Article

Comparative Studies of Digestion Techniques for the Dissolution of Neodymium-Based Magnets

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Abstract: The digestion of neodymium (NdFeB) magnets was investigated in the context of recycling rare earth elements (i.e., Nd, Pr, Dy, and Tb). Among more conventional digestion techniques (microwave digestion, open vessel digestion, and alkaline fusion), focused infrared digestion (FID) was tested as a possible approach to rapidly and efficiently solubilize NdFeB magnets. FID parameters were initially optimized with unmagnetized magnet powder and subsequently used on magnet pieces, demonstrating that the demagnetization and grinding steps are optional.

Keywords: NdFeB magnets; critical metals; rare earth elements (REEs); recycling; focus infrared digestion; ICP-OES; electronic waste

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1. Introduction

As electronic devices play an increasingly more important role in our lives, society needs to develop strategies to recover valuable metals from end-of-life electronic products. This need is driven by critical metal supply concerns, and by environmental issues with the rapid generation of electronic waste (e-waste) worldwide [1]. The annual global production of e-waste was approximately 53.6 million metric tons (Mt) in 2019 and is expected to increase to 74 Mt by 2030 [1]. Because e-waste contains up to 69 elements from base to precious metals [1], e-waste mining has been proposed as a promising and cost-effective alternative to conventional mining [2]. However, it is estimated that less than 20% of the discarded e-waste is recycled at this time. This low recycling rate is partly attributed to the lack of proper recycling methods for most metals [1]. Therefore, there is a sustainable need to propose new and alternative strategies for e-waste recycling.

Besides precious and base metals, e-wastes also contain rare earth elements (REEs), which are increasingly used in high technology and clean energy applications [3]. REEs are present, for example, in common electronic components such as speakers, hard disk drives, and vibrators [4]. While REEs have relatively low concentrations in most bulk e-waste, the volume of end-of-life electronic devices discarded annually represents a great recycling opportunity. The presence of REEs within these devices comes mostly from neodymium (NdFeB) magnets [5]. NdFeB magnets are typically composed of up to 31 wt% REE [6]. Apart from Nd, which is the main REE, Dy, Pr, and Tb are also added to the magnet in various proportions depending on the application and quality of the magnets required [7]. The possibility of digesting NdFeB magnets into their isolated REE constituents is therefore a critical aspect of an effective recycling strategy.

While the recycling of REEs derived from NdFeB magnets in end-of-life electronic devices is not yet performed commercially, Rademaker et al. [7] emphasized that it would be technically feasible if efficient physical dismantling, separation, hydrometallurgical, and refining methods were available in the future. One challenge associated with REEs

is the difficulty of isolating individual REEs from their neighbouring elements in the periodic table [8]. However, most separation techniques for REEs require the dissolution of solid matrices, and NdFeB magnets are no exception. Therefore, digestion of such magnets in a rapid, efficient, and cost-effective manner is an important aspect of a REEs recycling strategy.

Numerous researchers have investigated the dissolution of REEs from NdFeB magnets via various hydrometallurgical approaches (Table 1). Most procedures used variable acid types and concentrations and a two-step sample pre-treatment prior to the acid dissolution. This sample pre-treatment was driven by the need to demagnetize and pulverize the magnet to facilitate its manipulation and dissolution. These steps are time-consuming and potentially hazardous from a chemical and health perspective. For example, as the grinding of magnets leads to small particles, they can be inhaled and deposited within the respiratory system. The exposed magnet surface is increased for smaller particulates which can facilitate the ignition of metallic powders. Hoogerstraete et al. [9] reported a fire after opening a grinding mill containing NdFeB magnets. Sometimes, the heat generated during the grinding process can create a vacuum upon cooling, rendering the opening of the grinding mill challenging. Moreover, even though rare-earth magnets are brittle because they consist of agglomerated particulates (pressed and/or sintered), they are still a hard material and are sufficiently abrasive to damage steel, which can lead to premature wear of the equipment used for e-waste recycling. Grinding NdFeB magnets also requires powerful and resistant grinding equipment [10]. There is therefore a significant interest in assessing the dissolution performances of analytical procedures that do not require grinding and demagnetization processes.

