REEs      | 26.10| 63.50| 0.73| 0.68| 2.68| 2.99| -   | -   | 0.02| -   | -   | 0.70| -   | -    | [51]  |
| Medium REEs      | 25.38| 61.09| 1.00| 2.62| 1.08| 1.42| -   | -   | -   | 0.02| -   | 0.95| 2.03| -    | [52]  |
| Medium REEs      | 28.00| 68.00| 1.00| -   | 1.00| -   | -   | -   | -   | -   | 0.95| 1.00| 3.00| -    | [53]  |
| Medium REEs      | 23.70| 66.10| 0.91| 1.22| 2.24| 3.34| -   | -   | -   | -   | -   | 0.15| 2.03| -    | [54]  |
| Medium REEs      | 24.43| 64.07| 0.97| -   | -   | 1.67| -   | -   | 0.37| -   | -   | 0.15| -   | -    | [8]   |
| High REEs        | 19.40| 66.30| 0.96| 6.43| 5.21| -   | 0.77| -   | -   | -   | -   | 0.87| -   | -    | [31]  |
| High REEs        | 30.73| 61.60| 0.96| 4.39| -   | -   | -   | 1.58| -   | -   | -   | 0.83| -   | -    | [25]  |
| High REEs        | 18.80| 63.90| 1.02| 5.98| 5.93| 0.42| -   | -   | 1.51| -   | -   | 1.04| -   | -    | [55]  |
| High REEs        | 25.95| 58.16| 1.00| 0.34| 4.21| 4.22| -   | -   | -   | -   | -   | 0.34| 0.02| -    | [34]  |
| High REEs        | 25.95| 58.16| 1.00| 0.07| 4.21| 4.22| -   | -   | 0.83| -   | -   | 0.34| 0.02| -    | [56]  |
| High REEs        | 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$_2$Fe$_{14}$B [54,57], which accounts for 96–98%. Herbst et al. indicated the unit cell structure of Nd$_2$Fe$_{14}$B. The space group is P4$_2$/mnm, and there are four Nd$_2$Fe$_{14}$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$_2$Fe$_{14}$B, NdO, Nd$_2$O$_3$, and the minor NdFe$_4$B$_4$ 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$_2$Fe$_{14}$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$_2$Fe$_{14}$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.](image1)

![Figure 6. SEM-EDS analysis of NdFeB permanent magnets [54]; published by Elsevier, 2014.](image2)

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$_2$Fe$_{14}$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$_1$Fe$_4$B$_4$ 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].

![Image of EDX mapping](https://example.com/edx_mapping.png)

**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.
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$_2$O$_3$ and insoluble Fe$_2$O$_3$ 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$_4$NO$_3$) 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 $P_{O_2} \leq 10^{-20}$ 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$_2$N] 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$_2$O$_2$. 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$_2$O$_3$-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$_4$Cl 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.
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### 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 \( \text{H}_2\text{C}_2\text{O}_4 \) at 110 \(^\circ\)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 \( \text{Ca(OH)}_2 \), the B can be recovered from the highly acidic waste water by formation of \( \text{CaB}_2\text{O}_5 \cdot \text{H}_2\text{O} \) [84,85].

Abrahami et al. indicated the feasibility of directly leaching of NdFeB magnet scrap by \( \text{H}_2\text{SO}_4 \), 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...
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 H2SO4 (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 HNO3 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 H2SO4 and H2C2O4 by Makarova et al. [60]. The scanning Kelvin probe force microscopy results showed that the Local Volta potential difference between Nd2Fe14B \( \phi \)-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 Nd2Fe14B grains (\( \phi \)-phase), then whole grains of the \( \phi \)-phase eventually falls off from the surface.

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

![Figure 12. Schematic illustration of leaching process on the surface of NdFeB magnet scrap in (a) H2SO4, (b) mixture of H2SO4 and H2C2O4 [60]; published by Elsevier, 2020.](image)

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$_2$C$_2$O$_4$ 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            | Low recovery                                  |
|                              | The process is simple| Product is impurity                           |
|                              |                     | Hard to obtain single REE                     |
| Solvent extraction           | High recovery       | High cost                                     |
|                              | Can obtain high purity single REE | The process is complicate                     |
|                              |                     | Generation of large amount of waste           |
| Ionic liquids extraction     | High recovery       | Environmentally friendly                      |
|                              | Can obtain high purity single REE | Efficient                                     |
|                              |                     | 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$_2$C$_2$O$_4$ [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$_2$C$_2$O$_4$ 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$_2$SO$_4$/NaCl or H$_2$SO$_4$/ethanol were used as precipitating agents. But in a mixed aqueous solvent of 3.0 mol/L HCl and 0.2 mol/L H$_2$C$_2$O$_4$ via hydrothermal treatment at 110 °C for 360 min. About 99% of Nd contained in the magnet scrap was recovered as Nd$_2$(C$_2$O$_4$)$_3$·xH$_2$O 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$_3$PO$_4$ and ascorbic acid via selective precipitation process [31]. Nd also can be recovered as Mn$_2$O$_3$-type Nd$_2$O$_3$, with the recovery of Nd of 97% via oxalic acid precipitation from NdFeB magnet scrap [74].
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$_2$C$_2$O$_4$ [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$_2$C$_2$O$_4$ 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$_2$SO$_4$/NaCl or H$_2$SO$_4$/ethanol were used as precipitating agents. But in a mixed aqueous solvent of 3.0 mol/L HCl and 0.2 mol/L H$_2$C$_2$O$_4$ via hydrothermal treatment at 110 °C for 360 min. About 99% of Nd contained in the magnet scrap was recovered as Nd$_2$(C$_2$O$_4$)$_3$·xH$_2$O with a purity of 99.8% [56].

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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$_2$C$_2$O$_4$. 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$_2$O$_3$ 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$_2$SO$_4$·6H$_2$O) 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$_2$SO$_4$ 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].
Metals scrap HNO₃ 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].

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

Although these methods can effectively separate Nd from other metals, due to the difficulty of filtering NdF₃ (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 (Nd₂(SO₄)₃, Na₂SO₄·6H₂O) 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 H₂SO₄ 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].

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 H₂C₂O₄-NH₃ 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 Fe₂O₃, Fe₂O₃·Nd₂O₃, and Pr₂CoO₄. These valuable elements can be directly used as raw materials for the preparation of recycled NdFeB magnetic powder [37].
such as Fe₂O₃, Fe₂O₃·Nd₂O₃, and Pr₂CoO₄. These valuable elements can be directly used as raw materials for the preparation of recycled NdFeB magnetic powder [37].

