URBAN MINING OF RARE EARTH ELEMENTS FROM RARE EARTH MAGNETS - HYDROMETALLURGICAL PROCESSING

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ABSTRACT

The concerns and impact of increasing volumes of waste electrical and electronic equipment (WEEE) reported in developed countries, will soon be a problem facing local municipalities. Contained in this waste is a critical raw material group of rare earth elements (REEs), and its use in electrical and electronic equipment has increased significantly in recent years as the demand for these products rises. With the growing volumes of WEEE, the responsible management of associated solid wastes are yet to be addressed practically in South Africa.

Hydrometallurgy by acid dissolution is one of the techniques used for the recovery of REEs and their compounds from neodymium-iron-boron (NdFeB) magnets. These are predominantly based on inorganic acids such as hydrochloric, nitric, and sulphuric acids which offer a good transition of the metals into dissolvable salts. The first stage operation in the extraction of REEs from waste (NdFeB) magnets includes the physical processes of demagnetization, crushing, and grinding to obtain waste permanent magnet (WPM) powders, while the chemical process is then initiated by leaching the WPM powder with an acid.

This work presents results from hydrometallurgical leaching experiments utilizing nitric acid for the recovery of neodymium and iron from crushed NdFeB magnets removed from discarded hard disk drives. Leaching experiments were performed using varying particle sizes to investigate optimal conditions for the extraction based on three variables, which were, the concentration of acid, leaching temperature, and leaching time. The results show that for the selected particle size the optimal leaching conditions for neodymium were obtained using 6.7M nitric acid, a temperature of 333.15 K and a leaching time of 60 minutes with a solid recovery rate above 99%.

KEYWORDS

Rare Earth Elements, hydrometallurgical processing, waste permanent magnets, waste electrical and electronic equipment

INTRODUCTION

The implementation of the commercial processes for waste electrical and electronic equipment recycling, especially Rare Earth Element (REE) recycling is limited to date (Binnemans et al., 2021). Commercially available processes are mostly focused on the recovery of scrap magnets from the waste electrical and electronic equipment (WEEE), and repurposing them by utilising the magnet-to-magnet approach. European Union's SUSMAGPRO programme funds four recycling plants with a combined planned capacity of NdFeB magnet powder recovery equal to 116 tonnes per year. Four REE reprocessing plants across Europe are also funded by this programme (SUSMAGPRO plants.). Urban Mining Company, based in the USA and funded by the US Department of Defence, obtained a patent for a technology called M2M used to reprocess scrap NdFeB magnets into new magnets (Binnemans et al., 2021).

The focus of this work was to optimize the extraction of REEs from NdFeB magnets through the comminution and leaching processes. Rare Earth Elements refer to 17 elements in the periodic table, namely lanthanides and two additional elements: scandium and yttrium (Binnemans et al., 2013). The two main groups of REEs can be categorised into two sets, with light rare earth elements (LREEs) ranging from lanthanum (La) to gadolinium (Gd) and heavy rare earth elements (HREEs) from terbium (Tb) to lutetium (Lu), including scandium and yttrium. This distinction is based on the atomic number and ionic diameter of REE atoms and refers to the different geochemical behaviour of both groups (Shannon, 1976).

According to Erust et al. (2021), China has monopolised the production of raw REE ores since the 1990s with approximately 95% of global production. Rich deposits allow China to fulfil approximately 90% of the global demand for rare earth metals and 75% of the demand for neodymium-iron-boron (NdFeB) magnets. Neodymium (Nd) and dysprosium (Dy) are arguably the most important REEs in the modern industry (Sarfo, 2019). Global demand for new sources of REEs increased significantly since 2006 which is related to the more restrictive export of rare earth metals by China (He, 2014).

