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Article

Recovery of Rare Earth Elements from the Leaching Solutions of Spent NdFeB Permanent Magnets by Selective Precipitation of Rare Earth Oxalates

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Abstract: After mechanical pre-treatment, the typical hydrometallurgical route of NdFeB magnet recycling starts with leaching in acidic solutions. However, due to the high concentration of iron ions in the leaching solution, the selective recovery of rare earths from the solution is challenging. In our work, the selective precipitation of rare earth oxalates as a potential separation method was proposed. The precipitation of neodymium oxalate was first tested on model solutions, which was then followed by experimental tests carried out on real solutions after the leaching of NdFeB magnets. The recovery of rare earths in the form of oxalates was investigated with the use of different amounts of oxalic acid in relation to its stoichiometric amount. The most efficient separation of rare earths was observed in the case where sulfuric acid was used for leaching. The use of oxalic acid in stoichiometric amounts resulted in the precipitation of about 93% of all rare earths present in the solution, whereas the concentration of Fe and other elements (Ni, Co, and B) practically did not change. An increase in oxalic acid of 20% and 40% more than the stoichiometric amount (100%) led to the increase in the precipitation efficiency of rare earths to 96.7% and 98.1%, respectively. However, the use of oxalic acid in a 1.4 ratio caused a 7% decrease in Fe concentration, which suggests Fe co-precipitation. In order to investigate a possibility of further increasing the separation of rare earths from iron, an additional method was tested, in which iron was first oxidized from Fe²⁺ to Fe³⁺ before the precipitation of rare earth oxalates.

Keywords: hydrometallurgy; recycling; neodymium; e-waste; REEs extraction; selective precipitation; NdFeB magnets



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1. Introduction

Rare earth elements (REEs) are indispensable in the development of high-tech applications, such as electric and hybrid vehicles, wind turbines, variety of electronics, photovoltaic films, and catalysts. These wide application areas are the result of specific magnetic, catalytic, and phosphorescent properties of REEs and lead to the high demand of raw REE materials [1–3]. Due to the high demand and supply risk, REEs belong to Critical Raw Materials according to the recently updated list of the European Commission [4]. The European Union depends on external imports to cover its demand for REEs. Almost all of these imports (98%) are covered by China, which is the leading global producer of REEs. However, China recently announced restrictions on REE exports, citing the increase in their domestic demand and the environmental impact of continuous mining operations [3].

Permanent magnets, based on (Nd, Pr, Dy)-Fe-B alloys, have the best quality compared to other types of permanent magnets [5] and are essential in electronics and the clean energy industry, i.e., computer hard drives, hybrid and electric vehicles, as well as wind turbines.

They consist of 27–32 wt.% of REEs, 67–73 wt.% of Fe, about 1 wt.% of B and other minor metals. It is predicted that from 2022 to 2035, the clean energy transition, meaning the transition to electric vehicles and wind power, will play a key role in the growing demand for REEs [6]. The gap between the high industrial demand for REEs in magnets and their supply requires new resources of these elements, other than traditional primary REE ores [3]. Secondary raw materials, i.e., end-of-life electronics or wind turbines, seem to have great potential in becoming an important source of REEs. Some of the devices using permanent magnets (hybrid and electric vehicles and wind power generators) will work for many years, but others, such as computer hard disk drives, reach their end of life relatively quickly due to the rapid aging of electronic devices. Therefore, the recycling of NdFeB magnets from waste hard disk drives (HDDs) could be one of the alternative sources of REEs.

Various technologies (hydrometallurgy, electrochemistry, gas-phase extraction, membrane separation, biological extraction, and pyrometallurgy) have been investigated to recover REEs from end-of-life magnets. Descriptions of them have been given in recently published works [1,2,7–10]. Among all available technologies, magnet-to-magnet recycling seems to be the least time-consuming method to produce new magnets from waste magnets, and it has been implemented on an industrial scale [11,12]. Habibzadeh et al. [13] have recently reviewed the research carried out so far on magnet-to-magnet technology. Despite the already-available technologies and the many studies conducted, less than 1% of REEs used today are recycled, and there is a need to develop a simple, effective, and economically viable recycling method.

Hydrometallurgical routes for the recycling of magnets consist of several unit operations, such as demagnetization; crushing and milling; roasting; leaching; the separation of rare earths from iron via, i.e., solvent extraction; and finally, the precipitation of rare earths in different chemical forms [1,2,7–10]. The combination of so many unit operations, although easy to carry out on a laboratory scale, negatively affects the applicability of hydrometallurgical methods on an industrial scale. The grinding and roasting operations consume a lot of energy and negatively affect the economics of the recycling. Additionally, solvent extraction requires the use of large amounts of complex and expensive solvents.

In the leaching stage of the hydrometallurgical process, mineral inorganic agents, such as nitric acid, sulfuric acid, hydrochloric acid, and sodium hydroxide, are typically used [14]. Lee et al. [15] carried out leaching processes with all four inorganic agents and demonstrated that hydrochloric and sulfuric acids performed best to dissolve 100% of Nd from waste magnets. In the recent study of Stein et al. [16], it was demonstrated that organic acetic and citric acids also have potential as leaching agents for NdFeB magnets; however, the REE dissolution rates were found to be much lower in comparison to inorganic acids. With the additional use of microwaves, 57% of Nd and 58% of Pr were leached with 0.5 M citric acid, and 65% of Nd and 65% of Pr were leached with 0.5 M acetic acid. Belfqueh et al. [17] evaluated different organic acids as alternative leaching agents for NdFeB magnets and indicated that acetic acid shows the highest leaching performance, allowing the dissolution of 90% of Nd, Dy, and Pr while applying an acid concentration of 1.6–10 M, a solid/liquid ratio 0.5%–5%, and a temperature of 60 °C.