Most dissolution approaches reported in the literature (Table 1) use elevated temperatures to accelerate NdFeB dissolution, usually heated with conventional heat sources such as hotplates and ovens. Recently, Helmezi et al. [11] reported a rapid digestion of REEs in phosphoric acid by short-wavelength focused infrared radiation (FIR). They reported excellent recoveries and reproducibilities for REEs in various certified reference materials such as OREAS-465 (carbonatite supergene REE-Nb ore), OKA-2 (rare earths and thorium ore), and REE-1 (rare earths, zirconium, and niobium ore). These results suggest that FIR digestion could be a potential alternative to other heat sources for magnet dissolution and, potentially, alleviate previously mentioned sample pretreatments.

Table 1. Hydrometallurgical techniques published on the recycling of REEs from NdFeB magnets.

Magnets Source	Studied Elements	Demagnetization	Particles Size	Pre-Treatment	Leaching Method	Solubilization REEs ^a /Fe (%)	References
Magnetic sludge	Nd, Dy, Fe, B	(Not magnetized)	<250 µm	Drying of the sludge	1 M HNO ₃ + 0.3 M H ₂ O ₂ , 80 °C, 10 mL/g, 5 min	98, 81/15	Rabatho, et al. (2013) [12]
Manufacturing waste magnets	Nd, Fe, B	350 °C, 15 min	<297 µm	-	3 N H ₂ SO ₄ , 27 °C, 50 mL/g, 15 min (ultrasound)	100/100	Lee, et al. (2013) [10]
Manufacturing waste magnets	Nd, Dy, Fe	(Not magnetized)	not mentioned	Roasting at 400 °C, 2 h	1 M acetic acid, 90 °C, 100 mL/g, 400 rpm, 3 h	94, 93/1	Yoon, et al. (2015) [13]
HDD	Nd, Pr	320 °C, time not mentioned	<250 µm	-	2 M H ₂ SO ₄ , 70 °C, 20 mL/g, 15 min	90/not mentioned	München, Bernardes, and Veit (2018) [14]
Wind turbine	Nd, Pr, Dy, Fe, B, Al, Co	310 °C, 60 min	<149 µm	Roasting at 850 °C, 6 h	0.5 M HCl, 10 mL/g, 500 rpm, 5 h	98, 97/<1	Kumari, et al. (2018) [15]
HDD	Nd, Dy, Fe	350 °C, 60 min	<100 µm	900 W microwave, opened vessels, 5 min	0.5 M HCl, 70 °C, 25 mL/g, 900 rpm, 2 h	56/low (not mentioned)	Tanvar, Kumar, and Dhawan (2019) [16]

Table 1. Cont.

Magnets Source	Studied Elements	Demagnetization	Particles Size	Pre-Treatment	Leaching Method	Solubilization REEs ^a /Fe (%)	References
HDD	Nd, Dy, Fe	350 °C, 30 min	<500 µm		2 M H ₂ SO ₄ , 27 °C, 20 mL/g, 15 min	100/100	Erust, et al. (2019) [17]
HDD	Fe, Nd, Co, Ni	400 °C, 45 min	<420 µm	-	1.3 M (NH ₄) ₂ S ₂ O ₈ , 75 °C, 50 mL/g, 15 min	99/64	Ciro, et al. (2019) [18]
HDD	Nd, Pr, Dy, Fe	350 °C, 3 h	~2 mm	-	1 M H ₂ SO ₄ , 25 °C, 20 mL/g, 90 min	100/100	Kumari, et al. (2020) [19]
HDD	Nd, Pr, Dy, Tb, B, Fe, Al, Cu, Ni, Co	350 °C, 60 min	<250 µm	-	1.6 N HCl or H ₂ SO ₄ , 20 mL/g, 5 min	100/100	Present work
HDD	Nd, Pr, Dy, Tb, B, Fe, Al, Cu, Ni, Co	No demagnetization	Coarsely broken	-	1.6 N HCl or H ₂ SO ₄ , 20 mL/g, ~30 min for 6 × 3 × 2 mm pieces	100/100	Present work

^a Presented as “Nd” (or mixed REEs) or “Nd, Dy” percentages.