NdFeB magnets are mainly composed of iron, neodymium, and boron with additives in the form of other REEs such as praseodymium (Pr) and dysprosium (Dy) or other metals, i.e., cobalt (Co). The final composition of the permanent magnet is defined by the future application (Tunsu, 2018). To prevent corrosion of the permanent magnets common additives are nickel, used for coating the manufactured product or the addition of 1-2% of cobalt to the alloy (Gruber et al., 2020; Lee et al., 2017). The Curie temperature is an important parameter of the permanent magnets which is a critical temperature of transition between ferromagnetic and paramagnetic properties of the material (Fabian et al., 2013). The alloy used to manufacture NdFeB magnets is enriched by the addition of praseodymium (Pr) which increases the Curie temperature of the alloy and dysprosium (Dy) which increases its coercivity (Yang et al., 2017). According to Sarfo (2019), market demand for neodymium, dysprosium, yttrium, europium, and terbium is nearing the quantities obtained from geological deposits. Thus, the collection and recycling of NdFeB magnets and other WEEE are critical to meet the goals of the sustainable growth of this sector of industry (Chu, 2010).

Examples of some key applications of neodymium magnets include wind turbines, electric cars, hard disk drives (HDDs) and military equipment (Xie et al., 2014). These products require high strength durability and coercive forces because they work under a high load (Xie et al., 2014). One of the promising sources of waste magnets that can be used in the recycling process is hard disk drives (HDDs). Each HDD contains between 1 and 30 g of neodymium magnets with a Nd and Dy content of approximately 31% and 4-7%, respectively (Erust et al., 2021).

The recycling of NdFeB magnets is necessary to meet global demands for REEs which can possibly delay the depletion of the known deposits (Reisdörfer et al., 2019) and address unsustainable mining practices. The three possible approaches to REE recycling include magnet-to-magnet, pyrometallurgical and hydrometallurgical methods. The magnet-to-magnet approach

refers to the production of new magnets from spent magnets. The waste magnets are refurbished and prepared for sintering with the addition of approximately 3% of fresh permanent magnet alloy. Greater than 90% of REEs are recovered with less than 5% freshly mined rare earth metals (Jin et al., 2016). The most important disadvantage of this approach is the decrease in the final product quality, mostly due to the inconsistency in the composition of the final product. A number of applications report the use of these magnets in electrical engines, wind turbines generators or magnetic separators (Nlebedim et al., 2018).

The pyrometallurgical approach is primarily used in the processing of freshly mined ores with high concentrations of REEs (Tunsu, 2018). However, this method can be also utilized in the recycling of non-ferrous metals from WEEE (Cui et al., 2008). Reduction reactions at increased temperatures form the basis of the pyrometallurgical approach (Binnemans et al., 2013; Y. Yang et al., 2017). The main disadvantages of this approach are high energy consumption used to reach the required temperatures, low selectivity of the process, and high levels of pollution in the form of emissions of gas and solid particles into the air (Tunsu, 2018).

One of the most important approaches used in the recovery of rare earth elements from WEEE is hydrometallurgy (Gruber et al., 2020). Leaching is a well-established hydrometallurgical technique that uses chemical reactions to convert metals into ions of soluble salts (Behera et al., 2016; Lee et al., 2013, 2017; Ni'am et al., 2019; Sahin et al., 2017; Tunsu, 2018). REEs react with acids such as sulfuric acid, nitric acid, and hydrochloric acid to form hydrogen gas and cations in salts containing sulfate, nitrate, and chloride anions, respectively. The low energy consumption, reduced gas emissions and adaptability to varied materials by adjustment of the reagents to achieve lower environmental impact (Reisdörfer et al., 2019). However, the amount of acidic waste generated in liquid form poses a significant drawback to this approach (Gruber et al., 2020). In hydrometallurgical processes, NdFeB magnets are demagnetized and comminuted to small diameter particles preferable in leaching processes. Then WPM powder is digested with acid to obtain mixtures containing ions of metals present in the alloy used to manufacture magnets. This approach is based on the use of inorganic acids such as hydrochloric, nitric, and sulfuric acid which, according to the literature allow for high leaching recoveries (Erust et al., 2021; Lee et al., 2013; Ni'am et al., 2019). Leaching is affected by WPM powder modification, type of acid, particle size, the concentration of acid, solid-to-liquid ratio, stirring speed, the temperature of the solution, and contact time with leachate (Ni'am et al., 2019). Lee et al. (2013) conducted batch experiments to establish optimal leaching conditions for Nd recovery from permanent magnets. The authors concluded from the large list of parameters investigated, that for WPM powder of particle size less than 297 μm optimal leaching conditions were obtained by using 3M H_2SO_4 and HCl over 15 minutes using a solid/liquid ratio of 0.02. Ni'am et al. (2019) reported that optimal WPM leaching conditions were obtained by utilizing 5 M HCl at a temperature of 368 K for 24 h using 0.02 solid-liquid ratio, 800 rpm stirring speed, and 0.250 mm particle size of the WPM powder.

