Leaching of Rare Earth Elements from NdFeB Magnets without Mechanical Pretreatment by Sulfuric (H$_2$SO$_4$) and Hydrochloric (HCl) Acids

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Abstract: A simplified approach for rare earth elements leaching from NdFeB (neodymium-iron-boron) magnets was investigated. The possibility of simplifying the magnet recycling process by excluding grinding, milling and oxidative roasting unit operations was studied. Attempts to skip the demagnetization step were also conducted by using whole, non-demagnetized magnets in the leaching process. The presented experiments were conducted to optimize the operating conditions with respect to the leaching agent and its concentration, leaching time, leaching temperature and the form of the feed material. The use of hydrochloric and sulfuric acids as the leaching agents allowed selective leaching of NdFeB magnets to be achieved while leaving nickel, which is covering the magnets, in a solid state. The application of higher leaching temperatures (40 and 60 °C for sulfuric acid and 40 °C for hydrochloric acid) allowed us to shorten the leaching times. When using broken demagnetized magnets as the feed material, the resulting rare earth ion concentrations in the obtained solutions were significantly higher compared to using whole, non-demagnetized magnets.

Keywords: extractive metallurgy; recycling; rare earth elements; urban mining

1. Introduction

Between 20 and 25% of the worldwide mining output of rare earth elements (REEs) is used for the manufacturing of neodymium–iron–boron (NdFeB) permanent magnets [1]. These magnets contain approximately 30% of the REEs (mainly neodymium, praseodymium, dysprosium and terbium). All of these rare earth elements are considered as critical raw materials (CRMs) by the European Commission [2]. The demand for CRMs is expected to increase significantly in the coming years, as one of the EU goals is to meet climate and energy targets [3]. The global production of NdFeB magnets rapidly increased from about six thousand tons in 1996 to about 63 thousand tons in 2008 [4], and in 2016, the production reached about 90 thousand tons [5]. It has been predicted that the manufacturing of NdFeB magnets could account for up to 50% of the REE demand by 2035 [6,7]. These magnets are essential in energy saving and digital equipment such as hard disk drives (HDDs), highly efficient air conditioners, hybrid and electric vehicles as well as wind power generators [8,9]. Some of the aforementioned devices (hybrid and electric vehicles, wind power generators) will work for many years, while others reach end-of-life relatively quickly and can potentially be recycled. Computer hard disk drives belong to this group. Due to the rapid aging of electronic devices, computers (and the hard disk drives within them),

for example, are often replaced with new equipment. Therefore, the recycling of NdFeB magnets from waste hard disk drives (HDDs) can be a significant source of REEs [10]. In recent years, great efforts have been made to develop suitable recycling methods for the magnets, as described in several review articles [6,11–14] and presented in Table 1.

Table 1. Selected methods of recycling of NdFeB permanent magnets.

Method	Description	References
Hydrometallurgy	Leaching of the magnets or magnets scrap (acidic or alkaline treatment), followed by separation of REEs using solvent extraction, ion exchange technology or selective precipitation	[5,6,15–19]
Ionometallurgy	Use of ionic liquids in the liquid–liquid extraction of REEs present in NdFeB magnets	[20–25]
Electrochemical leaching	Electrochemical leaching of REEs is achieved at lower cell voltages by adding oxalic acid in the sulfuric acid leach solution. Separation of REEs is achieved by precipitation using $H_2C_2O_4$	[26]
Acid baking with water leaching and ultrasonic spray pyrolysis	Magnets are crushed, grinded and sieved. Nitric acid is used for acid baking without dilution. After calcination, water leaching is used for selective separation of REEs, which is followed by ultrasonic spray pyrolysis	[1]
Electroslag remelting	Melting of a relatively large batch of magnetic slag material as a consumable anode or by addition to a molten bath	[16]
Melt spinning	Remelting of magnet scraps by induction heating and conversion of the material into a master alloy	[27]
Treatment with liquid metals	Selective extraction of neodymium from magnet scrap with liquid magnesium or molten silver	[28–30]
Chlorination roasting	REE extraction from neodymium magnet sludge by chlorination with $FeCl_2$	[31–33]
Sulfation roasting	REE extraction by suitable selective roasting and water leaching treatment after completely transforming powdered samples into sulfate mixture	[34]
Oxidation roasting	Oxidation of NdFeB magnets at a high temperature followed by selective leaching. Before roasting, the magnets are demagnetized, crushed and grinded	[35–37]
Hydrogen decrepitation (HD) process and re-sintering	NdFeB magnet scrap recycling by processing it in hydrogen, then milling, aligning, pressing and re-sintering it	[38–40]

Although different methods for NdFeB magnet recycling have been reported in the literature, only one piece of technology has been applied in practice by the Urban Mining Technology Company [40]. Zakotnik and Tudor [40] reported that the process applied at a commercial scale completely recovers the properties of the starting scrap magnets and it is based on hydrogen decrepitation (HD) and re-sintering. Although this method has

many advantages, it does not allow for the recovery of REEs in a form that can be used for applications other than magnets.

Hydrometallurgical methods, intensively investigated, consist of several operations (Figure 1), namely, demagnetization, crushing and milling, roasting, leaching, the separation of lanthanides from iron and finally, the separation of individual lanthanides [6,11–14]. 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. These advantages and disadvantages of using the hydrometallurgical method for magnets recycling were explained in detail in a work by Yang et al. (2017) [6]. The grinding step, although valuable, as it increases the surface area of particles, is also the most energy consuming step in the recycling process [41,42]. Additionally, the roasting step used in many methods described in the literature [31–37] consumes a lot of energy [33]. Therefore, the grinding and roasting operations negatively affect the economics of the recycling process by increasing its costs. The main goal of the present study was to investigate the possibility of simplifying the process of hydrometallurgical NdFeB magnet recycling by eliminating the grinding/milling and oxidative roasting steps. Directly after demagnetization, the broken magnets were subjected to a leaching process. A few leaching tests were also conducted with magnets, which were not demagnetized. The main objective of the present work was the elaboration of a simple, cheap, effective and upscalable method of permanent magnet leaching. This study did not focus on the separation of the rare earth ions from other metal ions present in the solution after leaching.
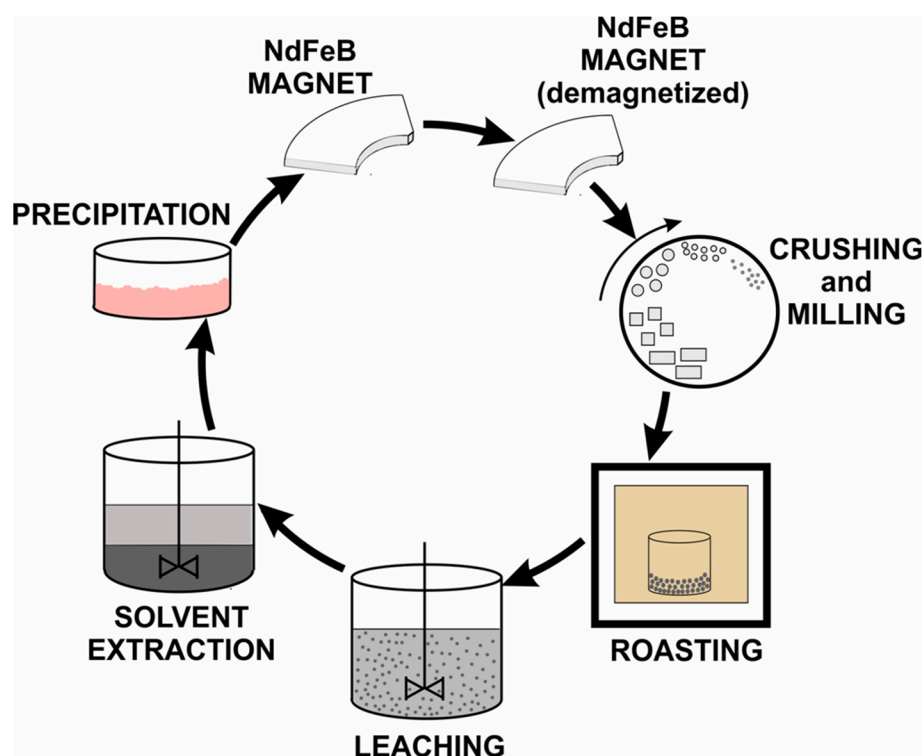