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,
Metals extraction mechanism shows as the following equation [99]:

\[ \text{Mn}^+ + n \text{HA} = \text{MAn}^{\text{org}} + n \text{H}^+ (\text{aq}) \] (1)

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 | 
\[ \text{C}_2\text{H}_5 \]
\[ \text{CH}_3\text{(CH)}_2\text{CH}-\text{CH}_2\text{O} \]
\[ \text{P} \equiv \text{O} \]
\[ \text{C}_2\text{H}_5 \] |
| | EHEHPA | 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester | 
\[ \text{C}_2\text{H}_5 \]
\[ \text{CH}_3\text{(CH)}_2\text{CH}-\text{CH}_2\text{O} \]
\[ \text{P} \equiv \text{O} \]
\[ \text{C}_2\text{H}_5 \] |
| | PC88A | 2-Ethylhexyl phosphonic acid mono 2-ethylhexyl ester | 
\[ \text{C}_2\text{H}_5 \]
\[ \text{CH}_3\text{(CH)}_2\text{CH}-\text{CH}_2\text{O} \]
\[ \text{P} \equiv \text{O} \]
\[ \text{C}_2\text{H}_5 \] |
| | 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 | 
\[ (\text{R}_1, \text{R}_2=\text{C}_8) \]
\[ \text{H}_3\text{C} \]
\[ \text{H}_3\text{C} \]
\[ \text{N} \]
\[ \text{CH}_3 \]
\[ \text{Cl}^- \]
| Neutral extractant | TBP | Tri-n-butyl phosphate | 
\[ \text{CH}_3\text{(CH)}_2\text{O} \]
\[ \text{P} \equiv \text{O} \]
\[ \text{O(CH)}_2\text{CH}_3 \] |
| | TODGA | Tetraoctyldiglycol amide | 
\[ \text{C}_6\text{H}_{17} \]
\[ \text{C}_6\text{H}_{17} \]
\[ \text{O} \]
\[ \text{O} \]
\[ \text{N} \]
\[ \text{C}_6\text{H}_{17} \]
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]:

\[ \text{M}^{n+} + n\text{HA} = \text{MA}_{n\text{org}} + n\text{H}^+_{\text{aq}} \] (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, H₂SO₄ and HNO₃ 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 HNO₃ were poorer than those from HCl and H₂SO₄ 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 > 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 EPEHHA, 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].

\[ \text{Nd}^{3+} + \frac{3 + x}{2}H_2\text{A}_{2\text{org}} = \text{NdA}_{3x}\text{HA}_{\text{org}} + 3\text{H}^+ \] (2)
\[
\text{Nd}^{3+} + 1.5\text{H}_2\text{A}_2\text{org} = \text{NdA}_3\text{H}_{\text{org}} + 3\text{H}_{aq}^+
\]  

where \(\text{H}_2\text{A}_2\) and \(\text{org}\) 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 \((D_{\text{Dy}}/D_{\text{Nd}})\) 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 \(\text{RNH}_2\) denotes the Primene JMT in the organic phase, \(\text{Ln}\) denotes the rare earth ion and \(\text{R}_4\text{N}^+\text{NO}_3^-\) the quaternary ammonium nitrate salt.

\[2\text{RNH}_2 + \text{H}_2\text{SO}_4 = (\text{RNH}_3)_2\text{SO}_4\]  

\[2\text{La}(\text{SO}_4)_2^{3-} + 3(\text{RNH}_3)_2\text{SO}_4 = 2(\text{RNH}_3)_3\text{La}(\text{SO}_4)_3 + 3\text{SO}_4^{2-}\]  

\[\text{Ln}^{3+} + 3\text{NO}_3^- + x(\text{R}_4\text{N}^+\text{NO}_3^-)^- = \text{Ln}(\text{NO}_3)_3 x\text{R}_4\text{N}^+\text{NO}_3^-\]  

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$_2$O$_3$ from a light rare earth nitrate liquor used a 0.50 mol/L Aliquat 336 nitrate in Shellslol 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 actinoids 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].

\[
\text{REE}^{3+} + m\text{H}_2\text{A}_2 = \text{REEA}_3(\text{HA})_{2m-3} + 3\text{H}^+ \quad (7)
\]

where $\text{H}_2\text{A}_2$ 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].

\[
\text{REE}^{3+} + 3\text{Cl}^- + m\text{H}_2\text{A}_2 = \text{REECl}_3(\text{HA})_{2m}, \quad (8)
\]

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 HNO₃ 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).

\[
\text{RE}^{3+} + \text{Cl}^- + 2\text{H}_2\text{A}_2 = \text{REClA}_2\cdot2\text{HA} + 2\text{H}^+ \quad (\text{RE} = \text{Pr, Nd}) \quad (9)
\]

\[
\text{RE}^{3+} + (x + 1)\text{Cl}^- + 2\text{H}_2\text{A}_2 + x\text{NR}_3 = \text{RECl(HA)}_2 + x\text{R}_3\text{NHCl} + (2 - x)\text{H}^+ \quad (\text{RE} = \text{Pr, Nd}) \quad (10)
\]

where the value of x (0 ≤ x ≤ 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. Reaction for extracting Nd with this mixture is shows in Equation (11) [136].

\[
\text{Nd}^{3+} + \text{Cl}^- + (\text{HB})_2 + 2\text{R}_3\text{N} = \text{NdClB}_2\cdot2\text{R}_3\text{N} + 2\text{H}^+ \quad (11)
\]

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 HNO₃ 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 HNO₃ medium with a mixture of neutral organophosphorus reagents gave synergistic behavior and forming a neutral complex of the form of \(M(\text{NO}_3)_3(\text{TOPO})(\text{TRPO})\), 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.

\[
M^{3+} + 3\text{NO}_3^- + \overline{\text{TOPO}} + \overline{\text{TRPO}} = M(\text{NO}_3)_3(\text{TOPO})(\text{TRPO}) \quad (12)
\]

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 \([\text{C}_n\text{mim}]\), were the first potential ILs to be used for extracting REEs. \([\text{C}_8\text{mim}][\text{PF}_6]\) was first tested for separating Ce (IV) from HNO₃ solutions containing La (III) and Th (IV) [142]. It was found that the distribution ratios of Ce (IV) and Th (IV) using pure \([\text{C}_8\text{mim}][\text{PF}_6]\) as the extract phase was similar to that using HDEHP or DEHPA in n-heptane, which indicated that \([\text{C}_8\text{mim}][\text{PF}_6]\) 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.

\[ \text{REE}^3+ + \text{C}_m^m + \text{C}_{IL}^+ = \text{ML}_{m,IL}^+ + \text{C}_m^m \]  

(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.](image)

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\(_{4}\)mim][Tf\(_2\)N] and [N\(_{1444}\)][Tf\(_2\)N] was higher than that in ILs with a hydrophobic cation such as [C\(_{10}\)mim][Tf\(_2\)N], [P\(_{66614}\)][Tf\(_2\)N], or [N\(_{1888}\)][Tf\(_2\)N] [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\(_{4}\)mim][Tf\(_2\)N] 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\(_2\)N]\(^-\) was transferred to the aqueous phase to keep the charge neutrality, and [C\(_{4}\)mim\(^+\)][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.

\[ \text{REE}^{3+} + 4\text{Htta} + [\text{C}_4\text{mim}][\text{Tf}_2\text{N}]_{IL} = [\text{C}_4\text{mim}^+][\text{REE(tta)}^{4-}]_{IL} + 4\text{H}^+ + [\text{Tf}_2\text{N}]^- \]  

(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\(_n\)mim][Tf\(_2\)N]/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.

\[
M^{3+} + 3HL_{\text{IL}} = ML_{3,\text{IL}} + 3H^+
\]  