Reisdörfer et al. (2019) characterized roasted and unroasted NdFeB magnet powders sourced from HDDs. Roasting is performed at high temperatures to convert the elements in the sample into oxides. This enhances the selectivity of Nd in the leaching procedure. Unroasted NdFeB powders contained 32.36% of Nd and 58.5% of Fe. Lee et al. (2013) reported similar values, with 31.27% of Nd, 59.62% of Fe, and 1.26% of B. It must be noted that the Nd percentages of 25.19% and 32.36%, with and without roasting, respectively, were considerably higher than the amounts typically found in mineral ores. The extraction of Nd from bastnasite is about approximately 18.5 wt%, while percentages in the range of 15-20% are extracted from monazite. Gruber and Carsky (2020) determined the chemical composition of different NdFeB magnets by dissolution in acid and analysis by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES).

The hydrometallurgical approach has been successfully adopted to recover REEs from other sources such as coal fly ash (CFA) (Cornelius et al., 2021; Yang et al., 2021) and printed circuit boards (PCB) (Maurice et al., 2021; Xia et al., 2022). Cornelius et al. (2021) were able to achieve a high yield of 530.2 ppm of REEs from the CFA. The first step of CFA processing was a wet magnetic separation of magnetic (MF) and non-magnetic fractions (NMF) of the ash suspended in water in a 1:2 ratio. The analysis of the fractions showed that REEs were present in NMF. The next step of the process was so-called zeolitization performed by mixing the NMF with 8M NaOH solution. The solid phase which was separated from the solution was then filtered and contacted with H_2SO_4 to precipitate Si-compounds. The concentration of REEs in the remaining mixture obtained by this method was approximately 3 times higher than the concentration of REEs in Earth's crust (Rudnick et al., 2003). CFA may be a prospective source of REEs for the industry (Cornelius et al., 2021). Yang et al. (2021) studied the leaching of the REEs from CFA using a mixture of 0.1M citric acid with 0.5M trisodium citrate, and 0.5M ethylenediaminetetraacetic acid (EDTA). Reported recovery values for total RRE yield in the samples were 11% for citric acid/trisodium citrate mixture and 33% for EDTA. This indicates that leaching using inorganic acids is a preferred method of REE processing.

Maurice et al. (2021) and Xia et al. (2022) reported experiments using PCBs. The recovery of the REEs from PCBs is economically challenging, as PCBs containing very low amounts of REEs require large-scale, centralised operations (Maurice et al., 2021). Xia et al. (2022) developed a multistage Nd recovery process for PCBs using an automized separation method. The distribution of the metals was based on the differences in physicochemical properties of the electronic components and compounds used in manufacturing. According to the authors (Xia et al., 2022) the use of HNO_3 as a leaching agent and oxalic acid as a precipitation agent results in 91.1% of neodymium present in the initial mass of PCBs. This can be restored in the form of high purity (99.6%) neodymium oxide.