Figure 1. The traditional route of NdFeB magnet recycling using hydrometallurgy.

2. Materials and Methods

2.1. Materials

NdFeB magnets used in the study came from end-of-life hard disk drives (HDDs) obtained from different types of Desktop PCs (3.5″ HDDs) and Notebooks (2.5″ HDDs). All the HDDs were disassembled manually. The characteristics of NdFeB magnets and other main HDD components can be found in our previous work [43]. This previous study showed that magnets are highly heterogenous, as their chemical composition varies in a wide range (24–29 wt% of Nd, 2–13 wt% of Pr, 0.08–1.42 wt% of Dy, 53–62 wt% of

Fe, 3.4–6.4 wt% of Ni, 0.85–0.96 wt% of B, 0.54–3.6 wt% of Co) and these variations do not depend on the HDD parameters (for example, the capacity or physical volume). The diversity of the chemical composition of magnets was also summarized in a review by Zhang et al. (2020) [14].

The main phase of the NdFeB magnet is $Nd_2Fe_{14}B$, which was the only crystalline phase identified using X-ray diffraction (XRD) method in our previous study [43]. This phase was also the only crystalline phase identified in NdFeB magnet powders in studies by Kaya et al. [1] and Lim et al. [44].

Sintered NdFeB magnets are difficult to separate from the steel plates due to the generated magnetic field and the layer of glue setting the magnets into position. Therefore, a demagnetization process was performed by heating the magnet assembly above the Curie temperature, which, according to data in the literature, is 312 °C [45,46]. In this work, the process of demagnetization was conducted at 350 °C in a muffle furnace for 30 min. Under these conditions, all the magnets were separated from the steel plates.

In leaching experiments, both non-demagnetized magnets fixed on steel plates as well as demagnetized magnets broken into pieces were used as feed materials (Figure 2). The leaching of non-demagnetized magnets was performed in order to verify if the demagnetization step can be omitted.
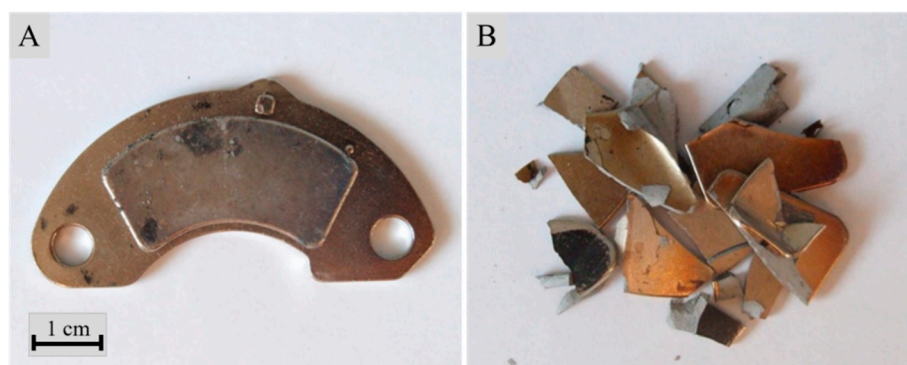
Figure 2. The whole magnet without demagnetization, glued to a steel plate (**A**); pieces of demagnetized and broken magnets (**B**).

The NdFeB magnets from HDDs differ in shape and weight. The mass of magnets in one PC HDD fluctuated from 6 to 19 g and in one laptop HDD from 7 to 12 g. All of the NdFeB magnets were covered with a nickel layer that protects the magnets from corrosion.

The solutions of leaching agents were prepared by an appropriate dilution of commercially available concentrated sulfuric acid (H_2SO_4, min. 95%, especially pure, POCH SA, Gliwice, Poland) and hydrochloric acid (HCl, 35%, especially pure, POCH SA, Gliwice, Poland). Ethylenediaminetetraacetic acid disodium salt (quality level 100, Merck Group, Darmstadt, Germany) and calcium chloride ($CaCl_2$, min. 96%, CHEMPUR, Piekary Śląskie, Poland) were used for the analysis of acid concentration.

2.2. Leaching Procedure

The leaching experiments were performed in a rotary reactor driven by an evaporator (Rotavapor R-210/215, Büchi, Flawil, Switzerland) presented in Figure 3. Due to the physical form of the magnets (big pieces of magnets or whole magnets with steel plates), these experiments could not be performed in a typical reactor with a mechanical stirrer. All of the leaching processes were carried out under atmospheric pressure with a rotation speed of 40 rpm in a temperature range varying from room temperature (approximately 20 °C) to 60 °C. In the case of using whole magnets, the mass of the feed material was 40.9 ± 1.5 g, i.e., the sum of the weight of magnets (approximately 14 g) and steel plates (approximately 27 g). The mass of broken magnet pieces used in one batch was 13.5 ± 0.3 g. The volume of the leaching solution varied within the range of 100–200 mL, and it was

selected in a way that the initial number of hydrogen ions was the same in each experiment. Detailed parameters of the leaching experiments are presented in Table 2.

Figure 3. The rotary reactor driven by an evaporator (Buchi, Rotavapor R-210/215) used in the leaching experiments.

Table 2. The parameters of leaching processes in solutions of H_2SO_4 and HCl (RT = room temperature).

Leaching Agent (Solution Volume)	Temperature /°C	Acid Concentration /mol·L^{-1}	Mass of Magnets /g	Form of Magnets
H_2SO_4 (200 mL)	RT, 40, 60	1.0	13.5 ± 0.3	Demagnetized, broken
H_2SO_4 (100 mL)	RT, 40, 60	2.0	13.5 ± 0.3	Demagnetized, broken
H_2SO_4 (200 mL)	RT, 40, 60	1.0	40.9 ± 1.5 g Magnet and plate	Whole, without demagnetization
H_2SO_4 (100 mL)	RT, 40, 60	2.0	40.9 ± 1.5 g Magnet and plate	Whole, without demagnetization
HCl (200 mL)	RT, 40	2.0	13.5 ± 0.3	Demagnetized, broken
HCl (100 mL)	RT, 40	4.0	13.5 ± 0.3	Demagnetized, broken
HCl (200 mL)	RT, 40	2.0	40.9 ± 1.5 g Magnet and plate	Whole, without demagnetization
HCl (100 mL)	RT, 40	4.0	40.9 ± 1.5 g Magnet and plate	Whole, without demagnetization

The reaction progress was monitored directly on the basis of the change in acid concentration. Stabilization of the concentration indicated the end of the leaching process. At the same time, samples of the solution were taken and analyzed for concentration of REEs, iron and other magnet components.