In this article, we compared the dissolution of intact and pulverized magnets (both magnetized and demagnetized) by focused infrared digestion (FID) to other, more conventional dissolution techniques (microwave digestion, hot plate, and alkaline fusion).

2. Materials and Methods

2.1. Materials and Reagents

Two different samples were used in this study. The first sample, for method comparison and optimization, was prepared from magnets obtained from hard disk drives (HDD) collected in electronic waste bins located on the main campus at Laval University (Quebec City, QC, Canada) and separated from their brackets. The second sample, for the study concerning the dissolution of unaltered magnets, consisted of cylindrical magnets of 0.751 ± 0.006 g (6 mm in diameter and 2 mm in height) manufactured as one single batch, purchased from MagnetsShop (Culver City, CA, USA). These magnets were physically cleaved into similar fractions to enable the acid to penetrate beyond the protective Ni-Cu-Ni coating.

Nanopure water (18.2 MΩ·cm at 25 °C) obtained using a Milli-Q system (Millipore, Bedford, MA, USA) was used to dilute the solutions. Standard solutions (1 g·L⁻¹) of Al, B, Co, Cu, Dy, Fe, Nb, Nd, Ni, Pr, Rh (ISTD), and Tb, purchased from PlasmaCal (SCP Science, Baie d’Urfée, QC, Canada), were used to prepare calibration standards. Concentrated ACS-grade H₂SO₄ (Fisher, Ottawa, ON, Canada), and trace metal grade HCl and HNO₃ (VWR, Mississauga, ON, Canada) were used for sample digestion. Unless stated otherwise, all the confidence intervals represent a confidence level of 95%.

2.2. Demagnetisation and Grinding

Hard disk drive magnets (237 g) were demagnetized by thermal demagnetization based on the procedure proposed by Tanvar et al. [16]; the intact magnets were heated in a muffle furnace at 350 °C in a porcelain crucible for 1 h. Then, the demagnetized magnets were placed in a steel dish with grinding rings and ground with an 8500 Shatterbox mill (SPEX SamplePrep, Metuchen, NJ, USA) during successive cycles lasting 70, 50, and 40 s. Between each cycle, the ground sample was sifted through a 250 µm (mesh #60) brass sieve. Pieces larger than 250 µm were reintroduced to the steel dish for the next cycle. The resulting powder had a final mass of 216 g, representing 91% of the original mass. The difference between the initial and final masses can be explained by the presence of

unground particles (13 g) that were larger than 250 µm after the last grinding cycle, and losses during grinding and sieving operations.

The particle size of the ground magnets was analyzed with 53 and 150 µm (mesh #270 and #100) sieves with a W.S. Tyler RX-29 Ro-Tap Sieve shaker (Laval Lab, Laval, QC, Canada) for 15 min, and each collected fraction was weighed. The mass loss from sieving represents less than 0.5% of the total mass used. For all the grinding and sieving steps, the sieves used were W.S. Tyler 12 inch (30.5 cm) brass sieves (Laval Lab, *ibid.*) with a PM4000 balance (Mettler Toledo, Mississauga, ON, Canada).

2.3. Elemental Analyses

The elemental composition of magnets was determined by inductively coupled plasma–optical emission spectroscopy (ICP-OES, iCAP 7000 Series, Thermo Scientific, Montréal, QC, Canada) equipped with a pneumatic concentric nebulizer. Table 2 presents the ICP-OES operating conditions. X-ray fluorescence (XRF) analyses were also used on some digestion residues to determine their elemental constituents. XRF analyses were performed in 3 replicates of 30 s for each filter (Na-S, Ni-Ag, Cr-Co, and Cl-V) using a MiniPal4 (Malvern Panalytical, Québec, QC, Canada).

Table 2. ICP-OES operating conditions.