(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$_8$mim][Tf$_2$N] 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$_2$SO$_4$ solution. The ILs were confirmed to be applicable for the separation of REEs from a variety of resources [147]. Finally, they used [C$_4$mim][Tf$_2$N]/DODGAA to recover REEs from waste fluorescent lamps, the [C$_4$mim][Tf$_2$N]/DODGAA showed a high affinity for REEs in liquid-liquid extraction [148]. [C$_4$mim][Tf$_2$N]/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$_6$mim][DEHP], [C$_6$mpyr][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$_6$mim][DEHP] and [C$_6$mpyr][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$_6$mim][Tf$_2$N]/DEHPA and [C$_6$mpyr][Tf$_2$N]/DEHPA systems, the Equation (16) can be proposed for the extraction mechanism of Nd by DEHPA in [C$_6$mim][NTf$_2$] and [C$_6$mpyr][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$_6$mim][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.

\[
Nd^{3+} + 3\text{DEHPA} = Nd(\text{DEHP})_3 + 3H^+
\]  

(16)
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Figure 18. Different Nd³⁺ extraction behaviors in [C₆mpyr][Tf₂N]/DEHPA and [C₆mim][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 [C₆mim][DEHP]/[C₆mim][NTf₂] and [C₆mpyr][DEHP]/[C₆mpyr][NTf₂] ionic liquid extraction systems. A separation factor of 340 is obtained for Nd over La in the [C₆mim][DEHP]. Pr is weakly extracted by the [C₆mpyr][DEHP]/[C₆mpyr][NTf₂] system, but rather strongly by the [C₆mim][DEHP]/[C₆mim][NTf₂] 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][Tf₂N], 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][Tf₂N]-H₂O systems. The leaching of the roasted NdFeB was tested using a 1:1 wt/wt [Hbet][Tf₂N]-H₂O 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 H₂C₂O₄ 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 Nd₂O₃ and Dy₂O₃ 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].
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][NO₃] to extract Nd from La ions, and the Nd extraction behavior of [A336][DGA] in [A336][NO₃] 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][NO₃] is significant different from that of extraction systems with molecular diluents. A rational mechanism for extracting Nd by [A336][DGA] in [A336][NO₃] at pH 2–5 with 0.1 M salting-out agent in the feed phase is shown as Equation (17).

$$Nd^{3+} + 3NO_3^- + [A336][DGA] = Nd(NO_3)_3\bullet[A336][DGA]$$  \hspace{1cm} (17)

A comparative study was carried out between Bi-ILs [A336][CA-12] (tricaprylmethylammonium secoctylyphenoxy acetic acid)/[A336][CA-100] (tricaprylmethylammonium secononylphenoxy acetic acid), organic carboxylic acids CA-12/CA-100 and neutral organophosphorus extractants TBP/P350 for extracting REEs in HNO₃ 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].

| 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 NdBeFe magnet scrap leach liquor.
A comparative study showed that the extraction efficiency of Bi-ILs trioctylmethylammoniumbis
(2,4,4-trimethylpentyl)phosphate (R4NCy) and trioctylmethylammonium di(2-ethylhexyl)phosphate
(R4ND) 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: R4NCy >
R4ND > 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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References
1. Jiles, D. Introduction to Magnetism and Magnetic Materials, 2nd ed.; Chapman & Hall: New York, NY, USA, 1998.
2. Coey, J.M.D. Permanent magnet applications. J. Magn. Magn. Mater. 2002, 248, 441–456. [CrossRef]
3. Shaw, S.; Constantinides, S. Permanent magnets: The demand for rare earths. In Proceedings of the 8th International Rare Earths Conference, Hong Kong, China, 13–15 November 2012.
4. Yang, Y.; Walton, A.; Sheridan, R.; Güth, K.; Gauß, R.; Gutlfleisch, O.; Buchert, M.; Steenari, B.-M.; Van Gerven, T.; Jones, P.T.; et al. REE Recovery from end-of-life NdFeB permanent magnet scrap: A critical review. J. Sustain. Metall. 2016, 3, 122–149. [CrossRef]
5. Sagawa, M.; Fujimura, S.; Yamamoto, H.; Matsuura, Y.; Hiraga, K. Permanent magnet materials based on the rare earth-iron-boron tetragonal compounds. IEEE Trans. Magn. 1984, 20, 1584–1589. [CrossRef]
6. Peiró, L.T.; Ménendez, G.V.; Ayres, R.U. Material flow analysis of scarce metals: Sources, functions, end-uses and aspects for future supply. Environ. Sci. Technol. 2013, 47, 2939–2947. [CrossRef] [PubMed]
7. Japan Oil Gas and Metals National Corporation. Mineral Resources Material Flow; Japan Oil Gas and Metals National Corporation: Tokyo, Japan, 2008. Available online: mric.jogmec.go.jp/public/report/2012-12/2012120122_REs.pdf (accessed on 29 May 2020).
8. Mochizuki, Y.; Tsubouchi, N.; Sugawara, K. Selective recycling of rare earth elements from Dy containing NdFeB magnets by chlorination. ACS Sustain. Chem. Eng. 2013, 1, 655–662. [CrossRef]
9. Zakotnik, M.; Tudor, C.O.; Peiró, L.T.; Afjuny, P.; Skomski, R.; Hatch, G.P. Analysis of energy usage in Nd–Fe–B magnet to magnet recycling. Environ. Technol. Inno. 2016, 5, 117–126. [CrossRef]
10. Lee, K.; Yoo, K.; Yoon, H.-S.; Kim, C.J.; Chung, K.W. Demagnetization followed by remagnetization of waste NdFeB magnet for reuse. Geosyst. Eng. 2013, 16, 286–288. [CrossRef]
11. Sheridan, R.S.; Williams, A.J.; Harris, I.R.; Walton, A. Improved HDDR processing route for production of anisotropic powder from sintered NdFeB type magnets. J. Magn. Magn. Mater. 2014, 350, 114–118. [CrossRef]
12. Guttfleisch, O.; Güth, K.; Woodcock, T.G.; Schultz, L. Recycling used Nd-Fe-B sintered magnets via a hydrogen-based route to produce anisotropic, resin bonded magnets. Adv. Energy Mater. 2013, 3, 151–155. [CrossRef]

13. Itoh, M.; Masuda, M.; Suzuki, S.; Machida, K.-I. Recycling of rare earth sintered magnets as isotropic bonded magnets by melt-spinning. J. Alloy. Compd. 2004, 374, 393–396. [CrossRef]

14. Li, C.; Liu, W.Q.; Yue, M.; Liu, Y.Q.; Zhang, D.T.; Zuo, T.Y. Waste Nd-Fe-B sintered magnet recycling by doping with rare earth rich alloys. IEEE Trans. Magn. 2014, 50, 2015403. [CrossRef]

15. Hogberg, S.; Holboll, J.; Mijatovic, N.; Jensen, B.B.; Bendixen, F.B. Direct reuse of rare earth permanent magnets-coating integrity. IEEE Trans. Magn. 2017, 53, 1–9. [CrossRef]

16. Xia, M.; Abrahamsen, A.B.; Bahl, C.R.H.; Veluri, B.; Søegaard, A.I.; Bøjsøe, P. Hydrogen decrepitation press-less process recycling of NdFeB sintered magnets. J. Magn. Mater. 2017, 441, 55–61. [CrossRef]