In a leaching process where the complete dissolution of a magnet is achieved, the solution contains large amounts of Fe ions, which cause a great challenge for the separation and recovery of REEs [14]. There are several studies regarding the recovery of rare earths from leaching solutions in the form of oxalates [18–22]. In the recycling method proposed by Vander Hoogerstraete et al. (2014) [19], NdFeB magnets were first crushed, milled, and roasted. Roasted magnets were leached with 12.0 M HCl and 3.5 M NH₄Cl at 100 °C, after which, Fe was left in the solid residue. REEs were separated from cobalt and other metals present in the leaching solution via solvent extraction with ionic liquid trihexyl(tetradecyl)phosphonium chloride. After solvent extraction, rare earths were precipitated in the form of oxalates, which were then further calcinated to rare earth oxides. The proposed method seems very promising and effective; however, the process

consumes energy through roasting, crushing, milling, and calcination. In order to simplify the hydrometallurgical process, Liu et al. [21] proposed introducing oxalic acid already in the leaching process as an extractant, through which, the simultaneous extraction of rare earths and iron was achieved. The precipitation rate of rare earth oxalates reached 93% at the most optimal conditions of 90 °C for 6 h in the aqueous solution of 2 M oxalic acid with a liquid/solid ratio of 60 mL/g. In another study by Liu et al. [23], NdFeB sludge was leached with hydrochloric acid followed by a precipitation stage with oxalic acid, which resulted in the selective separation and precipitation of REEs and Fe. REE recovery of 98.28% was achieved. In a recent study by Makarova et al. [22], oxalic acid was added in a mixture with sulfuric acid in chemical and electrochemical leaching. It was discovered that electrochemical leaching intensifies the dissolution of magnets, and it was also indicated that the concentration of oxalic acid has a high influence on rare earth element concentrations in both solution and precipitate. In the most optimal conditions, the achieved purity of REE oxalates was up to 93% [22].

Based on the literature studies, oxalic acid seems to be a promising precipitation agent as it does not introduce new metals to the solution. Moreover, after the use of oxalic ions for the precipitation of rare earths, the remaining solution contains high concentration of H⁺ ions and could be potentially reused in the leaching process. Additionally, precipitated rare earth oxalates can be further calcinated to rare earth oxides, which can be then integrated with the production of rare earth oxides from primary ores.

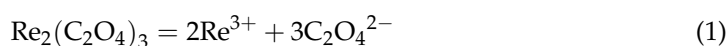
In our previous study, we proposed a simplified process of hydrometallurgical NdFeB magnet recycling [24]. Its simplicity is a result of omitting the unit operations of crushing, grinding, and roasting before leaching. The use of hydrochloric and sulfuric acids as the leaching agents allowed for the selective leaching of broken Nd-Fe-B magnets, while leaving nickel, which covered the magnets, in a solid state. In our current study, we focused on the separation of rare earths from iron and other elements present in the leaching solution. The main aim of our study was to simplify the separation process via the direct precipitation of rare earth oxalates and by leaving iron and other elements in the leaching solution. In this study, oxalic acid was used as a precipitant, and its concentration was one of the investigated variables. Additionally, the precipitation of rare earth oxalates was studied before and after the oxidation of iron from Fe²⁺ to Fe³⁺. Precipitation tests were carried out on two different types of solutions: hydrochloric leaching solutions and sulfuric leaching solutions. Due to the complexity of the actual leaching solutions, the experiments were first performed on model solutions.

2. Materials and Methods

2.1. Background of the Methodology

It was shown in the authors' previous study [24] that after the leaching of demagnetized and broken NdFeB magnets with HCl and H₂SO₄, the obtained solutions contained high concentrations of Fe (38–64 g·L^{−1}) and Nd (17–29 g·L^{−1}). The solutions may have also contained other rare earths—Pr (1–5 g·L^{−1}), Dy (0.2–2 g·L^{−1}), and Tb (0.02–0.3 g·L^{−1})—and also traces of other elements (B, Co, and Ni) with concentrations between 0.001 and 1 g·L^{−1}. The precipitation methodology applied in this study aimed to separate Fe from rare earth ions through the selective precipitation of rare earth oxalates.

According to the literature [25], the rare earth oxalate dissolution reaction can be described with Equation (1):



where Re represents the rare earth element. The dissolution of iron(II) oxalate can be expressed with Equation (2).



Oxalate ions may further react with protons to form oxalic acid, as presented in Equations (3) and (4).

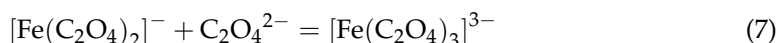
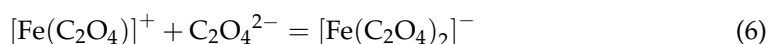
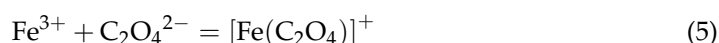


The solubility of rare earth oxalates in water is very low in comparison to the solubility of iron(II) oxalate. The solubility products for selected rare earths oxalates as well as the solubility product of iron(II) oxalate are presented in Table 1.

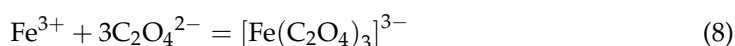
Table 1. Solubility products of selected oxalates [25,26].

Oxalate	Solubility Product
$\text{Nd}_2(\text{C}_2\text{O}_4)_3$	1.08×10^{-33}
$\text{Dy}_2(\text{C}_2\text{O}_4)_3$	2.0×10^{-31}
FeC_2O_4	3.2×10^{-7}

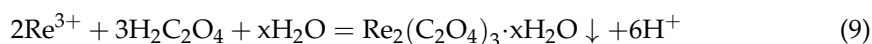
Furthermore, if Fe is present in the solution at the +3 oxidation state, oxalic acid can deactivate the iron cations through the formation of highly stable complexes, and depending on the conditions, i.e., pH and concentrations of Fe and oxalic acid, the complexes with one, two, or three ligands in the coordination sphere may exist in aqueous solution [27], as presented in Equations (5)–(7).



The above reactions can be summarized with one simplified reaction, expressed with Equation (8):



Based on the collected information, it was expected that when oxalic acid is added to the solution after the leaching of NdFeB magnets, the rare earths will first precipitate in the form of oxalates, according to Equation (9), whereas Fe^{2+} ions remain in the solution until the amount of $\text{C}_2\text{O}_4^{2-}$ ions reaches the saturation of iron(II) oxalate. On the other hand, if Fe^{2+} is oxidized to Fe^{3+} , iron will be left in the solution in the form of an iron(III) oxalate complex, and rare earths will precipitate in the form of oxalates when the oxalic ions are added to the system, according to Equation (9).



In order to test this approach, the precipitation tests were first conducted on model solutions followed by experiments on real solutions obtained after the leaching of magnets [24].