Instrumental Parameters	iCAP 7000 Series ICP-OES
RF Power (W)	1150
Plasma gas flow (L/min)	12
Auxiliary gas flow (L/min)	0.5
Nebulizer gas flow (L/min)	0.5
Analysis mode	Radial (Fe, Nd), Axial (others)
Stabilization Time (s)	5
Sample flow rate (mL/min)	1.8
Wavelength (nm)	Al(309.271), B(249.773), Co(228.616), Cu(224.700, 324.754), Dy(353.170), Fe(238.204, 259.940), Nb(309.418), Nd(401.225, 406.109), Ni(216.556, 221.647), Pr(422.535), Tb(350.917)

2.4. Leaching

2.4.1. Total Dissolution of the NdFeB Magnets

To evaluate the elemental composition of ground magnets, four dissolution techniques were used: (1) closed-vessel acid digestion (CVAD, SCP Science, Baie d’Urfée, QC, Canada); (2) microwave (MWD, CEM corporation, Matthews, NC, USA); (3) focused infrared digestion (FID, Coldblock, Niagara Falls, ON, Canada), and (4) alkaline fusion (AF, Malvern Panalytical, Québec, QC, Canada). Table 3 presents the conditions used for each type of dissolution technique. Note that for FID and AF, the temperature ramping was extremely rapid, and boiling and melting temperatures, respectively, were obtained in less than a minute in both cases. The choice of a mixture of concentrated HCl and HNO₃ in an 8-to-2 ratio for acid digestion was based on the operating conditions reported by Berghof [20] for the dissolution of permanent magnets. The choice of 3 M of HNO₃ as a dissolution medium for alkaline fusion was based on the procedure published by Milliard et al. [21] concerning the dissolution of refractory species in environmental matrices.

2.4.2. Leaching Experiments

Experiments on the leaching of elements from the NdFeB powder were conducted with 1 g of ground magnetic material by FID using the design of experiments (DOE) performed using JMP Pro (Version 14.3, SAS Institute, Cary, NC, USA). The parameters used for this optimization process on the FID are presented in Table 4.

Table 3. Operating conditions used for the complete dissolution of ground magnets.

Digestion Technique	CVAD	MWD	FID	AF ^a
Instrument	DigiPrep Jr 12 pos.	Mars 5	6 channels ColdBlock	M4 Fluxer
Amount of ground magnet used (g)	0.5	0.25	1.0	0.1
Volume of acid (mL)	30 mL	10 mL	25 mL	100 mL
Nature of the acid used	HCl:HNO ₃ (8:2)	HCl:HNO ₃ (8:2)	HCl:HNO ₃ (8:2)	3 M HNO ₃
Digestion procedure	Ramp <i>ca.</i> 30 min, 240 min at 100 °C	Ramp 25 min, hold 15 min, 1600 W at 100%	15 min at 100% power for both lamps	See Milliard et al. [21]

^a Fusion was performed using a 20:1 (~2 g) ratio of LiT/LiB/LiBr 49.5/49.5/1% flux to sample (Malvern Panalytical, Québec, QC, Canada), which was subsequently dissolved under the acidic conditions presented.

Table 4. Values used during DOE optimization process of the focused infrared digestion of ground magnets.

Nominal Variables	Value 1	Value 2	
Acid type	HCl	H ₂ SO ₄	
Numerical Variables	Low-Value	Mid-Value	High-Value
Acid concentration (N)	1	2	3
Acid-to-sample ratio (mL/g)	10	20	30
Dissolution time (s)	300	450	600
Lamp power (%)	80	90	100

After optimization, the following optimal leaching methodology was used for FID: either 20 mL (1.6 N) or 10 mL (3.2 N) of HCl or H₂SO₄, per gram of ground NdFeB, is necessary to quantitatively (>99.9%) solubilize the rare earth elements in 5 min with a lamp power of 100%. For the trials on unaltered magnets, 7.5 mL of 3.2 N of H₂SO₄ was used for about 0.75 g of magnetic material.

3. Results and Discussion

3.1. Particle Size Distribution of the Ground Demagnetized NdFeB Magnets

The particle size plays an important role in the dissolution process of ground magnets. The particle size distribution of ground NdFeB magnets obtained from HDD are presented in Table 5.

Table 5. Mass percentage composition as a function of the particle size of the ground NdFeB magnet powder obtained from HDD.

Particle Size (µm)	Mass Percentage (%)
<53	42
54–150	34
151–250	24

The particle size distribution shows that most of the ground magnet powder (76%) was reduced to particles smaller than 151 µm. The three fractions were pooled together and used for the remaining trials.