17. Sheridan, R.S.; Sillitoe, R.; Zakotnik, M. Anisotropic powder from sintered NdFeB magnets by the HDDR processing route. J. Magn. Magn. Mater. 2012, 324, 63–67. [CrossRef]

18. Zakotnik, M.; Harris, I.R.; Williams, A.J. Possible methods of recycling NdFeB-type sintered magnets using the HD/degasging process. J. Alloy. Compd. 2008, 450, 525–531. [CrossRef]

19. Bian, Y.Y.; Guo, S.; Tang, K.; Jiang, L.; Lu, C.; Lu, X.; Ding, W. Recovery of rare earth elements from permanent magnet scrap by pyrometallurgical process. Rare Met. 2015. [CrossRef]

20. Hua, Z.; Wang, L.; Wang, J.; Xiao, Y.; Yang, Y.; Zhao, Z.; Liu, M. Extraction of rare earth elements from NdFeB scrap by AlF3-NaF melts. Mater. Sci. Tech. 2014, 31, 1007–1010. [CrossRef]

21. Hua, Z.; Wang, J.; Wang, L.; Zhao, Z.; Li, X.; Xiao, Y.; Yang, Y. Selective extraction of rare earth elements from NdFeB scrap by molten chlorides. ACS Sustain. Chem. Eng. 2014, 2, 2536–2543. [CrossRef]

22. Saito, T.; Sato, H.; Ozawa, S.; Yu, J.; Motegi, T. The extraction of Nd from waste Nd-Fe-B alloys by the glass slag method. J. Alloy. Compd. 2003, 353, 189–193. [CrossRef]

23. Takeda, O.; Okabe, T.H.; Umetsu, Y. Phase equilibrium of the system Ag-Fe-Nd, and Nd extraction from magnet scrap using molten silver. J. Alloy. Compd. 2004, 379, 305–313. [CrossRef]

24. Moore, M.; Gebert, A.; Stoica, M. A route for recycling Nd from Nd-Fe-B magnets using Cu melts. J. Alloy. Compd. 2015, 647, 997–1006. [CrossRef]

25. Bian, Y.; Guo, S.; Jiang, L.; Liu, J.; Tang, K.; Ding, W. Recycling of rare earth elements from NdFeB magnet by VIM-HMS method. ACS Sustain. Chem. Eng. 2016, 4, 810–818. [CrossRef]

26. Bia, Y.; Tang, K.; Gabriella, R. A thermodynamic assessment of the Nd-C system. Calphad 2015, 51, 206–210. [CrossRef]

27. Miura, K.; Itoh, M.; Machida, K.I. Extraction and Recycling Characteristics of Fe element from Nd-Fe-B sintered magnet powder scrap by carbonylation. J. Alloy. Compd. 2008, 466, 228–232. [CrossRef]

28. Firdaus, M.; Rahmdhani, M.A.; Durandet, Y.; Rankin, W.J.; McGregor, K. Review of high-temperature recycling of rare earth (Nd/Dy) from magnet waste. J. Sustain. Metall. 2016, 2, 276–295. [CrossRef]

29. Uda, T. Recycling of rare earths from magnet sludge by FeCl2. Mater. Trans. 2002, 43, 55–62. [CrossRef]

30. Itoh, M.; Miura, K.; Machida, K.I. Novel rare earth recycling process on Nd-Fe-B magnet scrap by selective chlorination using NH4Cl. J. Alloy. Compd. 2009, 477, 484–487. [CrossRef]

31. Yamada, E.; Murakami, H.; Nishihama, S.; Yoshizuka, K. Separation process of dysprosium and neodymium from waste neodymium magnet. Sep. Purif. Technol. 2018, 192, 62–68. [CrossRef]

32. Padhan, E.; Sarangi, K. Recycling of Nd and Pr from NdFeB magnet leachates with bi-functional ionic liquids based on Aliquat 336 and Cyanex 272. Hydrometallurgy 2017, 167, 134–140. [CrossRef]

33. Padhan, E.; Nayak, A.K.; Sarangi, K. Recovery of neodymium and dysprosium from NdFeB magnet swarf. Hydrometallurgy 2017, 174, 210–215. [CrossRef]

34. Riaño, S.; Binnemans, K. Extraction and separation of neodymium and dysprosium from used NdFeB magnets: An application of ionic liquids in solvent extraction towards the recycling of magnets. Green Chem. 2015, 17, 2931–2942. [CrossRef]

35. Kim, D.; Powell, L.; Delmau, L.H.; Peterson, E.S.; Herchenroeder, J.; Bhave, R.R. Selective extraction of rare earth elements from permanent magnet scraps with membrane solvent extraction. Environ. Sci. Technol. 2015, 49, 9452–9459. [CrossRef] [PubMed]

36. Dupont, D.; Binnemans, K. Recycling of rare earths from NdFeB magnets using a combined leaching/extraction system based on the acidity and thermomorphism of the ionic liquid [Hbet][TF2N]. Green Chem. 2015, 17, 2150–2163. [CrossRef]
37. Gergoric, M.; Ekberg, C.; Foreman, M.R.S.J.; Steenari, B.-M.; Retegan, T. Characterization and leaching of rare earths: A critical review. *J. Clean. Prod.* **2013**, *51*, 1–22. [CrossRef]

38. Binnemans, K.; Jones, P.T.; Blanpain, B.; Van Gerven, T.; Yang, Y.; Walton, A.; Buchert, M. Recycling of rare earths. Available online: [http://minerals.usgs.gov/minerals/pubs/commodity/rare_earths/index.html#myb](http://minerals.usgs.gov/minerals/pubs/commodity/rare_earths/index.html#myb) (accessed on 29 May 2020).

39. Alonso, E.; Sherman, A.M.; Wallington, T.J.; Everson, M.P.; Field, R.; Roth, R.; Kirchain, R.E. Evaluating rare earth element availability: A case with revolutionary demand from clean technologies. *Environ. Sci. Technol.* **2012**, *46*, 3406–3414. [CrossRef] [PubMed]

40. Schulze, R.; Buchert, M. Estimating of global REE recycling potentials from NdFeB magnets: Complete leaching, iron removal and electrolysis. *J. Sustain. Metall.* **2017**, *3*, 638–645. [CrossRef]

41. Seo, Y.; Morimoto, S. Comparison of dysprosium security strategies in Japan for 2010–2030. *Resour. Policy* **2014**, *39*, 15–20. [CrossRef]

42. Binnemans, K.; Jones, P.T.; Blanpain, B.; Van Gerven, T.; Yang, Y.; Walton, A.; Buchert, M. Recycling of rare earths: A critical review. *J. Clean. Prod.* **2013**, *51*, 1–22. [CrossRef]

43. Guyonnet, D.; Planchon, M.; Rollat, A.; Escalon, V.; Tuduri, J.; Charles, N.; Vaxelaire, S.; Dubois, D.; Fargier, H. Material flow analysis applied to rare earth elements in Europe. *J. Clean. Prod.* **2015**, *107*, 215–228. [CrossRef]

44. Schüler, D.; Buchert, M.; Liu, R.; Dittrich, S.; Merz, C. Development of a recycling process for NdFeB magnets using molten Mg and Nd-Fe-B magnets. *J. Alloy. Compd.* **2014**, *586*, S143–S149. [CrossRef]

45. Itakura, T.; Sasai, R.; Itoh, H. Resource recycling from Nd-Fe-B sintered magnet by hydrothermal treatment. *J. Alloy. Compd.* **2006**, *408–412*, 1382–1385. [CrossRef]

46. Gutfleisch, O.; Willard, M.A.; Bruck, E.; Chen, C.; Sankar, S.G.; Liu, J. Magnetic materials and devices for the 21st century: Stronger, lighter, and more energy efficient. *Adv. Mater.* **2011**, *23*, 821–842. [CrossRef] [PubMed]

47. Önal, M.A.R.; Borra, C.R.; Guo, M.X.; Blanpain, B.; Gerven, T.V. Hydrometallurgical recycling of NdFeB magnets: Complete leaching, iron removal and electrolysis. *J. Rare Earth.* **2017**, *35*, 574–584. [CrossRef]

48. Critical Materials Strategy; U.S. Department of Energy, Advanced Research Projects Agency-Energy: Washington, DC, USA, 2010.