2.2.1. Thermodynamic Analysis of Nickel Digestion in Acids

In order to support the literature information about possible selective leaching of NdFeB magnets, thermodynamic analysis of nickel digestion in mineral acids was performed. The values of enthalpy, entropy and free energy at different temperatures (20, 40 and 60 °C) of nickel reactions with HCl, HNO_3 and H_2SO_4 were calculated with HSC software (version 9.4.1).

2.2.2. Analysis of Liquors

Concentrations of the elements were determined using an optical Jobin Yvon sequential ICP-OES instrument (Jobin Yvon 38S, HORIBA Jobin Yvon SAS, Longjumeau, France). The type-curve method was used for calibration. The standard solutions of B, Co, Fe and Ni

were prepared by dilution of a commercial multi-element solution (Merck Group, quality level MQ100, 1000 mg/L). The multi-element standard solutions of Dy, Nd, Tb and Pr were prepared from commercial one-element solutions (Merck Group, quality level MQ100, 1000 mg/L). The concentrations of standard solutions used for calibration covered the range 0–5.0 mg/L.

2.2.3. Analysis of Acid Concentrations

The concentration of the acid during leaching could not be controlled using the traditional acid-base titration method (direct titration with sodium hydroxide), because of the presence of many metal ions that can undergo hydrolysis, which leads to the production of hydrogen cations. Therefore, a method based on the masking of metal ions with an ethylenediaminetetraacetic acid (EDTA) disodium salt as well as fixing an equivalent point by potentiometric titration was used in this work. This method was developed in the 1970s at the Institute of Inorganic Chemistry and Rare Elements of Wroclaw University of Technology [47].

The disodium salt of ethylenediaminetetraacetic acid dissociates into ions in aqueous solutions according to reaction (1).

$$Na_2H_2Y \rightarrow H_2Y^{2-} + 2Na^+ \tag{1}$$

The addition of disodium EDTA salt to a solution containing metal ions (B^{2+}, Ni^{2+}, Co^{2+}, Fe^{3+}, Nd^{3+}, Pr^{3+}, Dy^{3+}, Tb^{3+}) results in the formation of very stable metal complexes, and hydrogen ions are released according to reaction (2)

$$Me^{n+} + H_2Y^{2-} \leftrightarrows MeY^{(n-4)} + 2H^+ \tag{2}$$
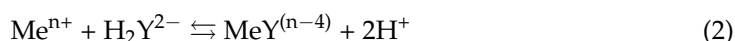
where Me = B, Ni, Co, Fe, Nd, Pr, Dy, Tb.

The course of the reaction above causes an increase in the total concentration of hydrogen ions in the analyzed solution (they come from both the mineral acid and the product of the complex formation). Therefore, the result of analysis of acid concentration would be burdened with a significant error. In order to prevent this error, an indirect masking of ions was carried out. In order to mask the ions, an analyzed sample of the solution was introduced into an appropriately prepared solution of disodium EDTA and calcium chloride. Before adding the sample, the pH of the disodium EDTA and calcium chloride solution was adjusted to 5.5. After introducing the sample into the prepared solution, an exchange reaction between the unstable calcium complex and the ions of the masked metals takes place according to reaction (3)

$$Ca(EDTA)^{2-} + Me^{2+} \rightarrow Me(EDTA)^{2-} + Ca^{2+} \tag{3}$$

This reaction does not produce hydrogen cations. Therefore, the change in the solution pH after the addition of the analyzed sample is the result of acid concentration change. Thus, re-adjusting the solution pH to a value of 5.5 allows the acid concentration in the added sample to be determined.

2.2.4. Analysis of Solid Residue

The chemical compositions of solid residues from leaching were analyzed with EDS (Energy Dispersive Spectroscopy) method. The fragments of solid residue were hot mounted in a phenolic formaldehyde resin at a temperature of 167 °C and under 6 MPa pressure. Subsequently, a metallographic cross-section was prepared by grinding and polishing. After ensuring the electrical conductivity of the specimen, its chemical composition was studied with a Scanning Electron Microscope JEOL JSM-6610A (JEOL, Akishima, Japan) equipped with a JED-2300 EDS detector (Si-Li type, Mini-cup). An accelerating voltage of 20 kV was used, and the beam conditions were set to achieve at least 6000 counts per second with the detector dead time not exceeding 10%.

3. Results and Discussion

3.1. Theoretical Studies on Selective Leaching

As mentioned in the introduction, the goal of the study was to propose a simple leaching process that allowed the selective digestion of REEs and iron, while keeping nickel in the solid form. Prior to the leaching tests, the standard reduction potentials of the magnet components were analyzed and information concerning the reactivity of these components with mineral acids was collected from the literature. The standard reduction potentials of magnet components are presented in Table 3. When a magnet is immersed in an acid solution, a galvanic contact cell is formed. The metal with higher potential (nickel) plays the role of the cathode; metals with lower potentials play the role of the anode. Accordingly, they should dissolve, whereas on the cathode, one should observe the evolution of hydrogen. The selective dissolution of magnets during leaching with HCl and HO_4, while leaving nickel in the solid state, is very likely according to the collected data.

Table 3. Standard reduction potentials of the main components of NdFeB magnets [48,49].

Component	Standard Reduction Potential/V
Nickel (Ni^{2+}/Ni)	−0.23
Iron (Fe^{2+}/Fe)	−0.44
Boron (H_3BO_3/B)	−0.89
REEs (Ln^{3+}/Ln)	from −2.52 to −2.25

As the REEs and Fe are present in magnets mostly as a metallic alloy ($Nd_2Fe_{14}B$), it can be assumed that the leaching reactions of the main components of magnets will proceed according to the following reactions (4)–(6) [26,37,44,50]:
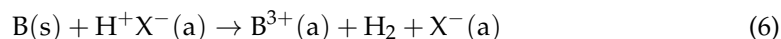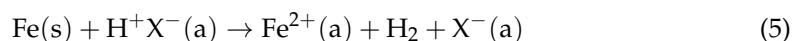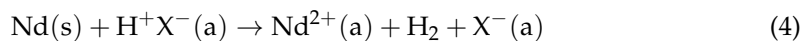
$$Nd(s) + H^+X^-(a) \rightarrow Nd^{2+}(a) + H_2 + X^-(a) \tag{4}$$

$$Fe(s) + H^+X^-(a) \rightarrow Fe^{2+}(a) + H_2 + X^-(a) \tag{5}$$

$$B(s) + H^+X^-(a) \rightarrow B^{3+}(a) + H_2 + X^-(a) \tag{6}$$

Table 4 presents the results of the thermodynamic analysis of nickel reactions with HCl, H_2SO_4 and HNO_3. Based on the literature data, it was expected that nickel will not be dissolved in low-concentrated solutions of HCl and H_2SO_4. Thermodynamic calculations confirmed this information concerning HCl and very likely H_2SO_4. The same calculation performed for nitric acid showed unequivocally that nickel will be dissolved in nitric acid with the formation of gaseous nitric oxide. The evolution of nitrogen oxides would require an additional system for their utilization, thus complicating the recycling process. Therefore, nitric acid was excluded as a leaching agent. For comparison, the same thermodynamic data were also calculated for neodymium dissolution in HCl and H_2SO_4.