3.2. Elemental Composition of Ground Demagnetized NdFeB Magnets

To properly assess various leaching approaches, the elemental composition of the powdered magnet must be known exactly. Four total dissolution approaches were compared: closed-vessel acid digestion (CVAD), microwave digestion (MW), focused infrared digestion (FID), and alkaline fusion (AF). The elemental composition was determined by ICP-OES. The instrument response was validated by analyzing Al, Cu, Dy, Fe, Nb, Nd, Ni,

and Pr in the certified reference material REE-1 (CanmetMINING, Ottawa, ON, Canada). The REE-1 material was prepared for ICP-OES analysis by AF using 0.4 g of the material with 1.2 g of flux. Other parameters were as presented in Table 3. Table 6 presents the elemental composition of powdered NdFeB magnets determined by ICP-OES based on the total dissolution technique used.

Table 6. Elemental composition (%) of the powdered NdFeB sample determined by ICP-OES based on the total digestion used.

Element	Digestion Technique			
	Closed-Vessel Acid (<i>n</i> = 6)	Microwave (<i>n</i> = 2)	Focused Infrared (<i>n</i> = 3)	Alkaline Fusion (<i>n</i> = 3)
Fe	64 ± 1	67 ± 2	65 ± 2	67 ± 3
Nd	24.5 ± 0.7	25.6 ± 0.9	26.0 ± 0.6	25 ± 2
Pr	3.4 ± 0.1	3.6 ± 0.1	3.5 ± 0.2	3.3 ± 0.3
Ni	1.8 ± 0.2	N.D.	1.9 ± 0.1	1.7 ± 0.3
Dy	1.57 ± 0.04	1.61 ± 0.08	1.5 ± 0.2	1.5 ± 0.1
B	1.04 ± 0.02	0.93 ± 0.03	1.0 ± 0.1	N.M.
Co	1.02 ± 0.02	1.02 ± 0.01	1.00 ± 0.07	1.0 ± 0.1
Al	0.43 ± 0.02	0.50 ± 0.01	0.5 ± 0.1	0.49 ± 0.07
Nb	0.44 ± 0.08	0.4 ± 0.1	0.223 ± 0.005	0.35 ± 0.02
Cu	0.20 ± 0.02	N.D.	0.17 ± 0.03	0.16 ± 0.02
Tb	0.07 ± 0.02	0.09 ± 0.05	0.09 ± 0.03	0.08 ± 0.01
Total	99 ± 2%	101 ± 4%	100 ± 4%	100 ± 6

N.M.—not measurable, due to the addition of borate flux. N.D.—not determined.

The results obtained from four distinct digestion approaches for ground magnets led to a relatively consistent elemental composition except for Nb. This suggests that the sample used was sufficiently homogeneous to be used for leaching comparisons, which is discussed in the next section. As the digestates were filtered prior to ICP-OES analysis, a black residue was noticeable on the filters used for the samples digested by CVAD and FID. Pre-weighed filters were used to determine the mass fraction of the undissolved magnet powder. After filtration, they were washed with water, dried, and weighed using an analytical balance. The filters were then subjected to elemental analysis by XRF (Figure 1). It was determined that the residue represents $0.40 \pm 0.08\%$ ($\sigma = 1$ SD) of the ground magnet mass used initially.

Figure 1. XRF spectrum of the residue present after FID.

The XRF analysis showed that the residue is composed of Nb and Fe. Nb is present in some NdFeB magnets to increase resistance to corrosion and enhance some magnetic properties [22,23]. Its presence in our powdered sample is not unexpected, because of the refractory nature of niobium oxides [24]. We suspect that the presence of Fe is the result of incomplete washings of the filter surface. Except for traces of Nd and Fe, all four digestion techniques were effective to completely dissolve ground demagnetized magnets.

3.3. Leaching of Powdered and Demagnetized Magnets

While complete dissolution of the magnets is mandatory for comparing the digestion techniques and determining the degree of leaching, it is not necessary from the perspective of developing a hydrometallurgical strategy for the recycling of rare earth elements in magnets. Helmeczi et al. [11] recently reported the rapid dissolution of REEs in mineral and environmental matrices using FID. As FID also demonstrated equivalent dissolution performances to other digestion techniques for the complete digestion, this approach was investigated for leaching purposes through a design of experiments (DOE) approach.