49. Brown, D.; Ma, B.; Chen, Z. Developments in the processing and properties of NdFeb-type permanent magnets. *J. Magn. Magn. Mater.* **2002**, *248*, 432–440. [CrossRef]

50. Zhou, S.; Dong, Q.; Gao, X. Sintered NdFeB Rare Earth Permanent Magnetic Materials and Technology; Metallurgical Industry Press: Beijing, China, 2011.

51. Önal, M.A.R.; Borra, C.R.; Guo, M.X.; Blanpain, B.; Gerven, T.V. Hydrometallurgical recycling of NdFeB magnets: Complete leaching, iron removal and electrolysis. *J. Rare Earth.* **2017**, *35*, 574–584. [CrossRef]

52. Gutfleisch, O.; Willard, M.A.; Bruck, E.; Chen, C.; Sankar, S.G.; Liu, J. Magnetic materials and devices for the 21st century: Stronger, lighter, and more energy efficient. *Adv. Mater.* **2011**, *23*, 821–842. [CrossRef] [PubMed]

53. Guyonnet, D.; Planchon, M.; Rollat, A.; Escalon, V.; Tuduri, J.; Charles, N.; Vaxelaire, S.; Dubois, D.; Fargier, H. Material flow analysis applied to rare earth elements in Europe. *J. Clean. Prod.* **2015**, *107*, 215–228. [CrossRef]

54. Schüler, D.; Buchert, M.; Liu, R.; Dittrich, S.; Merz, C. Development of a recycling process for NdFeB magnets using molten Mg and Nd-Fe-B magnets. *J. Alloy. Compd.* **2014**, *586*, S143–S149. [CrossRef]

55. Herbst, J.F.; Croat, J.J.; Pinkerton, F.E. Relationships between crystal structure and magnetic properties in Nd_{2}Fe_{14}B. *Phys. Rev. B* **1984**, *29*, 4176. [CrossRef]

56. Chung, K.W.; Kim, C.J.; Yoon, H.S. Novel extraction process of rare earth elements from NdFeB powders via alkali treatment. *Arch. Metall. Mater.* **2015**, *60*, 1301–1305. [CrossRef]

57. Zhou, S.; Dong, Q.; Gao, X. Sintered NdFeB Rare Earth Permanent Magnetic Materials and Technology; Metallurgical Industry Press: Beijing, China, 2011.

58. Önal, M.A.R.; Borra, C.R.; Guo, M.X.; Blanpain, B.; Gerven, T.V. Hydrometallurgical recycling of NdFeB magnets: Complete leaching, iron removal and electrolysis. *J. Rare Earth.* **2017**, *35*, 574–584. [CrossRef]

59. Itakura, T.; Sasai, R.; Itoh, H. Resource recycling from Nd-Fe-B sintered magnet by hydrothermal treatment. *J. Alloy. Compd.* **2006**, *408–412*, 1382–1385. [CrossRef]

60. Chung, K.W.; Kim, C.J.; Yoon, H.S. Novel extraction process of rare earth elements from NdFeB powders via alkali treatment. *Arch. Metall. Mater.* **2015**, *60*, 1301–1305. [CrossRef]
61. Önal, M.A.R.; Borra, C.R.; Guo, M.; Blanpain, B.; Gerven, T.V. Recycling of NdFeB magnets using sulfation, selective roasting, and water leaching. *J. Sustain. Metall.* **2015**, *1*, 199–215. [CrossRef]

62. Jha, M.K.; Kumari, A.; Panda, R.; Kumar, J.R.; Yoo, K.; Lee, J.Y. Review on hydrometallurgical recovery of rare earth metals. *Hydrometallurgical* **2016**, *165*, 2–26. [CrossRef]

63. Jyothi, R.K.; Thenepalli, T.; Ahn, J.W.; Parhi, P.K.; Chung, K.W.; Lee, J.-Y. Review of rare earth elements recovery from secondary resources for clean energy technologies: Grand opportunities to create wealth from waste by saving energy. *J. Clean. Prod.* **2020**, *267*, 122048. [CrossRef]

64. Kumari, A.; Panda, R.; Jha, M.K.; Kumar, J.R.; Lee, J.Y. Process development to recover rare earth metals from monazite mineral: A review. *Miner. Eng.* **2015**, *79*, 102–115. [CrossRef]

65. Lee, J.C.; Kim, W.B.; Jeong, J.; Yoon, I.J. Extraction of neodymium from Nd-Fe-B magnet scraps by sulfuric acid. *J. Korean Inst. Met. Mater.* **1998**, *36*, 967.

66. Niinae, M.; Yamauchi, K.; Nakahiro, Y. Study on recycling of rare earth magnet scrap. *J. Mining Mater. Pro. Ins.* **1994**, *110*, 337.

67. Koyama, K.; Kitajima, A.; Tanaka, M. Selective leaching of rare-earth elements from an Nd-Fe-B magnet. *Kidorui (Rare Earths)* **2009**, *54*, 36–37.

68. Koyama, K.; Tanaka, M. The Latest Technology Trend and Resource Strategy of Rare Earths; Machida, K., Ed.; CMC Press: Tokyo, Japan, 2011; pp. 127–131.

69. Kumari, A.; Sinha, M.K.; Pramanik, S.; Sahu, S.K. Recovery of rare earths from spent NdFeB magnets of wind turbine: Leaching and kinetic aspects. *Waste Manag.* **2018**, *75*, 486–498. [CrossRef]

70. Hoogerstraete, T.V.; Wellsell, S.; Verachtert, K.; Binnemans, K. Removal of transition metals from rare earths by solvent extraction with an undiluted phosphonium ionic liquid: Separations relevant to rare-earth magnet recycling. *Green Chem.* **2013**, *15*, 919–927. [CrossRef]

71. Hoogerstraete, T.V.; Binnemans, K. Highly efficient separation of rare earths from nickel and cobalt by solvent extraction with the ionic liquid trihexyl(tetradecyl) phosphonium nitrate: A process relevant to the recycling of rare earths from permanent magnets and nickel metal hydride batteries. *Green Chem.* **2014**, *16*, 1594–1606.