Besides iron and REEs, magnets also contain about 1 wt% of boron [43]. According to the literature, boron is insoluble in non-oxidizing acids [48]. However, in the case of magnets, the situation is different. NdFeB magnets have a ferromagnetic matrix phase of $Nd_2Fe_{14}B$, which is surrounded by intergranular regions containing a neodymium-rich phase and a boron-rich phase [51]. Several authors [52–54] have informed that the neodymium-rich phase dissolves preferentially due to the formation of a galvanic couple owing to the negative standard potentials of rare earths. This is followed by the boron-rich phase dissolution and finally by the dissolution of the matrix phase.

All these considerations indicate that the dissolution of magnets in sulfuric and hydrochloric acids is possible. In addition, it is expected that the nickel covering the magnets will stay in the solid residue of the leaching process.

Table 4. Thermodynamic data for dissolution of nickel in HCl, H_2SO_4 and HNO_3 as well as for Nd in HCl and H_2SO_4. The values were calculated per 1 mol of metal (Me).

T/°C	ΔH^0/kJ·mol^{-1} of Me	ΔS^0/kJ·K^{-1}·mol^{-1} of Me	ΔG^0/kJ·mol^{-1} of Me
	Ni + 2HCl(a) = NiCl$_2$ + H$_2$(g)		
20	−53.8	−22.5	−46.0
40	−54.7	−29.5	−45.4
60	−55.6	−32.5	−44.8
	Ni + H$_2$SO$_4$(a) = NiSO$_4$ + H$_2$(g)		
20	−50.6	27.0	−58.5
40	−45.2	44.9	−59.3
60	−39.4	62.9	−60.3
	1.5 Ni + 4HNO$_3$(a) = 1.5 Ni(NO$_3$)$_2$ + NO(g) + 2 H$_2$O		
20	−282.2	−106.6	−250.9
40	−284.3	−113.6	−248.7
60	−286.4	−120.1	−246.4
	Nd + 3HCl(a) = NdCl$_3$(a) + 1.5H$_2$(g)		
20	−798.4	140.6	−839.7
40	−815.1	85.6	−841.9
60	−831.4	35.1	−843.1
	Nd + 1.5H$_2$SO$_4$(a) = 0.5Nd$_2$(SO$_4$)$_3$(a) +1.5H$_2$(g)		
20	−694.2	−80.8	−670.5
40	−696.7	−89.3	−668.7
60	−697.3	−91.1	−666.9

3.2. Preliminary Leaching Tests and Assumptions of the Leaching Process

In order to verify the theoretical considerations concerning the leaching of magnets with sulfuric and hydrochloric acids, a few experiments were conducted using NdFeB magnets after demagnetization. Before the experiments, the nickel layer was damaged, in order to assure contact between the magnet and the leaching solution. These experiments were conducted under atmospheric pressure, at room temperature and without mixing. Chemical analysis of the obtained solutions by ICP-OES showed the presence of iron ions (40–60 g·L^{-1}) and neodymium ions (10–20 g·L^{-1}). Nickel ions, as expected, were not detected in the solutions.

After conducting the preliminary tests, it was decided that the leaching would be carried out using big pieces of magnets after demagnetization and whole magnets without demagnetization, covered with a nickel layer. Due to the difficulty in determining the contact area during leaching as well as the inhomogeneity of feed material, the assessment of the leaching efficiency will be based on acid consumption.

Assuming that the average iron concentration in the magnet is about 57 wt% and the REE concentration is about 35% [43], the average acids consumption during the leaching of 100 g of magnets can be estimated as 1.38 and 2.76 mol for sulfuric and hydrochloric acid, respectively. Taking into account the maximum concentration of iron and REEs in the magnets, 62 and 42 wt%, respectively [43], the maximum acid consumption can be approximately 1.55 and 3.10 mol of sulfuric and hydrochloric acid, respectively. The solid/liquid ratio used in experiments was determined from the amount of acid necessary for the complete digestion of the magnets, and some excess acid to prevent the hydrolysis of metal ions.

The following considerations apply to the adopted leaching experiments:

- the crushing and milling of magnets, as well as oxidative roasting unit operations will be omitted;
- − broken demagnetized magnets or whole magnets without demagnetization will be used as feed material in the leaching process;
- the leaching process will lead to the complete dissolution of the magnets, and it will leave nickel in the solid phase;

- due to the physical form of the feed material, mechanical stirring is impossible; therefore, a rotary reactor will be used,
- the reaction surface (the surface of magnets not covered by nickel layer) is unknown and can change randomly;
- feed material is not homogenous and, therefore, only concentration of metals, without efficiency, will be determined in the leaching experiments;
- the concentration of leaching agents (hydrochloric and sulfuric acid) will be high enough to dissolve magnets, but not too high in order to avoid a violent evolution of hydrogen;
- the solid-to-liquid ratio will be defined by the requirement that a slight concentration of acid after the completed leaching process should be maintained;
- a moderate leaching temperature ($\leq 60\ ^\circ$C) will be applied.

The main goal of the leaching experiments was to determine the optimal conditions for a simple technological treatment of end-of-life permanent magnets and the subsequent recovery of the REEs within.

3.3. Leaching in H_2SO_4 Solutions

The leaching experiments in H_2SO_4 solutions were conducted for both types of feed material (whole magnets and broken magnets after demagnetization). Figures 4 and 5 show the concentrations of sulfuric acid (Figures 4A,B and 5A,B), concentrations of neodymium (Figures 4C,D and 5C,D) and iron (Figures 4E,F and 5E,F) in the solutions as a function of the leaching time with starting acid concentrations of 1 and 2 M. The results of broken, demagnetized magnets are shown in Figure 4, and the whole magnets in Figure 5.

In our study, the leaching yield could not be calculated, as the starting composition of the feed material varied in a wide range. However, the progress of the leaching process was determined by analyzing the acid concentration during the experiments. The stabilization in the acid concentration corresponds to the practical completion of the leaching process. Moreover, it was observed that the concentrations of neodymium and iron ions in the solutions stabilized at the same time when the concentration of acid in these solutions stabilized.