3.3.1. Design of Experiments

While the previous digestion procedure, which used a mixture of HCl and HNO₃, was certainly effective to completely dissolve powdered magnets, total digestion is not necessary for the recycling of REEs. The cost of nitric acid and its oxidative characteristics have limited its use in the hydrometallurgical separation of REEs in favor of HCl and H₂SO₄ [25]. Thus, an investigation of the leaching of ground demagnetized magnets was performed in either HCl or H₂SO₄. Five parameters were assessed through a DOE approach (Table 7). A first assessment of the DOE results showed that no parameter had a statistically significant impact on the dissolution. However, by removing either the acid type, dissolution time, or lamp power factors, the results showed that the concentration of acid, the acid-to-sample ratio, and their two-factor interaction were the only significant factors in the leaching of REEs. This suggests that the number of moles of acid was the main parameter for this leaching optimization. Experimentally, it was also determined that the low value used for the dissolution time (i.e., 300 s) set in the DOE was exceedingly sufficient to completely dissolve powdered magnets.

Table 7. Statistical importance of the DOE factors according to a 5- and 4-factor analysis.

Source	Log Worth ^a for 5 Factors	Log Worth ^a for 4 Factors ^b
Concentration	1.734	<u>3.506</u>
Ratio	1.724	<u>3.484</u>
Concentration * Ratio	1.567	<u>3.142</u>
Acid	0.448	<u>0.706</u>
Intensity * Time	0.354	
Intensity * Ratio	0.240	0.360
Time * Acid	0.209	
Time	0.137	
Concentration * Acid	0.137	0.223
Ratio * Acid	0.131	0.215
Intensity * Acid	0.130	0.189
Intensity * Concentration	0.091	0.145
Intensity	0.089	0.127
Time * Ratio	0.064	
Time * Concentration	0.026	

^a A log worth value of minimum 2 is required for a factor to be considered significant. ^b Dissolution time (Time) factor removed.

To adequately determine the quantity of acid required per gram of powdered magnet to completely dissolve REEs, tests were performed in HCl and H₂SO₄ by varying the number of moles of acid used per gram of magnet. The results are presented for Nd as a representative of the REEs in Figure 2.

Figure 2. Nd dissolution yield (%) as a function of the amount of acid (HCl or H₂SO₄, in mmol) for 1 g of powdered magnet after a digestion by FID (300 s).

This test highlights the fact that the quantity of acid available to react with the powder is the limiting factor in the dissolution of REEs using FID. The required quantity of H₂SO₄ (16 mmol/g of ground magnet) is exactly half of the needed HCl (32 mmol/g), which is consistent with the balanced redox formulas (Equations (1) and (2)) for both acids. As two atoms of REEs are being oxidized to a trivalent oxidation state, six H⁺ cations need to be reduced, which can be found in either three molecules of H₂SO₄ or six of HCl, hence the need for twice as much HCl as H₂SO₄. A similar logic can be applied to iron, one of the main components of the magnet. Based on the composition of the powdered magnet, it was calculated (from composition obtained by FID) that approximately 34 mmol of H⁺ was required to oxidize and dissolve the magnet, which is coherent with the quantity found experimentally.

Based on these observations, the following final leaching methodology can be proposed for FID: either 20 mL of 1.6 N or 10 mL of 3.2 N of HCl or H₂SO₄ per gram of NdFeB powder will be sufficient to completely solubilize the rare earths.

As stated previously, FID totally leached REEs from magnets, even with the shortest dissolution time tested (5 min). This suggests that the power output associated with the FID is more than sufficient to enable the complete dissolution of REEs. Thus, the Nd dissolution yield was monitored for dissolution times ranging from 60 to 300 s to determine how long, at full lamp power, it would take to achieve complete dissolution. No statistical differences in Nd dissolution yield were noted in the time range selected, except for the trial that ran for only 60 s (94%).

3.3.2. Leaching Performance Comparisons (CVAD, FID)

To determine whether there is a significant advantage in using FID for the leaching of REEs from magnets, the FID approach was compared to closed-vessel acid digestion (CVAD). The digestion of powdered NdFeB magnet was easily achieved in 300 s. As with FID, shorter dissolution times (60 to 300 s) were also investigated with CVAD. However, this technique required longer times—more than 120 s—to achieve complete digestion and quantitative dissolution (84% and 95% for 60 and 120 s, respectively).