2.2. Precipitation of Rare Earth Oxalates

The possibility of the selective precipitation of lanthanide oxalates from the solution was first tested on model solutions which contained only Fe^{2+} and Nd^{3+} ions for simplicity. The concentrations of the Fe and Nd ions were similar to the concentrations of these ions obtained in the magnet leaching process [24]: $35 \text{ g} \cdot \text{L}^{-1}$ and $20 \text{ g} \cdot \text{L}^{-1}$ for Fe and Nd, respectively. Two different types of model solutions were prepared. Model solutions S1 and S2 were prepared by mixing FeCl_2 and NdCl_3 as well as FeSO_4 and $\text{Nd}_2(\text{SO}_4)_3$ solutions, respectively. Iron(II) chloride and iron(II) sulphate solutions were prepared via the dissolution of FeCl_2 and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in distilled water. NdCl_3 and $\text{Nd}_2(\text{SO}_4)_3$ solutions

were prepared via the dissolution of Nd_2O_3 in hot concentrated hydrochloric and sulfuric acid, respectively. The pH of each model solution was adjusted to 1.0 ± 0.2 , i.e., to a value close to the pH of the solutions after leaching the magnets, by adding hydrochloric acid and sulfuric acid to S1 and S2, respectively. Details about chemicals used in the experiments are presented in Table 2.

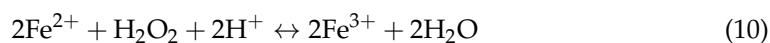
Table 2. Chemicals used in the experiments.

Chemical	Formula	Purity/Concentration	Supplier
Sulfuric acid	H_2SO_4	Min. 95%	POCH SA, Gliwice, Poland
Hydrochloric acid	HCl	35%	POCH SA, Gliwice, Poland
Iron(II) chloride	FeCl_2	98%	Sigma-Aldrich, Schnellendorf, Germany
Iron(II) sulphate heptahydrate	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	$\geq 99\%$	Merck, Darmstadt, Germany
Neodymium(III) oxide	Nd_2O_3	99.99%	Sigma-Aldrich, Schnellendorf, Germany
Oxalic acid dihydrate	$\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$	Min. 99.5%	POCH SA, Gliwice, Poland
Hydrogen peroxide	H_2O_2	30%	POCH SA, Gliwice, Poland

The volume of the solution was 50 mL in every precipitation test. The appropriate amount of oxalic acid was weighed on the scale; then, approximately every 2–3 min, a small amount of oxalic acid was added to the solution using a teaspoon. A magnetic stirrer was used to mix the solution while adding oxalic acid. The precipitation process was carried out at room temperature (20 °C) for about 30 min. The stoichiometric amount of oxalic acid was calculated based on the reaction presented in Equation (9). Different ratios between the added amount of oxalic acid and its stoichiometric amount were used in experiments, from 60 wt.% to 200 wt.%. After precipitation, the solid was separated from the solution via filtration. The solution was then subjected to the chemical analysis described in Section 2.3. The precipitate was washed several times with hot distilled water and dried at 50 °C for 24 h.

After experiments on model solutions, the same precipitation methodology was used for pregnant leach solutions. The leaching of NdFeB magnets was conducted according to the method described in our previous study [24]. Before leaching, magnets were demagnetized by being heated to 350 °C, and after that, they were broken into pieces. Two leaching series were performed with the use of hydrochloric and sulfuric acid with concentrations of $2 \text{ mol} \cdot \text{L}^{-1}$. NdFeB magnets used as feed in the leaching process came from end-of-life hard disc drives from different types of Desktop PCs and Notebooks. The weight of the magnets in each leaching experiment was $14 \text{ g} \pm 0.3 \text{ g}$, and the volume of the solution was 200 mL. Leaching was carried out in a rotary reactor driven by an evaporator (Büchi, Rotavapor R-210/215) at 40 °C using a mixing rate of 40 rpm for 6 h.

The oxidation state of iron in the leaching solution was determined with the potassium dichromate titration method, which allowed for the measurement of the concentration of Fe^{2+} ions, whereas the total concentration of iron was analyzed with the ICP-OES technique. The tests showed that the concentration of Fe^{2+} matched the concentration of total iron. Therefore, it was assumed that directly after leaching, Fe is present in the solution at the +2 oxidation state. The oxalate precipitation tests were conducted without iron oxidation and after the oxidation of iron ions to the +3 oxidation state. In order to oxidize Fe^{2+} to Fe^{3+} , twice the stoichiometric amount of hydrogen peroxide (30%-solution, Equation (10)) was added to the pregnant leach solution. The oxalate precipitation procedure was the same in both scenarios, with and without the oxidation of iron.



2.3. Chemical Analysis

The concentrations of the elements in solution were determined using an optical Jobin Yvon sequential ICP-OES instrument (Jobin Yvon 38S, HORIBA Jobin Yvon SAS, Longjumeau, France). The details of the analytical procedure were presented in our previous work [24].

The qualitative analysis of precipitated solids was conducted with the X-ray diffraction (XRD) technique. Measurements were carried out via symmetric $\theta/2\theta$ Bragg-Brentano geometry using a Philips X'PERT system with a diffractometer equipped with a $\text{CuK}\alpha$ ($\lambda = 0.154 \text{ nm}$) source. The identification of the chemical compounds was carried out via the comparison of the obtained powder diffraction patterns from the analysis of precipitated solids with reference patterns collected in the database (International Centre for Diffraction Data PDF-2 base).

3. Results and Discussion

3.1. Precipitation of Neodymium Oxalate from Model Solutions

The first oxalate precipitation tests were conducted on the model solution. It was observed during the experiments that a light-pink-colored solid started to precipitate immediately after adding the first portions of oxalic acid. The concentrations of Fe and Nd in model solution S1 (with hydrochloric acid) before and after the precipitation of neodymium oxalate are presented in Figure 1. After oxalic acid was added to the solution using a 0.6 ratio compared to its stoichiometric amount, the concentration of Nd decreased from $23 \text{ g}\cdot\text{L}^{-1}$ to $8 \text{ g}\cdot\text{L}^{-1}$, when at the same time, the Fe concentration decreased slightly from $33 \text{ g}\cdot\text{L}^{-1}$ to $31.5 \text{ g}\cdot\text{L}^{-1}$. When the amount of oxalic acid added increased to its stoichiometric amount, the Nd concentration decreased to $3.5 \text{ g}\cdot\text{L}^{-1}$, whereas the Fe concentration did not change. The Fe concentration in the solution remained the same, approximately $31 \text{ g}\cdot\text{L}^{-1}$, with the increasing amount of oxalic acid being up to 1.4 times the stoichiometric amount. With an even higher amount of oxalic acid, the Fe concentration decreased significantly and reached $21 \text{ g}\cdot\text{L}^{-1}$ after the oxalic acid addition increased to twice its stoichiometric amount. Simultaneously, the Nd concentration decreased first to $3.5 \text{ g}\cdot\text{L}^{-1}$ at a 1.4 oxalic acid ratio and then to $2.7 \text{ g}\cdot\text{L}^{-1}$ when the oxalic acid ratio increased to 1.6. With a higher amount of oxalic acid being added, the Nd concentration remained similar, about $2.7 \text{ g}\cdot\text{L}^{-1}$. Therefore, the highest possible recovery of neodymium was 88.6%.