Leaching experiments were conducted in this work, using HNO_3 and WPM powder from HDDs. The effect of particle size, the concentration of nitric acid, temperature, and time of the extraction process are reported. The samples obtained from the leaching experiments were analysed using Inductively Coupled Plasma – Optical Emission Spectrometry (ICP-OES).

Materials and methodology

Materials and reagents

HDDs of various brands and models were sourced from discarded personal computers at the University of KwaZulu-Natal. Table 1 shows the chemical purities and supplier details of the chemicals used. A 12.3 M analytical reagent grade nitric acid and deionized water were used to prepare 6.7 M and 2.2 M nitric acid solutions for the leaching process. The concentrations of the nitric acid solutions were validated by titrating against standardized sodium hydroxide.

Table 1: Details of the chemicals used in this study.

Compound	Chemical Formula	Molecular Weight (g/mol)	CAS Number	Supplier	Mass Fraction Purity[a]
Nitric acid	HNO_3	63.01	7697-37-2	Merck	0.55
Sodium hydroxide	NaOH	40.00	1310-73-2	Merck	0.98
Potassium Hydrogen Phthalate (KPH)	$C_8H_5O_4K$	204.22	877-24-7	Sigma Aldrich	0.9995
Phenolphthalein	$C_{20}H_{14}O_4$	318.32	77-09-8	Sigma Aldrich	0.99

Note: (a) As stated by the supplier.

HDDs were manually dismantled to remove the NdFeB magnets attached to aluminium support. The remaining components were dispatched for waste treatment. Magnets of varied sizes and thicknesses were collected for further processing. The waste NdFeB magnets were the first demagnetization. To remove the magnetic properties of the magnets a heating method was adopted. The magnets were demagnetized in a preheated Scientific 909 furnace at 673 K for 30 minutes until a total loss of magnetic properties occurred. Then the demagnetized NdFeB magnets were comminuted batch-wise in a roller mill. The distance between rollers was adjusted to accommodate magnets of varied sizes.

The crushed material was screened by laboratory test sieves (apertures 100 µm, 150 µm, 200 µm, 300 µm, 355 µm, 425 µm, 500 µm, and 600 µm) to assess the grinding efficiency and assess the effect of particle size on the leaching efficiency. The sieve trays were agitated for approximately 10 minutes. Large shards were further crushed until an adequate amount of the desired particle size range (425-500 µm) was obtained. Table 2 shows the size distribution of WPM powder after the sieving procedure. The selection of particle size fraction of 100-150µm was guided by literature. However, disadvantages of small particle sizes include airborne dust leading to health and safety concerns. A particle size range of ≥ 600 µm was used to determine if additional crushing or grinding is required for efficient leaching to occur. The standard uncertainties for mass measurements were u = 0.03 g.

Table 2: Size distribution of the WPM powder particles.

Sieve Size (µm)	Mass retained (g)	Mass fraction	Cumulative Mass Passes (g)	Total Percent Passed (%)
600	339.273	0.554	273.029	44.59
500	40.878	0.067	232.151	37.91
425	37.242	0.061	194.909	31.83
355	32.685	0.053	162.224	26.49
300	30.386	0.050	131.838	21.53
200	57.498	0.094	74.34	12.14
150	28.789	0.047	45.551	7.44
100	33.857	0.055	11.694	1.91
Pan	11.694	0.019	0	0.00
Total	612.302	1	612.302	100

Note: (a) Standard uncertainties (u) are u (mass) = 0.03 g

Leaching procedure and conditions

Firstly, to evaluate the concentrations of REEs and metals present in the WPM powder, a solution of 50 ml of 12.3M HNO_3 and 50 ml of 6M H_2SO_4 was used as leachate. An approximate amount of 1g of WPM powder (particle size 425-500 µm) was digested. The sample was chosen based on the availability of the WPM powder fractions obtained in the sieving process. The leaching solution and WPM powder were stirred for 8 h to achieve full dissolution of the solids. This was thereafter diluted with distilled water in a 1:100 ratio to obtain samples for ICP-OES analysis. This procedure was performed in triplicate.