Comparisons of the dissolution yields for FID and CVAD are presented in Figure 3. Statistically, both techniques yielded similar results when 10 mL of acid was used. Samples prepared using 20 mL of acid per gram showed lower yields with CVAD than FID. This difference could be explained by the short digestion time used (300 s), which does not allow the larger volume of the solution (20 mL) to be properly heated; this highlights the importance of heat in the rapidity of the digestion process. When performed at room temperature and a contact time of 300 s, the dissolution yields of REEs (i.e., Nd, Pr, Dy, and Tb) reached 80–90% with H_2SO_4 and 30–45% with HCl. As dissolution at room temperature with H_2SO_4 was more effective, further trials used H_2SO_4 . However, it should be noted that HCl is also a very suitable acid for such purposes and could be a judicious choice if the subsequent separation scheme is performed in this media.

Figure 3. Comparison of FID and CVAD for the digestion of 1 g of magnet powder during 300 s with 10 mL of 3.2 N or 20 mL of 1.6 N of HCl or H_2SO_4 .

3.3.3. Magnet Pieces Leaching

To test the effectiveness of FID vs. conventional CVAD on magnet pieces, cylindrical magnets were cut in half and put in with 7.5 mL of 3.2 N of H_2SO_4 for 15 min under various conditions (Table 8). The volume of acid and the molarity were adjusted to correlate with the number of moles required for the complete dissolution of the magnet mass used.

Table 8. Dissolved magnet mass after 15 min of contact time with 3.2 N of H_2SO_4 ($n = 3$).

Conditions	Relative Dissolved Mass ^a (%)
Room temp., without agitation	5 ± 2
Room temp., with agitation ^b	5 ± 2
CVAD	34 ± 5
FID	62 ± 2

^a The coating of the magnets is not digested with the proposed methods and represents $1.9 \pm 0.2\%$ of the total mass of the magnets. ^b Agitation was performed by the magnets pieces themselves interacting with the magnet field of a stirring plate.

As observed with the ground magnet, once the optimal quantity of acid per gram of magnet is used, the temperature of the acid is a critical parameter for the rapid dissolution of unaltered magnets. These results support the idea that FID, as a powerful heating source, could be an effective method to rapidly dissolve NdFeB magnets for hydrometallurgical recycling.

To determine the required time for the complete dissolution of the magnet pieces by FID and CVAD, the amount of magnet digested was monitored as a function of digestion

time (10 to 35 min, Figure 4). The same parameters as previously described were used, but with 15 mL of 3.2 N of H_2SO_4 to avoid the complete evaporation of the acid due to an incomplete condensation of the acidic vapor inside the part of the digestion vessel surrounded by the Peltier cooling block. The temperature of H_2SO_4 was monitored using a thermocouple inserted into the solution while the lamps were on. It showed a working temperature of 103 °C after 1 min, which is close to the expected boiling point of a 2 M solution of H_2SO_4 (102 °C [26]).

Figure 4. Undissolved magnet mass percentage after digestion in H_2SO_4 by FID and CVAD.

When the remaining magnet mass in the digestion vessel was approximately 10% of its initial value, the efficiency of the digestion tended to decrease for the FID approach. This is likely due to the round shape of the magnets used, which resulted in a smaller contact surface as the digestion progressed. Nonetheless, this experiment demonstrates that dissolution of magnet pieces is faster by FID than by CVAD.

4. Conclusions

The results obtained in this study indicate that focused infrared digestion (FID) could be used as an effective method for the recycling of rare earth magnets, either for the complete dissolution of ground samples (apart from refractory niobium oxides), or for the quantitative dissolution of REEs on magnetized and coarse magnet pieces. The absence of magnetic constituents in the FID unit enables the digestion of the magnets without any prior demagnetization process. The FID method is safer than others because, due to its rapid digestion time, FID does not require crushing of the magnets into fine powders. Skipping the grinding step also facilitates the separation of the undigested Ni-Cu-Ni coating and could potentially help in hydrometallurgical separation later in the recycling process.

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