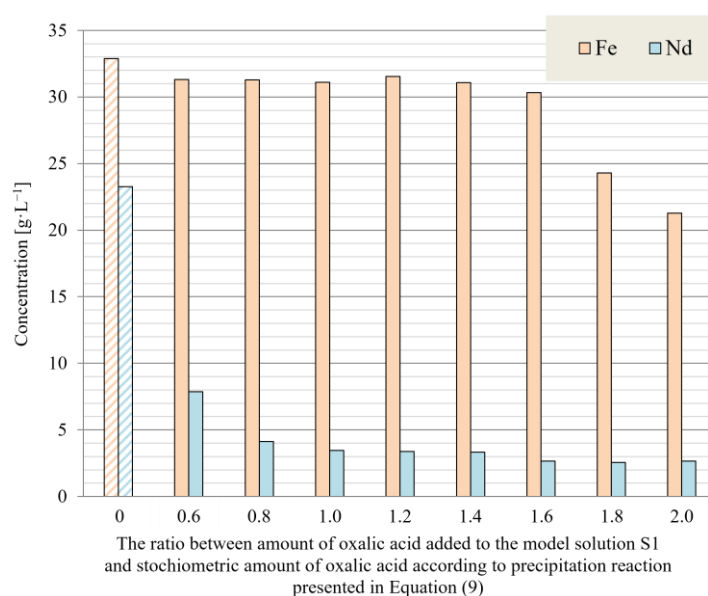


Figure 1. Concentrations of iron and neodymium in model HCl solution before and after precipitation of neodymium oxalate. The first two bars correspond to the concentrations of Fe and Nd before oxalates precipitation.

Based on the results, it can be stated that the amount of oxalic acid which does not cause the precipitation of iron (II) oxalate is 1.4 times the stoichiometric amount. This amount, however, only allowed about 85.7% of the Nd present in the model solution S1 to be precipitated.

The results of analogous tests of neodymium oxalate precipitation from the model solution S2 (with sulfuric acid) are shown in Figure 2. After adding oxalic acid to the model solution S2 in the stoichiometric amount, the concentration of Nd decreased from $19 \text{ g}\cdot\text{L}^{-1}$ to $8 \text{ g}\cdot\text{L}^{-1}$, which means that only 58% of the Nd was precipitated. When the amount of oxalic acid was increased by 20% in comparison to its stoichiometric amount, the Nd concentration decreased slightly to $7 \text{ g}\cdot\text{L}^{-1}$. When the amount of oxalic acid was increased further to 140% of its stoichiometric amount, the Nd concentration decreased to about $5 \text{ g}\cdot\text{L}^{-1}$, which means that 73% of the neodymium was precipitated. However, this increase in the amount of oxalic acid resulted in the decrease in the Fe concentration in the solution by 10%. This suggests that iron oxalate was co-precipitated together with neodymium oxalate. Therefore, the ratio of oxalic acid used should not be higher than 1.2 in relation to the stoichiometry.

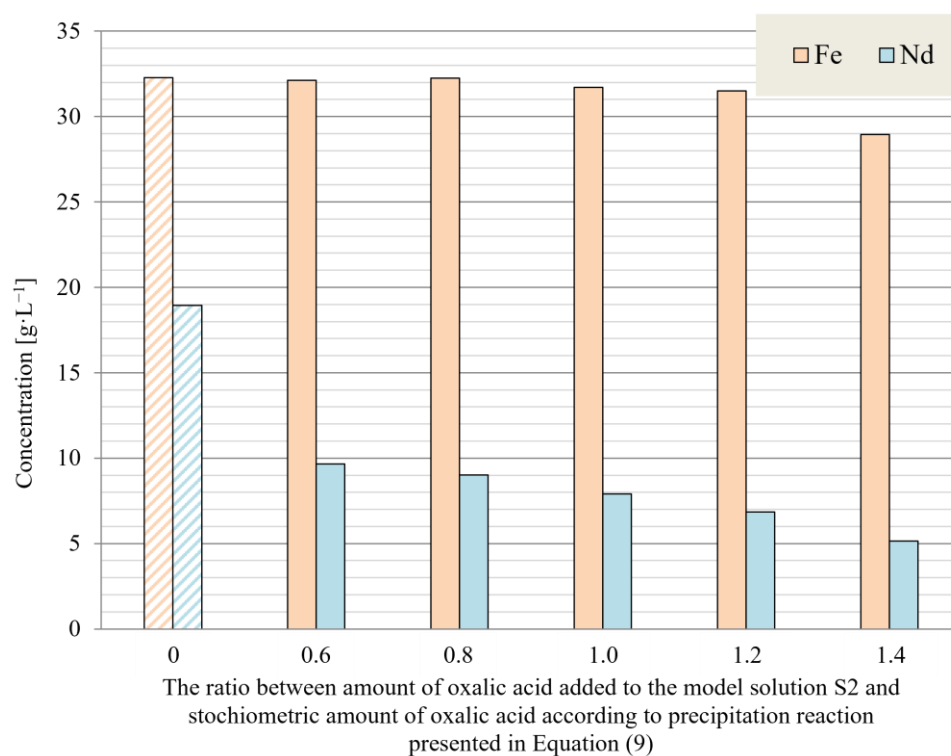


Figure 2. Concentration of iron and neodymium in model H_2SO_4 solution before and after precipitation of neodymium oxalate. The first two bars correspond to the concentrations of Fe and Nd before oxalates precipitation.