In the case of using demagnetized and broken magnets as the feed material, it is evident that the leaching rate increased with the increasing temperature (Figure 4). The practical completion of the leaching process in a 1 M solution of sulfuric acid took place after approximately 5 h at 40 $^\circ$C and after 4 h at 60 $^\circ$C. An increase in the acid concentration also shortened the leaching time. The completion of the leaching in a 2 M solution of acid took place after 2 h at a temperature of 60 $^\circ$C. The increase in acid concentration caused a significant increase in the concentration of neodymium and iron in the final solution (from 20.4 to 33 g$\cdot$L^{-1} and from 43.3 to 74.3 g$\cdot$L^{-1} at a temperature of 60 $^\circ$C for the solution of 1 and 2 M sulfuric acid, respectively). The high iron concentration in the solution using 2 M sulfuric acid at room temperature (Figure 4F) was due to the higher iron concentration in the magnets used for that experiment.

The chemical compositions of the leaching residues were analyzed with SEM-EDS. The residues obtained consisted of metallic nickel, as the EDS-spectra only showed nickel peaks (Supplementary Material, Figure S1A).

In order to verify if the operation steps of demagnetization and breaking the magnets before leaching can be omitted, identical process parameters (Table 2) were tested for the leaching of the whole (non-demagnetized) magnets glued to a metallic plate (Figure 2A). Prior to these experiments, the metallic layer of nickel was partially destroyed. The results obtained are presented in Figure 5.

The stabilization of the acid concentration, when using 1 M sulfuric acid as the starting solution, was achieved after six hours (Figure 5A). The concentrations of neodymium and iron did not stabilize after 7 h in the room temperature experiment. The increase in the leaching temperature from room temperature to 40 $^\circ$C and 60 $^\circ$C shortened the leaching time to 5 and 2 h, respectively. The leaching of the whole magnets in 2 M sulfuric

acid was much faster than leaching in 1 M acid solution (Figure 5B,D,F). The end of the leaching process in 2 M acid solution at room temperature appeared after approximately 5 h. Applying the leaching temperatures of 40 and 60 °C shortened the leaching times to approximately 4 and 2 h, respectively. During all the leaching tests, the dissolution of metallic plates, to which the magnets were glued, was not observed. However, only a partial dissolution of the magnets was observed and the solid residue after leaching consisted of the metallic plate, nickel and unreacted magnets.
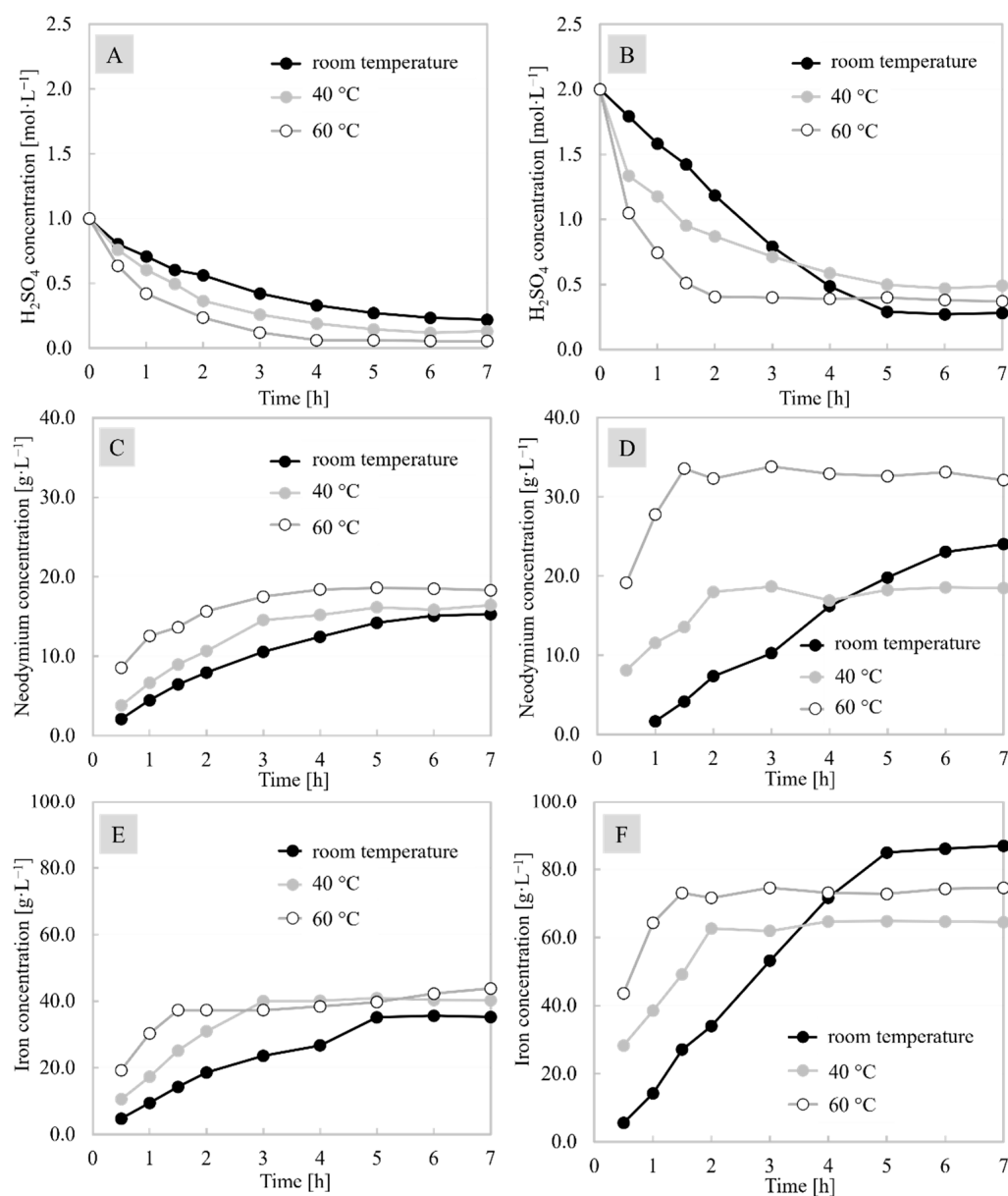
Figure 4. Leaching of demagnetized and broken NdFeB magnets in 1 M H_2SO_4 solution (left side) and in 2 M H_2SO_4 solution (right side). Different figures show the dependence between leaching time and the concentration of H_2SO_4 (**A**,**B**), neodymium (**C**,**D**) and iron (**E**,**F**).
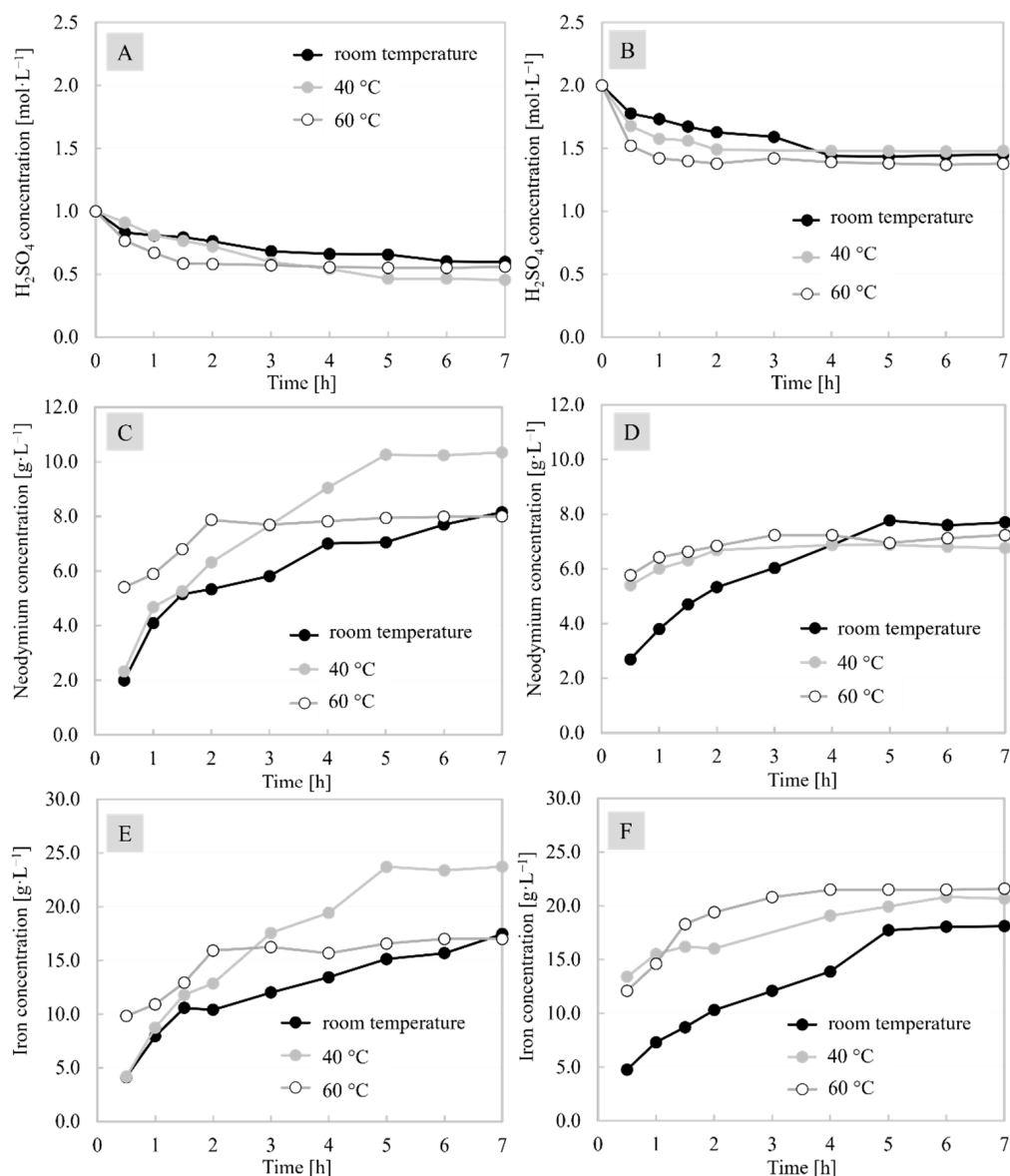
Figure 5. Leaching of the whole (non-demagnetized) NdFeB magnets in 1 M H_2SO_4 solution (left side) and 2 M H_2SO_4 solution (right side). Different figures show the dependence between leaching time and the concentration of H_2SO_4 (**A**,**B**), neodymium (**C**,**D**) and iron (**E**,**F**).