72. Martina, O.; Amy, V.B.; Bart, B.; Koen, B. Selective roasting of Nd-Fe-B permanent magnets as a pretreatment step for intensified leaching with an ionic liquid. *J. Sustain. Metall.* **2020**, *6*, 91–102.

73. Rabatho, J.P.; Tongamp, W.; Takasaki, Y.; Haga, K.; Shibayama, A. Recycling of Nd and Dy from rare earth magnetic waste sludge by hydrometallurgical process. *J. Mater. Cycles Waste* **2013**, *15*, 171–178. [CrossRef]

74. Kataoka, Y.; Ono, T.; Tsubota, M.; Kitagawa, J. Improved room-temperature-selectivity between Nd and Fe in Nd recovery from Nd-Fe-B magnet. *AIP Adv.* **2015**, *5*, 117212. [CrossRef]

75. Yoon, H.S.; Kim, C.J.; Chung, K.W.; Jeon, S.; Park, I.; Yoo, K.; Jha, M.K. The effect of grinding and roasting conditions on the selective leaching of Nd and Dy from NdFeB magnet scraps. *Metals* **2015**, *5*, 1306–1314. [CrossRef]

76. Xie, F.; Zhang, T.A.; Dreisinger, D.; Doyle, F. A critical review on solvent extraction of rare earths from aqueous solutions. *Miner. Eng.* **2014**, *56*, 10–28. [CrossRef]

77. Venkatesan, P.; Vander Hoogerstraete, T.; Hennebel, T.; Binnemans, K.; Sietsma, J.; Yang, Y. Selective electrochemical extraction of REEs from NdFeB magnet waste at room temperature. *Green Chem.* **2018**, *20*, 1065–1073. [CrossRef]

78. Venkatesan, P.; Sun, Z.H.I.; Sietsma, J.; Yang, Y. An environmentally friendly electro-oxidative approach to recover valuable elements from NdFeB magnet waste. *Sep. Purif. Technol.* **2018**, *191*, 384–391. [CrossRef]

79. Venkatesan, P.; Vander Hoogerstraete, T.; Binnemans, K.; Sun, Z.; Sietsma, J.; Yang, Y. Selective extraction of rare-earth elements from NdFeB magnets by a room-temperature electrolysis pretreatment step. *ACS Sustain. Chem. Eng.* **2018**, *6*, 9375–9382. [CrossRef]

80. Yoon, H.-S.; Kim, C.-J.; Chung, K.W.; Kim, S.-D.; Kumar, J.R. Process development for recovery of dysprosium from permanent magnet scraps leach liquor by hydrometallurgical techniques. *Can. Metall. Q.* **2015**, *54*, 318–327. [CrossRef]

81. Yoon, H.-S.; Kim, C.-J.; Chung, K.W.; Kim, S.-D.; Kumar, J.R. Recovery process development for the rare earths from permanent magnets scraps leach liquors. *J. Brazil. Chem. Soc.* **2015**, *26*, 1143–1151. [CrossRef]

82. Lyman, J.W.; Palmer, G.R. Recycling of rare earths and iron from NdFeB magnet scrap. *High Temp. Mater. Proc.* **1993**, *11*, 175–187.