The precipitated solids were analyzed via X-ray powder diffraction. Examples of XRD patterns of the obtained solids are presented in Figure 3. The main XRD peak positions and intensities correspond to $\text{Nd}_2(\text{C}_2\text{O}_4)_3\cdot 10\text{H}_2\text{O}$ according to the neodymium oxalate hydrate standard card (number 18-0858 in ICDD PDF2 database). The main peak positions according to the database are $2\theta = 8.835^\circ, 13.404^\circ, 17.478^\circ, 18.549^\circ$, and 25.427° . The obtained XRD patterns seemed very similar regardless of the oxalic acid amount that was used in the precipitation, which clearly indicates a very similar phase composition of the obtained precipitants.

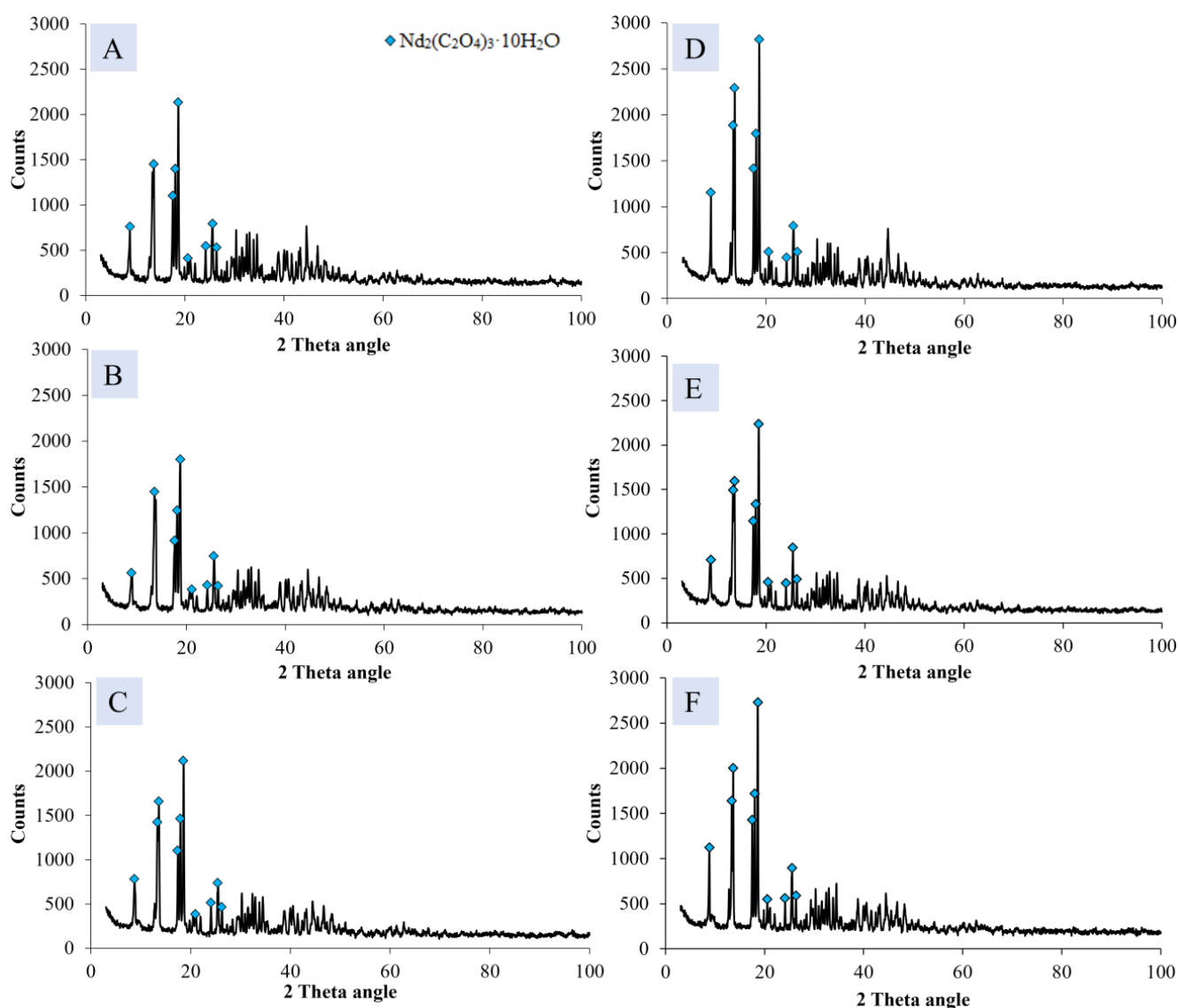


Figure 3. XRD diffractograms of solids precipitated after adding oxalic acid to the model solution S1 (A–C) and S2 (D–F). The ratio between the amount of oxalic acid added to the solution and the stoichiometric amount was (A,D)—1.0, (B,E)—1.2, and (C,F)—1.4. Blue diamond icons indicate peaks corresponding to $\text{Nd}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$.

3.2. Precipitation of Lanthanide Oxalates from Real Solutions after Leaching of Magnets with Hydrochloric and Sulfuric Acid Solutions

Precipitation tests conducted on model solutions confirmed the possibility of the selective precipitation of neodymium oxalate while leaving iron in the solution. Therefore, analogous tests were carried out on real solutions obtained after the leaching of NdFeB magnets in acidic solutions. The concentrations of all elements in the solution before and after the precipitation of oxalates were analyzed with the ICP-OES technique and are presented in Tables S1 and S2 in the Supplementary Materials. The concentrations of iron and rare earths in the solutions are shown in Figures 4 and 5.