3.4. Leaching in HCl Solutions

Hydrochloric acid was selected as the second leaching agent for NdFeB magnets. Leaching tests were conducted at room temperature and at 40 °C. Higher temperatures were not considered due to the high vapor pressure of gaseous HCl over the acid solutions. Leaching experiments were conducted both for demagnetized broken magnets and the whole magnets without demagnetization (Table 2).

The results of the leaching experiments performed on broken demagnetized magnets are presented in Figure 6. It was found that the leaching time is almost independent of the temperature. The end of leaching process took place after approximately 5 h. However, the concentration of neodymium and iron in the final solution was higher in the case of a higher temperature. This means that the efficiency of leaching is dependent on temperature. The leaching residues were analyzed with SEM-EDS and the results confirmed the presence of metallic nickel only (Figure S1B in Supplementary Material).
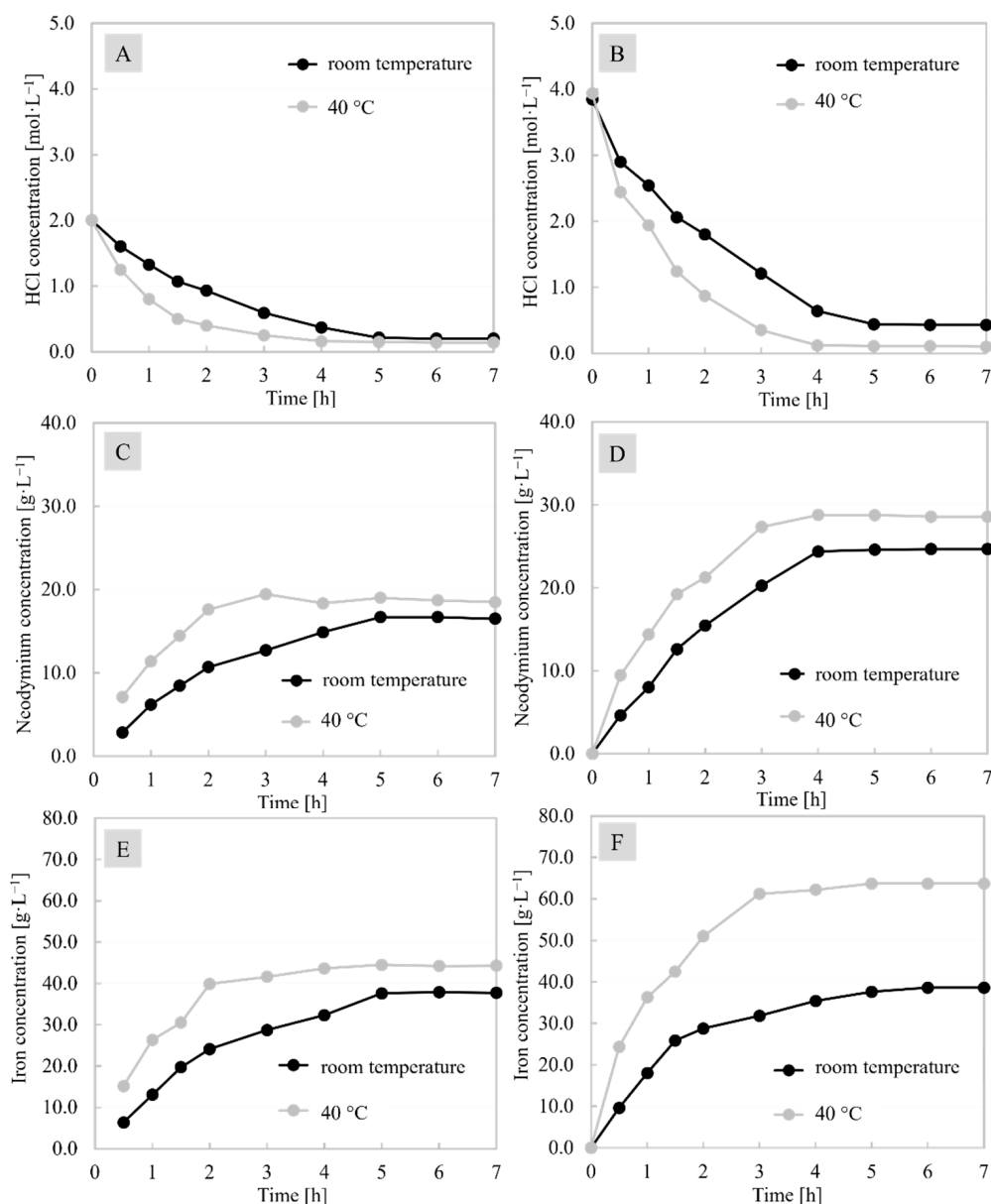
Figure 6. Leaching of demagnetized and broken NdFeB magnets in 2 M HCl solution (left side) and 4 M HCl solution (right side). Different figures show the dependence between leaching time and the concentration of HCl (**A**,**B**), neodymium (**C**,**D**) and iron (**E**,**F**).