83. Lee, C.-H.; Chen, Y.J.; Liao, C.H.; Popuri, S.R.; TSAI, S.L.; Hung, C.E. Selective leaching process for neodymium recycling from scrap Nd-Fe-B magnet. *Metall. Mater. Trans. A* **2013**, *44*, 5825–5833. [CrossRef]
84. Itakura, T.; Sasai, R.; Itoh, H. A novel recovery method for treating wastewater containing fluoride and fluoroboric acid. *Bull. Chem. Soc. Jpn.* 2006, 79, 1303–1307. [CrossRef]
85. Itakura, T.; Sasai, R.; Itoh, H. In situ solid/liquid separation effect for high-yield recycling of boron and fluorine from aqueous media containing borate or fluoroborate ions. *Bull. Chem. Soc. Jpn.* 2007, 80, 2014–2018. [CrossRef]
86. Auerbach, R.; Bokelmann, K.; Stauber, R.; Guttfleisch, O.; Schnell, S.; Ratering, S. Recycling of rare earth metals out of end of life magnets by bioleaching with various bacteria as an example of an intelligent recycling strategy. *Miner. Eng.* 2019, 134, 104–117. [CrossRef]
87. Yoon, H.-S.; Kim, C.-J.; Chung, K.-W.; Kim, S.-D.; Lee, J.-Y.; Kumar, J.R. Solvent extraction, separation and recovery of the dysprosium (Dy) and neodymium (Nd) from aqueous solutions: Waste recycling strategies for permanent magnet processing. *Hydrometallurgy* 2016, 165, 27–43. [CrossRef]
88. Reddy, B.R.; Kumar, J.R. Rare earths extraction, separation and recovery from phosphoric acid media. *Solvent Extr. Ion Exch.* 2016, 34, 226–240. [CrossRef]
89. Lee, J.Y.; Jha, A.K.; Kumari, A.; Kumar, J.R.; Jha, M.K.; Kumar, V. Neodymium recovery by precipitation from synthetic leach liquor of concentrated rare earth mineral. *J. Metall. Mater. Sci.* 2011, 53, 349–354.
90. Lee, J.Y.; Kim, C.J.; Lee, J.Y.; Kim, S.D.; Lee, J.C. Separation of neodymium from NdFeB permanent magnet scrap. *J. Korean Inst. Resour. Recycl.* 2003, 12, 57–63.
91. Lee, J.Y.; Jha, A.K.; Kumari, A.; Gupta, G.; Kumar, V. Neodymium recovery by precipitation from synthetic leach liquor of concentrated rare earth mineral. *Bull. Chem. Soc. Jpn.* 2012, 85, 953–958.
92. Itakura, T.; Sasai, R.; Itoh, H. In situ solid/liquid separation effect for high-yield recycling of boron and fluorine from aqueous media containing borate or fluoroborate ions. *Bull. Chem. Soc. Jpn.* 2007, 80, 2014–2018. [CrossRef]
93. Gergoric, M.; Ravaux, C.; Steenari, B.-M.; Espegren, F.; Retegan, T. Leaching and Recovery of Rare-Earth Elements from Neodymium Magnet Waste Using Organic Acids. *Metals* 2018, 8, 721. [CrossRef]
94. Saito, T.; Sato, H.; Motegi, T. Recovery of rare earths from sludges containing rare-earth elements. *Hydrometallurgy* 2016, 165, 27–43. [CrossRef]
95. Kołodyńska, D.; Hubicki, Z. Investigation of sorption and separation of lanthanides on the ion exchangers without external heating. *J. Asian Ceram. Soc.* 2018, 4, 155–158. [CrossRef]
96. Lee, J.Y.; Jha, A.K.; Kumari, A.; Kumar, J.R.; Jha, M.K.; Kumar, V. Neodymium recovery by precipitation from synthetic leach liquor of concentrated rare earth mineral. *J. Chin. Ceram. Soc.* 2011, 53, 349–354.
97. Sasai, R.; Shimamura, N. Technique for recovering rare-earth metals from spent sintered Nd-Fe-B magnets without external heating. *J. Chem. Technol. Biot.* 2004, 79, 207–214. [CrossRef]
98. Su, J.; Su, Y.; Lai, Z. Thermodynamic analysis on preparation of zinc doped CO2-Y planar hexagonal ferrite powder by chemical co-precipitation method. *Chin. J. Inorg. Chem.* 2008, 24, 1943–1948.
99. Huang, L.H. *Chemical Beneficiation*; Metallurgical Industry Press: Beijing, China, 2012.
100. Deshpande, S.M.; Mishra, S.L.; Gajankush, R.B.; Thakur, N.V.; Koppiker, K.S. Recovery of high purity Y2O3 by solvent extraction route using organo-phosphorus extractants. *Miner. Process. Extr. Metall. Rev.* 2002, 145–147. [CrossRef]
101. Lee, M.-S.; Lee, J.Y.; Kim, J.S.; Lee, G.S. Solvent extraction of neodymium ions from hydrochloric acid solution using PC88A and saponified PC88A. *Sep. Purif. Technol.* 2006, 425, 207–214. [CrossRef]
102. El-Kot, A.M. Solvent extraction of neodymium, europium and thulium by di-(2-ethylhexyl) phosphoric acid. *J. Rare Earths* 2012, 46, 72–78. [CrossRef]
103. Lee, M.-S.; Lee, J.Y.; Kim, J.S.; Lee, G.S. Solvent extraction of neodymium ions from hydrochloric acid solution using PC88A and saponified PC88A. *Sep. Purif. Technol.* 2005, 46, 72–78. [CrossRef]
104. Preston, J.S.; Preez, A.C. The separation of europium from a middle rare earth concentrate by combined chemical precipitation, soluation and solvent-extraction methods. *J. Chem. Technol. Biot.* 1996, 65, 93–101. [CrossRef]
105. Maharana, L.N.; Nair, V.R. Production of value added rare earths from monazite by solvent extraction. In *Light Metals*; Kvannde, H., Ed.; TMS 2005: Warrendale, PA, USA, 2005; pp. 1163–1166.
106. Mohammadi, M.; Forsberg, K.; Klof, L.; Cruz, J.M.D.L.; Rasmuson, A. Separation of Nd(III), Dy(III) and Y(III) by solvent extraction using D2EHPA and EHEHPA. *Hydrometallurgy* 2015, 156, 215–224. [CrossRef]
107. Sarangi, K.; Reddy, B.R.; Das, R.P. Extraction studies of cobalt(II) and nickel(II) from chloride solutions using Na-Cyanex 272: Separation of Co(II)/Ni(II) by the sodium salts of D2EHPA, PC88A and Cyanex 272 and their mixtures. *Hydrometallurgy* 1999, 52, 253–265. [CrossRef]
108. Thakur, N.V.; Jayawant, D.V.; Iyer, N.S.; Koppiker, K.S. Separation of neodymium from lighter rare earths using alkyl phosphonic acid, PC88A. *Hydrometallurgy* 1993, 34, 99–108. [CrossRef]
109. Devi, N.B.; Nathsarma, K.C.; Chakravortty, V. Separation and recycling of cobalt(II) and nickel(II) from sulphate solutions using sodium salts of D2EHPA, PC88A and Cyanex 272. *Hydrometallurgy* 1999, 49, 47–61. [CrossRef]
110. Devi, N.B.; Nathsarma, K.C.; Chakravortty, V. Separation of divalent manganese and cobalt ions from sulphate solutions using sodium salts of D2EHPA, PC88A and Cyanex 272. *Hydrometallurgy* 2000, 54, 117–131. [CrossRef]
111. Padhan, E.; Sarangi, K. Solvent extraction of Nd using organo-phosphorus extractants from chloride media. *Chem. Technol. Biotechnol.* 2015, 90, 1869–1875. [CrossRef]
112. Pavón, S.; Fortunya, A.; Collb, M.T.; Sastrec, A.M. Neodymium recovery from NdFeB magnet wastes using Primene 81R-Cyanex 572 IL by solvent extraction. *J. Environ. Manag.* 2018, 222, 359–367. [CrossRef] [PubMed]
113. Rice, A.C.; Stone, C.A. *Amines in Liquid–Liquid Extraction of Rare Earth Elements*; US Department of the Interior, Bureau of Mines: Washington, DC, USA, 1961; p. 5923.
114. Hsu, K.H.; Huang, C.H.; King, T.C.; Li, P.K. Separation of praseodymium and neodymium in high purity (99.9%) by counter-current exchange extraction and its mechanism. In *Proceedings of the International Solvent Extraction Conference’80 (ISEC’80)*, Liege, Belgium, 6–12 September 1980; Society of Chemical Industry: London, UK; Volume 2, pp. 80–82.
115. El-Yamani, I.S.; Shabana, E.L. Solvent extraction of lanthanum(III) from sulfuric acid solutions by Primene 81R. *J. Less-Common Metals* 1985, 105, 255–261. [CrossRef]
116. Huang, C.H.; Jin, T.Z.; Li, B.G.; Li, J.R.; Xu, G.X. Studies on extraction mechanism of the rare earths using alkyl phosphoric acid, PC88A or their mixtures. In *Proceedings of the International Solvent Extraction Conference—ISEC’86*; Dechema: Frankfurt, Germany, 1986; pp. 215–221.
117. Cerna, M.; Volaufova, E.; Rod, V. Extraction of light rare earth elements by amines at high inorganic nitrate concentration. *Hydrometallurgy* 1992, 28, 339–352. [CrossRef]
118. Lu, D.; Horing, J.S.; HOH, Y.C. The separation of neodymium by quaternary ammonium form didymium nitrate solution. *J. Less-Common Metals* 1989, 149, 219–224. [CrossRef]
119. Preston, J.S. The recycling of rare earth oxides from a phosphoric acid byproduct, Part 4: The preparation of magnet-grade neodymium oxide from the light rare earth fraction. *Hydrometallurgy* 1996, 42, 151–167. [CrossRef]
120. Mincher, B. Radiation chemistry in the reprocessing and recycling of spent nuclear fuels. In *Reprocessing and Recycling of Spent Nuclear Fuel*; Taylor, R., Ed.; Elsevier: Cambridge, UK, 2015; pp. 191–213.
121. Tachimori, S.; Sasaki, Y.; Suzuki, S. Modification of TODGA-n-dodecane solvent with a monoamide for high loading of lanthanides(III) and actinides(III). *Solvent Extr. Ion. Exch.* 2002, 20, 687–699. [CrossRef]
122. Marcus, Y. Principles of Solubility and Solutions. In *Solvent Extraction Principles and Practise*, 2nd ed.; Rydberg, J., Cox, M., Musicas, C., Choppin, G.R., Eds.; Marcel Dekker: New York, NY, USA, 2004; pp. 77–81.
123. Kim, D. A supported liquid membrane system for the selective recycling of rare earth elements from neodymium-based permanent magnets. *Sep. Sci. Technol.* 2017, 51, 1716–1726. [CrossRef]
124. Wang, X.; Li, W.; Meng, S.; Li, D. The extraction of rare earths using mixtures of acidic phosphorus based reagents or their thio-analogues. *J. Chem. Technol. Biot.* 2006, 81, 761–766. [CrossRef]
125. Santhi, P.B.; Reddy, M.L.P.; Ramamohan, T.R.; Damodaran, A.D. Liquid-liquid extraction of yttrium (III) with mixtures of organophosphorous extractants: Theoretical analysis of extraction behavior. *Hydrometallurgy* 1991, 27, 169–177. [CrossRef]
126. Tian, M.; Song, N.; Wang, D.; Quan, X.; Jia, Q.; Liao, W.; Lin, L. Applications of the binary mixture of sec-octylphenoxacyclic acid and 8-hydroxyquinoline to the extraction of rare earth elements. *Hydrometallurgy* 2012, 111–112, 109–113. [CrossRef]
127. Tian, M.; Jia, Q.; Liao, W. Studies on synergistic solvent extraction of rare earth elements from nitrate medium by mixtures of 8-hydroxyquinoline with Cyanex 301 or Cyanex 302. *J. Rare Earth.* 2013, 31, 604–608. [CrossRef]
128. Huang, X.; Li, J.; Zhang, Y.; Long, Z.; Wang, C.; Xue, X. Synergistic extraction of Nd$^{3+}$ and Sm$^{3+}$ with the mixtures of P2O4 and P507 in acidic sulfate solutions. *Chem. J. Nonferrous Met.* 2008, 18, 366–371.