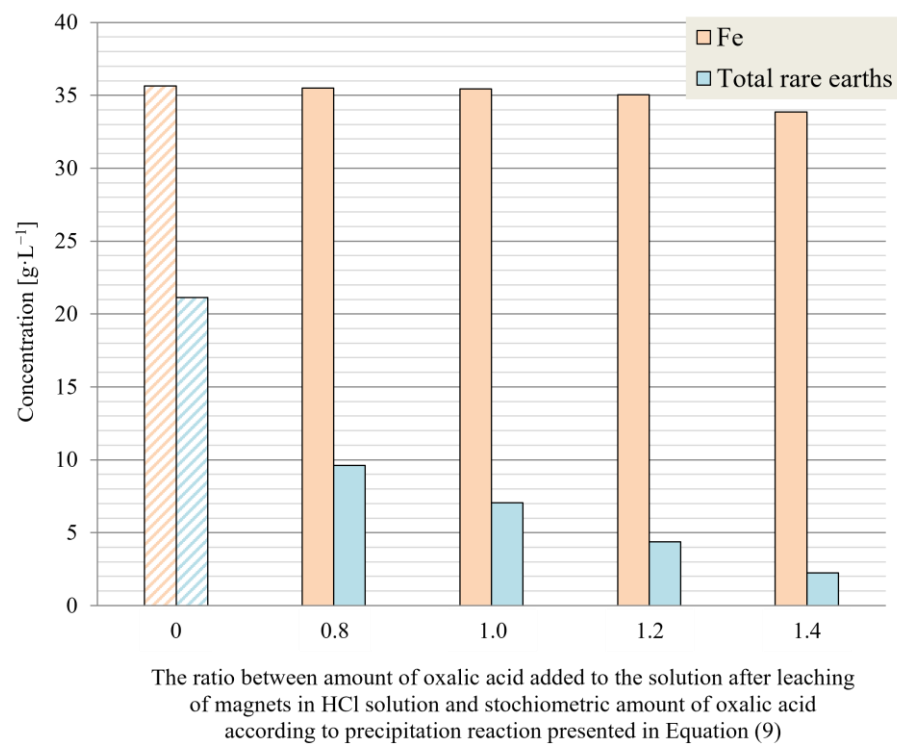


Figure 4. Iron and total rare earth element concentrations in the solution after the precipitation of rare earth oxalates with different amounts of oxalic acid added to the hydrochloric acid leaching solution. The first two bars correspond to the concentrations of Fe and REEs before oxalates precipitation.

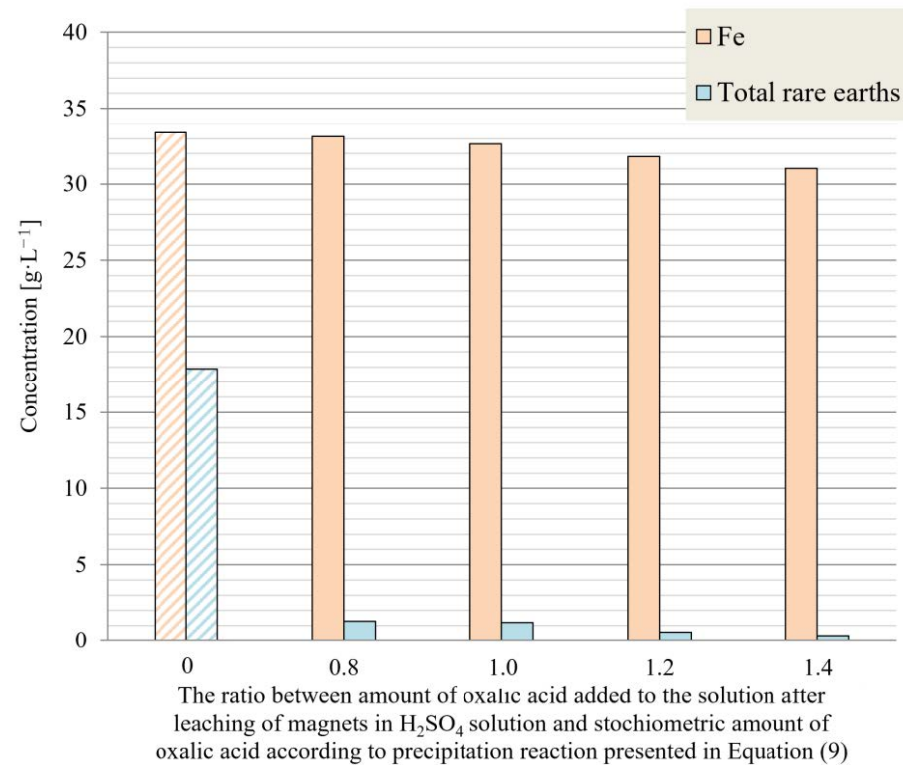


Figure 5. Iron and total rare earth concentrations in the solution after the precipitation of rare earth oxalates with different amounts of oxalic acid added to the sulfuric acid leaching solution. The first two bars correspond to the concentrations of Fe and REEs before oxalates precipitation.

It can be seen from Figure 4 that the total rare earth element concentration in the hydrochloric acid leaching solution decreased with an increasing amount of oxalic acid added. The total concentration of rare earths in the initial solution was $21 \text{ g}\cdot\text{L}^{-1}$, whereas after the addition of oxalic acid in a stoichiometric amount, their total concentration decreased to $7 \text{ g}\cdot\text{L}^{-1}$. Thus, about 66% of rare earths were recovered in the solid phase. An addition of oxalic acid to the solution in the ratio of 120% in relation to its stoichiometric amount decreased the concentration of rare earths in the solution to $4.4 \text{ g}\cdot\text{L}^{-1}$, resulting in 79% REE recovery. The use of oxalic acid in the ratio of 1.2 in relation to stoichiometry did not change the Fe concentration in the solution compared to its initial value. The addition of oxalic acid in the ratio 1.4 to its stoichiometric amount increased the rare earth precipitation to 89%; however, the Fe concentration simultaneously decreased from 35.6 to $33.9 \text{ g}\cdot\text{L}^{-1}$, which suggests that about 5% of the iron contained in the solution was co-precipitated with the rare earth oxalates.

The concentrations of iron and total rare earths in the sulfuric acid leaching solution before and after the precipitation of rare earth oxalates are presented in Figure 5. The concentration of Fe in the initial solution was $33.4 \text{ g}\cdot\text{L}^{-1}$, and it decreased slightly to $32.6 \text{ g}\cdot\text{L}^{-1}$ after the addition of oxalic acid in a stoichiometric amount. After an increase in the amount of oxalic acid to the ratio of 1.4 in relation to its stoichiometric amount, the iron concentration decreased to $31 \text{ g}\cdot\text{L}^{-1}$, indicating that 7% of iron from the solution was co-precipitated. At the same time, the total concentration of rare earths decreased from $17.9 \text{ g}\cdot\text{L}^{-1}$ to $1.2 \text{ g}\cdot\text{L}^{-1}$ after the addition of a stoichiometric amount of oxalic acid, which suggests that 93% of rare earths were recovered in the solid phase. An increase in oxalic acid amount increased the recovery of rare earths to 96.8% and 98.1% after 20 and 40% over the stoichiometric amount of oxalic acid was added, respectively.