The results of experiments performed with the whole magnets (without demagnetization) glued to the metallic plates are presented in Figure 7. The time at which the stabilization of the acid concentration occurs coincides with the time connected with the stabilization of the neodymium and iron concentration in the solution. In the case of leaching the whole magnets in 2 M hydrochloric acid, the stabilization in the acid concentration appeared after 5 h of leaching at room temperature and after 2–3 h at 40 °C. However, the concentrations of neodymium and iron obtained during leaching were significantly lower than in the case of the leaching of broken magnets. The increase in the acid concentration shortened the leaching time to about 3 h at 40 °C, but without a significant increase in the metals' concentration in the solution. Similarly, as in the case of leaching in sulfuric acid, only a partial dissolution of the magnets was observed and the solid residue after leaching consisted of the metallic plate, nickel and unreacted magnets. It is evident that the leaching of the broken magnets (Figure 6) was a much faster process in comparison to leaching of

the whole (non-demagnetized) magnets and the resulting metal concentrations in solutions were significantly higher with the broken magnets.
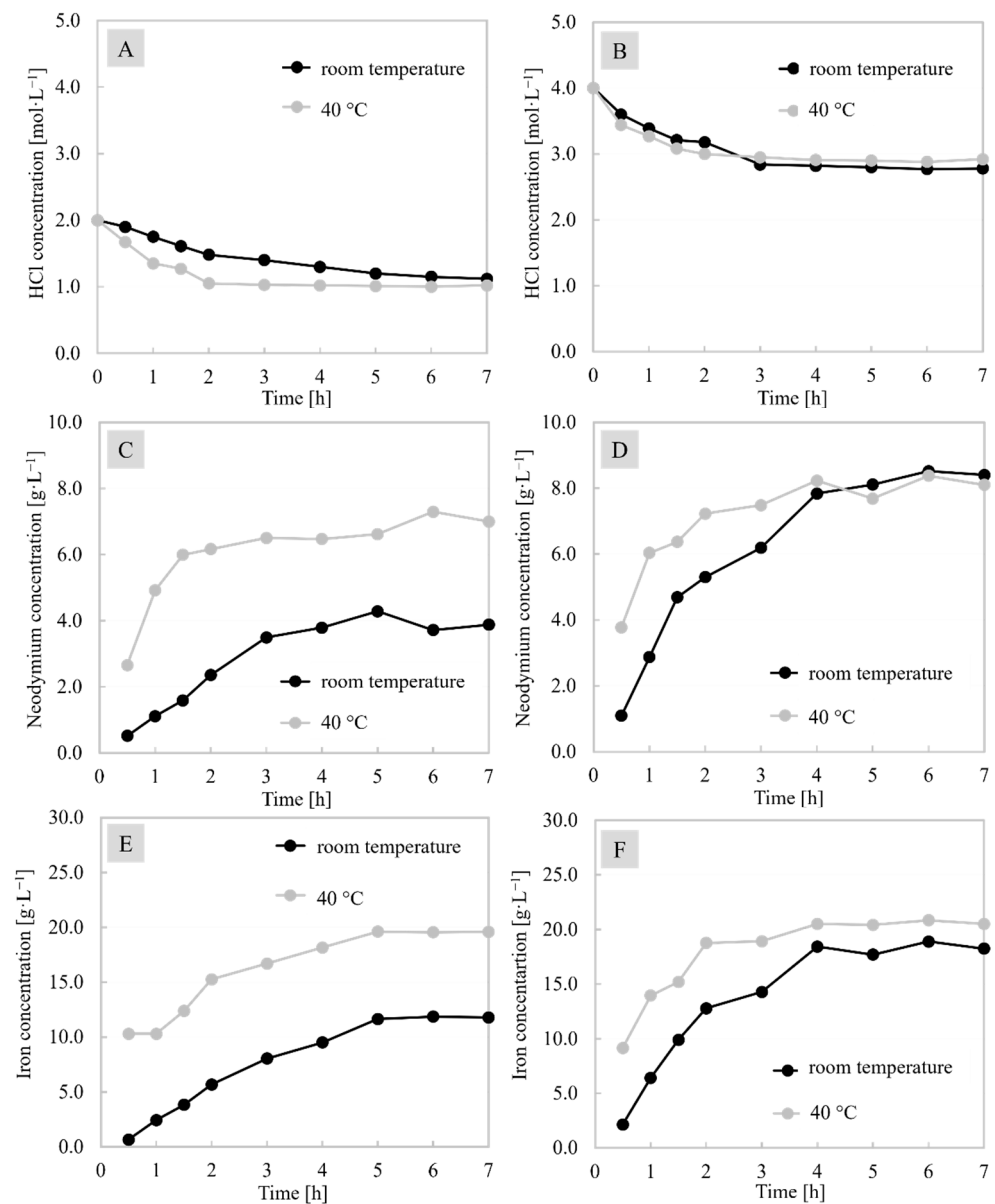
Figure 7. Leaching of the whole (non-demagnetized) NdFeB magnets in 2 M HCl solution (left side) and 4 M HCl solution (right side). Different figures show the dependence between leaching time and the concentration of HCl (**A**,**B**), neodymium (**C**,**D**) and iron (**E**,**F**).

4. Final Discussion

The data compiled regarding the concentrations of metal ions in the final solutions after seven hours of leaching in sulfuric and hydrochloric acid solutions are presented in Tables 5 and 6, respectively. The final solutions contained all the components of the magnets with the exception of nickel. Only traces of nickel (0.0027–0.0445 g·L^{-1}) were found in the leaching solutions, which means that the selective leaching of magnets while leaving nickel in the solid state was achieved. This is a positive result as it confirms the efficient separation of nickel from the other components, as well as the recovery of nickel at the leaching stage.

Table 5. Concentration of metal ions in the solutions obtained after the leaching of magnets in sulfuric acid for 7 h.