129. Luo, X.; Huang, X.; Zhu, Z.; Long, Z.; Liu, Y. Synergistic extraction of cerium from sulfuric acid medium using mixture of 2-ethylhexyl phosphonic acid mono 2-ethylhexyl ester and Di-(2-ethyl hexyl) phosphoric acid as extractant. *J. Rare Earth.* 2009, 27, 119–122. [CrossRef]

130. Baes, C.F.J. The extraction of metallic species by dialkylphosphoric acids. *J. Inorg. Nucl. Chem.* 1962, 24, 707–720. [CrossRef]

131. Sato, T. Liquid–liquid extraction of rare-earth elements from aqueous acid solutions by acid organophosphorus compounds. *Hydrometallurgy* 1989, 22, 121–140. [CrossRef]

132. Zhang, C.; Wang, L.; Huang, X.; Dong, D.; Long, Z.; Zhang, Y. Yttrium extraction from chloride solution with a synergistic system of 2-ethylhexyl phosphonic acid mono-(2-ethylhexyl) ester and bis(2,4,4-trimethylpentyl) phosphonic acid. *Hydrometallurgy* 2014, 147–148, 7–12. [CrossRef]

133. Liu, Y.; Jeon, H.S.; Lee, M.S. Solvent extraction of Pr and Nd from chloride solution by the mixtures of Cyanex 272 and amine extractants. *Hydrometallurgy* 2014, 150, 61–67. [CrossRef]

134. Panda, N.; Devi, N.B.; Mishra, S. Extraction of neodymium(III) using binary mixture of Cyanex 272 and Cyanex 921/Cyanex 923 in kerosene. *J. Radioanal. Nucl. Chem.* 2013, 296, 1205–1211. [CrossRef]

135. Liu, Y.; Jean, H.S.; Lee, M.S. Solvent extraction of Pr and Nd from chloride solution by the mixtures of Cyanex 272 and amine extractants. *Hydrometallurgy* 2014, 150, 61–67. [CrossRef]

136. Billard, I.; Ouadi, A.; Gaillard, C. Liquid-liquid extraction of actinides, lanthanides, and fission products by room temperature ionic liquids. *Ind. Eng. Chem. Res.* 2015, 44, 2349–2355. [CrossRef]

137. Nakashima, F.; Maruyama, T.; Goto, M. Feasibility of ionic liquids as alternative separation media for industrial solvent extraction processes. *Ind. Eng. Chem. Res.* 2005, 44, 4368–4372. [CrossRef]

138. Billard, I.; Ouadi, A.; Gaillard, C. Liquid-liquid extraction of actinides, lanthanides, and fission products by use of ionic liquids: From discovery to understanding. *Anal. Bioanal. Chem.* 2011, 400, 1555–1566. [CrossRef]

139. Wei, G.; Yang, Z.; Chen, C. Room temperature ionic liquid as a novel medium for liquid/liquid extraction of metal ions. *Anal. Chim. Acta* 2003, 488, 183–192. [CrossRef]

140. Rout, A.; Kotlarska, J.; Dehaen, W.; Binnemans, K. Liquid–liquid extraction of neodymium(III) by dialkylphosphate ionic liquids from acidic medium: The importance of the ionic liquid cation. *Phys. Chem. Chem. Phys.* 2013, 15, 16533–16541. [CrossRef]

141. Nakashima, F.; Maruyama, T.; Goto, M. Feasibility of ionic liquids as alternative separation media for industrial solvent extraction processes. *Ind. Eng. Chem. Res.* 2005, 44, 4368–4372. [CrossRef]

142. Nakashima, F.; Maruyama, T.; Goto, M. Feasibility of ionic liquids as alternative separation media for industrial solvent extraction processes. *Ind. Eng. Chem. Res.* 2005, 44, 4368–4372. [CrossRef]

143. Zhang, F.; Wu, W.; Bian, X.; Zeng, W. Synergistic extraction and separation of lanthanum (III) and cerium (III) using a mixture of 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester and di-2-ethylhexyl phosphoric acid. *Hydrometallurgy* 2014, 149, 238–243. [CrossRef]

144. Rout, A.; Kotlarska, J.; Dehaen, W.; Binnemans, K. Liquid–liquid extraction of neodymium(III) by dialkylphosphate ionic liquids from acidic medium: The importance of the ionic liquid cation. *Phys. Chem. Chem. Phys.* 2013, 15, 16533–16541. [CrossRef]
150. Liu, Y.; Chen, J.; Li, D. Application and perspective of ionic liquids on rare earths green separation. *Sep. Sci. Technol.* **2012**, *47*, 223–232. [CrossRef]

151. Rout, A.; Binnemans, K. Solvent extraction of neodymium(III) by functionalized ionic liquid trioctylmethylammonium dioctyl diglycolamate in fluorine-free ionic liquid diluent. *Ind. Eng. Chem. Res.* **2014**, *53*, 6500–6508. [CrossRef]

152. Wang, W.; Yang, H.; Cui, H.; Zhang, D.; Liu, Y.; Chen, J. Application of bifunctional ionic liquid extractants [A336][CA-12] and [A336][CA-100] to the lanthanum extraction and separation from rare earths in the chloride medium. *Ind. Eng. Chem. Res.* **2011**, *50*, 7534–7541. [CrossRef]

153. Rout, A.; Karmakar, S.; Venkatesan, K.A.; Srinivasan, T.G.; Vasudeva, P.R. Room temperature ionic liquid diluent for the mutual separation of europium(III) from americium(III). *Sep. Purif. Technol.* **2011**, *81*, 109–115. [CrossRef]

154. Sun, X.; Ji, Y.; Hu, F.; He, B.; Chen, J.; Li, D. The inner synergistic effect of bifunctional ionic liquid extractant for solvent extraction. *Talanta* **2010**, *81*, 1877–1883. [CrossRef] [PubMed]

155. Sun, X.; Waters, K.E. The adjustable synergistic effects between acid-base coupling bifunctional ionic liquid extractants for rare earth separation. *AIChE J.* **2014**, *60*, 3859–3868. [CrossRef]