As was shown in our previous study [24], the solution after the leaching of magnets also contained cobalt, nickel, and boron, the concentrations of which are presented in Tables S1 and S2 in Supplementary Materials. The concentrations of cobalt, nickel, and boron in the solutions did not change significantly in comparison to their initial concentrations regardless of the amount of oxalic acid added to the solution. Therefore, it can be stated that cobalt, nickel, and boron did not co-precipitate and can be separated from rare earth oxalates via simple filtration.

Based on the results presented in Figures 4 and 5, the addition of oxalic acid in a 1.2 ratio to its stoichiometric amount increased the recovery of rare earths in the form of oxalates to the solid phase and at the same time did not cause any significant co-precipitation of iron. In order to verify the qualitative composition of precipitated oxalates, the XRD technique was utilized. Figure 6 shows XRD patterns of solids precipitated after adding the stoichiometric amount of oxalic acid to the solution after leaching with HCl and H_2SO_4 , respectively. The obtained diffractograms are similar to the ones obtained for solids precipitated from the model solutions, shown in Figure 3. The main XRD peak positions and intensities correspond to $\text{Nd}_2(\text{C}_2\text{O}_4)_3\cdot 10\text{H}_2\text{O}$ according to the data for the standard card no. 18-0858. There was no visible difference between the peaks' positions on diffractograms of solids obtained after different amounts of oxalic acid were added the leach solution. A small change in the intensity of the recorded peaks indicated an insignificant change for the REEs' separation efficiency in the form of the precipitate obtained (its degree of crystallinity). Moreover, there were no visible peaks related to iron(II) oxalate, which suggests that perhaps the Co-precipitated Fe was washed out when the precipitate was washed with distilled water during filtration. It is also possible that the iron oxalate concentration was too low to be detected with the XRD technique.

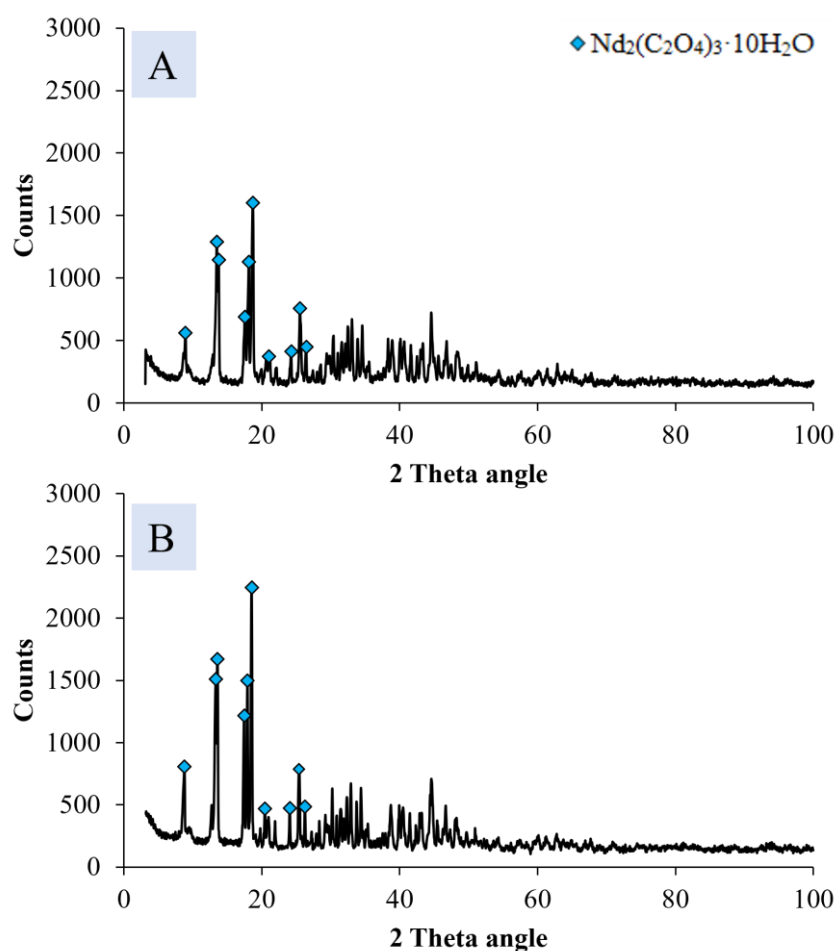


Figure 6. XRD diffractograms of precipitated rare earth oxalates: (A)—oxalates precipitated from the solution after leaching with HCl, (B)—oxalates precipitated from the solution after leaching with H_2SO_4 . Blue diamond icons indicate peaks corresponding to $\text{Nd}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$.

3.3. Precipitation of Rare Earth Oxalates after Iron Oxidation

As shown in Figures 1, 2, 4 and 5, it was not possible to precipitate all rare earths from the leaching solution. The maximum rare earth recovery from hydrochloric leaching solution reached 89% and 98% from the sulfuric leaching solution. The addition of extra amounts of oxalic acid in comparison to its stoichiometric amount allowed an increase in the recovery of rare earths in the form of oxalates, but at the same time, a small amount of iron started to co-precipitate. Therefore, another approach was tested in this study: Fe^{2+} ions were first oxidized to Fe^{3+} . It was expected that with the addition of oxalic acid, Fe^{3+} should form a stable complex ion resulting in iron being left in the solution, whereas rare earths precipitate in the form of oxalates.

During the addition of the first portions of oxalic acid to the solution after the oxidation of Fe^{2+} , no solid precipitation was observed, which was an opposite observation compared to the precipitation test, in which Fe was present at the +2 oxidation state. After only adding oxalic acid in the stoichiometric amount according to Equation (8), the solution had a dark green color, and a light-pink-colored solid began to precipitate from the solution.

Table 3 shows the concentrations of iron and rare earths in the solution after leaching (before Fe oxidation) and after the addition of oxalic acid (after Fe oxidation) in the ratio of 1.2 to its stoichiometric amount according to Equation (9). The concentration of iron in the solution after the oxalate precipitation practically did not change in the case of the sulfuric solution and only decreased slightly in the case of the hydrochloric solution. Concentrations of Pr, Dy, and Tb decreased to the level below the detection limits of the characterization technique, while the concentration of neodymium decreased to about $0.2 \text{ g} \cdot \text{L}^{-1}$. The

recovery of neodymium reached 98.8% and 99.2% in the case of the hydrochloric acid leaching solution and sulfuric acid leaching solution, respectively.

Table 3. Concentration of iron and rare earths in the solution before and after precipitation of rare earth oxalates.