Leaching Agent	Temperature	The State of Magnets	B	Co	Fe	Ni	Nd	Pr	Dy	Tb	Total REE
			$g \cdot L^{-1}$								
H$_2$SO$_4$ 1M	room temp.	demagnetized and broken	0.535	1.70	31.6	0.0027	15.1	0.535	0.585	0.243	16.463
		whole	0.237	0.769	17.5	0.0119	8.15	0.639	0.625	0.0125	9.426
	40 °C	demagnetized and broken	0.605	0.740	43.4	0.0031	15.9	6.20	0.0261	0.218	22.344
		whole	0.133	0.0047	23.7	0.0096	10.3	0.578	0.565	0.0032	11.446
	60 °C	demagnetized and broken	0.656	2.22	43.3	0.0210	20.4	2.15	1.109	0.200	23.859
		whole	0.259	0.849	17.0	0.0166	8.00	0.573	0.660	0.0209	9.2539
H$_2$SO$_4$ 2M	room temp.	demagnetized and broken	1.12	0.0124	86.1	0.0445	24.0	24.2	0.159	1.12	49.479
		whole	0.252	0.0056	18.1	0.0068	7.70	0.317	0.272	0.0029	8.292
	40 °C	demagnetized and broken	0.950	0.0173	64.7	0.0153	18.6	20.9	0.416	0.166	40.082
		whole	0.312	0.142	20.7	0.0105	6.76	2.52	0.567	0.0061	9.853
	60 °C	demagnetized and broken	1.32	4.48	74.3	0.0169	33.1	2.77	2.72	-	38.590
		whole	0.324	0.102	21.6	0.0123	7.24	2.45	0.643	0.0053	10.338

Table 6. Concentration of ions in the solutions obtained after the leaching of magnets in hydrochloric acid for 7 h.

Leaching Agent	Temperature	The State of Magnets	B	Co	Fe	Ni	Nd	Pr	Dy	Tb	Total REE
			$g \cdot L^{-1}$								
HCl 2M	room temp.	demagnetized and broken	0.570	1.09	37.9	0.0096	16.7	4.3	0.208	0.346	21.554
		whole	0.218	0.124	13.45	0	4.935	0.99	0.54	0.0009	6.466
	40 °C	demagnetized and broken	0.620	0.66	44.2	0.0128	18.7	4.787	0.82	0.0816	24.3886
		whole	0.281	0.975	16.55	0.0139	8.3	0.2965	0.865	0.0063	9.4678
HCl 4M	room temp.	demagnetized and broken	0.987	0.607	38.60	0.018	24.67	1.198	1.553	0.017	27.438
		whole	0.329	1.175	20.85	0.0068	8.4	0.3385	0.935	0.001	9.674
	40 °C	demagnetized and broken	1.159	0.670	63.70	0.022	28.57	1.493	1.771	0.0204	31.854
		whole	0.297	1.02	19.9	0.078	8.1	0.3195	0.845	0.0129	9.277

The presence of boron in the solutions after leaching can be explained by a phenomenon mentioned in the literature [51], according to which it is a result of galvanic cell formation during the leaching. NdFeB magnets have a matrix ferromagnetic Nd$_2$Fe$_{14}$B phase, which is surrounded by intergranular regions containing a neodymium-rich phase and a boron-rich phase. The neodymium-rich phase corrodes preferentially due to the formation of a galvanic couple owing to the highly negative standard potentials of rare earths. This is followed by the boron-rich phase dissolution, and this renders the matrix phase loose, enabling its dissolution.

Based on the data presented in Tables 5 and 6, similar concentrations of REEs were obtained in the leaching solutions when leaching the whole (non-demagnetized) magnets, independently of the leaching parameters. The total REE concentration was significantly lower in comparison with the leaching of broken magnets after demagnetization. The lower concentration naturally translates to the lower efficiency of the leaching process. It is very likely that the reason for such a phenomenon is the smaller reaction surface. During the leaching, the magnet always remains in the envelope formed by a layer of nickel, which limits the contact between the magnet and the leaching agent. The use of demagnetized pieces of broken magnets as the feed material allowed for much higher REE concentrations in the solutions to be achieved.

Based on the initial mass of magnets used in the leaching experiments and the mass of metals contained in the leaching solutions (calculated from the results of the chemical analyses presented in Tables 5 and 6), estimated leaching efficiencies were calculated. The mass of metals in the samples taken during the leaching experiments used for chemical analyses was taken into account in the calculations. The results are presented in Table 7. It is well visible that the leaching of broken, demagnetized magnets was characterized by high efficiency. In reality, the efficiency was higher because the mass of the metallic nickel covering the magnets was not taken into account in the calculations. According to the EDS analysis (Figure S1 in Supplementary Materials), the solid leaching residue only consisted of nickel.

Table 7. Calculated total leaching efficiencies based on the mass of magnets before leaching and the mass of metals in the leaching solutions.

Leaching Conditions	Mass of Magnets for Leaching g	Mass of Metals in Leaching Solution g	Efficiency of Leaching %
1 M H_2SO_4-RT	13.149	9.510	70.50
1 M H_2SO_4–40 °C	13.430	12.820	95.45
1 M H_2SO_4–60 °C	13.880	13.335	96.07
2 M H_2SO_4-RT	13.261	12.176	91.82
2 M H_2SO_4–40 °C	12.864	9.786	76.07
2 M H_2SO_4–60 °C	13.358	11.315	84.70
2 M HCl-RT	13.631	11.861	87.01
2 M HCl–40 °C	13.890	13.573	97.72

5. Conclusions

The use of hydrochloric and sulfuric acids as leaching agents allowed for the selective leaching of REEs and iron from NdFeB magnets, while leaving nickel in the solid phase. Nitric acid was excluded as a leaching agent because it also dissolves the nickel layer. An additional argument for excluding nitric acid was the formation of nitric oxides, requiring an additional system for their capture and utilization, thus complicating the recycling process on an industrial scale.

The first part of a hydrometallurgical recycling route for NdFeB magnets, the leaching process, was simplified by excluding grinding, milling and oxidative roasting unit operations, thus lowering the energy consumption of the process. Attempts to skip the demagnetization were also conducted and the whole, non-demagnetized magnets were tested in the leaching process. However, the efficiency of their leaching was significantly lower compared to broken and demagnetized magnets. Thus, it is preferable to use broken magnets after demagnetization. Their use as a feed material allowed very high leaching efficiencies to be achieved: the magnets were completely dissolved, leaving only nickel in the solid leaching residues. The concentrations of RE ions in the leaching solutions were generally 2–4 times higher compared to the non-demagnetized magnets. The application of higher leaching temperatures (40 and 60 °C for sulfuric acid and 40 °C for hydrochloric acid) resulted in shorter leaching times.

This is a fundamental study regarding the feasibility of a simplified process for the leaching of NdFeB magnets as a part of the hydrometallurgical magnet recycling route. At this stage, no calculations were performed regarding the economic benefits compared to other processes reported in the literature.

The leaching of REEs from NdFeB permanent magnets is the first step of a hydrometallurgical way of recovering REEs from the magnets. The solutions obtained after leaching will be subjected to further research in order to determine a complete process for REE recycling and recovery from permanent magnets.

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