Solution	After Leaching in HCl	After Precipitation of Rare Earth Oxalates	After Leaching in H ₂ SO ₄	After Precipitation of Rare Earth Oxalates
Fe (g·L ⁻¹)	45.000	42.000	45.400	45.200
Nd (g·L ⁻¹)	17.840	0.208	21.200	0.172
Pr (g·L ⁻¹)	7.600	0.000	3.600	0.000
Dy (g·L ⁻¹)	0.660	0.054	0.920	0.000
Tb (g·L ⁻¹)	0.034	0.000	0.118	0.000

3.4. Further Considerations

A schematic diagram of the proposed process for rare earths' recovery in the form of oxalates from NdFeB magnets is shown in Figure 7. In future studies, the possibility of regenerating leaching agents as well as water recovery in the proposed process should be investigated. The leaching and precipitation stages could be also tested at a larger scale to verify if the results from the laboratory scale could be applied at a larger scale.

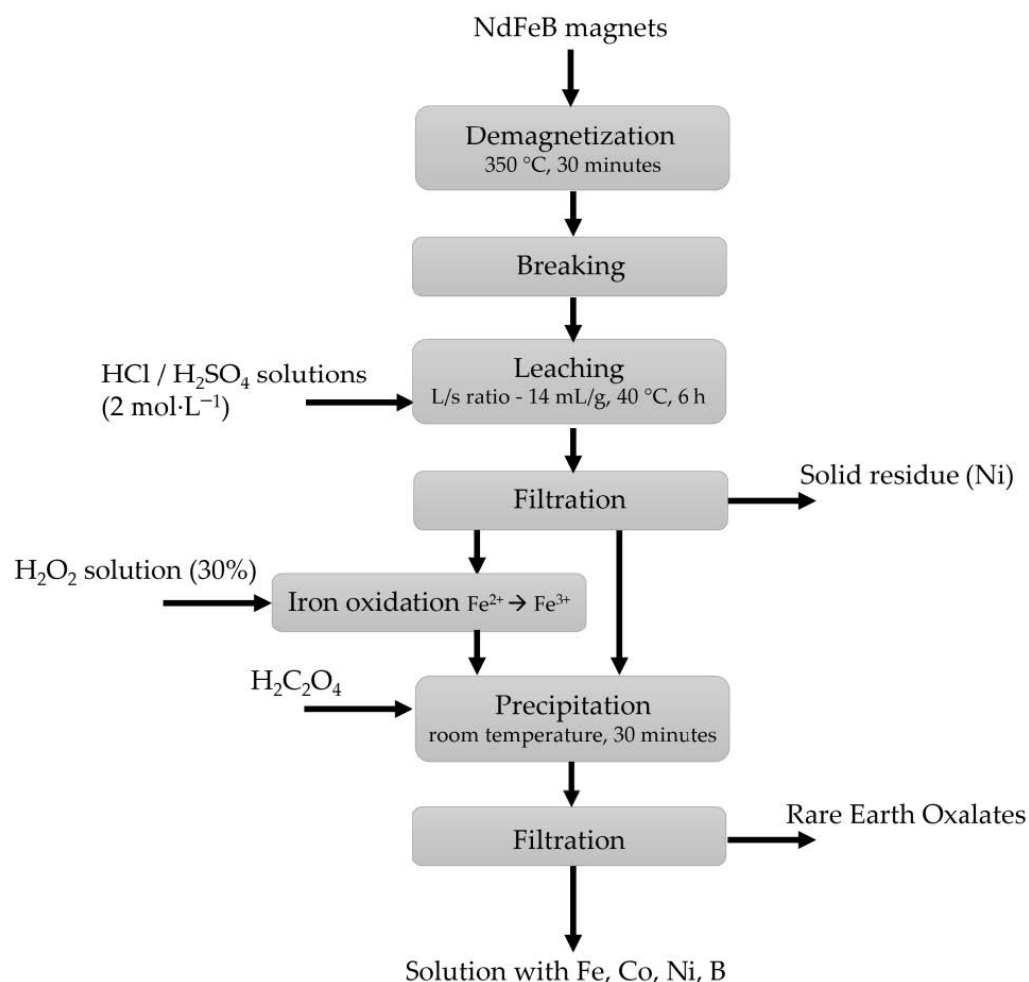


Figure 7. Proposed process of REE recovery from end-of-life NdFeB magnets.

There are many different hydrometallurgical routes of magnet recycling described in the literature. Despite the great efforts made by many research groups around the world, the recycling rates of rare earths remain very low. An economic analysis of different recycling routes should be conducted in the future in order to identify the most economically feasible solutions. Moreover, the proposed recycling processes should be critically analyzed from the perspective of environmental impacts. The Life Cycle Assessment (LCA) is a standardized methodology extensively used to study the environmental impacts of a product, process, or activity [28], and it is also increasingly used to evaluate the environmental impacts of metal recycling processes [29,30]. The combination of LCA and economic analysis would create a systematic evaluation method and help in optimizing the recycling routes.

4. Conclusions

In this study, the possibility of the selective separation of rare earths from NdFeB magnet leaching solutions was investigated. The solvent extraction step was omitted from the process. Rare earths were precipitated in the form of oxalates using oxalic acid as a precipitant. The main conclusions from this study can be formulated as follows:

- It is possible to selectively precipitate rare earth oxalates from leaching solutions without the co-precipitation of iron or other elements present in the solution.
- The amount of oxalic acid added to the solution had an influence on the rare earth and iron concentrations in the solution.
- The use of oxalic acid in stoichiometric amounts allowed for the selective precipitation of rare earth oxalates; however, the recovery rate of rare earths was not very high.
- The use of oxalic acid in a 1.2 ratio compared to its stoichiometric amount allowed the achievement of higher precipitation rates of rare earths. The addition 40% or more excess oxalic acid resulted in the co-precipitation of iron.
- Higher precipitation/recovery rates of rare earths can be achieved by adding an iron oxidation stage before the oxalate precipitation. However, in this scenario, much more oxalic acid must be used to first form the iron(III) oxalate complexes. Additionally, the oxidation of iron requires the use of a high amount of hydrogen peroxide.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/min13070846/s1>, Table S1: The concentrations of all elements in the hydrochloric leaching solution before and after precipitation of oxalates, analyzed with ICP-OES technique; Table S2: The concentrations of all elements in the sulfuric leaching solution before and after precipitation of oxalates, analyzed with ICP-OES technique.

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