Strong inorganic acids allow for high recovery of metals from magnets and dissolve metals more easily than weak organic acids. The solid REEs in the magnets are converted to ions [RE^{3+}] as follows (Erust et al., 2021):

$$\mathrm{RE} + 3H^{+}X^{-}_{(aq)} \rightarrow RE^{3+}_{(aq)} + 3\mathrm{X}^{-}_{(aq)} + 1.5H_{2\,(g)} \qquad (1)$$

Three main parameters considered for experiments were the concentration of acid, time, and temperature of the leaching process.

Leaching experiments were conducted batch-wise with a solid-to-liquid ratio of 0.02g/ml to compare to the literature (Erust et al., 2021; Lee et al., 2013). The findings of Lee et al. (2013)

and Erust et al. (2021) of a solid to liquid ratio of 0.02 g/ml were applied in the leaching experiments.

HNO_3 solutions were prepared as this acid has been used in previous work (Williams-Wynn et al., 2020). Solid recoveries were determined by measuring the difference in the mass of Nd and Fe in the NdFeB sample before and after leaching.

WPM powder of the desired particle size range and nitric acid of the selected concentration was placed in a glass beaker in a solid: liquid ratio of 0.02 g/ml. The temperature of the solution was monitored using an alcohol thermometer (temperature readability 0.1 K). The mixture was placed on a magnetic stirring plate with a heater (FMH STR-MH140) operating at 333 rpm at 298.15 K. Approximately 6 ml of the leached solution was sampled at 10-minute intervals using a syringe and injected through a microfilter (0.45µm) into sample vials. Micro-filter syringes were used to effectively filter the solids from the leachate, hence terminating the solid-liquid reaction. The leaching experiment was terminated after 30 minutes. A gravimetric filtration setup was used to separate the pregnant leach solution and unleached solids to obtain leaching recoveries. The pregnant leach solution was collected after each experiment. The concentration of Nd and Fe in the leached samples and mother liquor were analysed by ICP-OES.

The same procedure was conducted at temperatures of 318.15 K and 333.15 K, using a particle size of 425-500 µm. Particle size was chosen to assess the effect of temperature, the leaching time was set to 30 minutes, and a sample of approximately 6 ml was extracted every 10 minutes using disposable syringes. Once the leaching process was complete, the filtration step followed, and the pregnant leach solution and leachate samples were withdrawn, stored, and sent for ICP-OES analysis. Solid recoveries were determined using the following equation:

$$\text{Solid recovery (\%)} = \frac{m_1}{m_t} \times 100\% \tag{2}$$

where m_1 is the mass of metal digested in acid and m_t is the initial mass of a metal sample.

To determine the effect of time on the leaching process, Lee et al. (2017) used leaching times of 30, 60, 90, and 120 minutes. The procedure was conducted using 2.2M HNO_3 and a WPM powder particle size of 425-500 µm 298.15 K. The extended leaching test was conducted using WPM powder of 425-500 µm particle size and 12.3M HNO_3 at 298.15 K for 5 hours. Samples were withdrawn every 60 minutes.

Calibrations and Uncertainties

The standard uncertainties of composition and temperature in Table 3 were determined using guidelines issued by the National Institute of Standards and Technology (NIST). A coverage factor of *k=2* was used to calculate expanded uncertainties with a confidence level of approximately 95%.

Table 3: Standard Uncertainty Estimates used in this work.

Source of uncertainty	Deviation estimate	Distribution
Composition		
Mass balance uncertainty (g)	0.03^b	Rectangular
Repeatability of x_i (x_i)	0.18^a	Rectangular
Correlation of Nd calibration (x_i)	3.5^a	Rectangular
Correlation of Fe calibration (x_i)	1.1^a	Rectangular
Volume uncertainty, pipette (cm3)	0.05^b	Rectangular
Volume uncertainty, burette (cm3)	0.03^b	Rectangular
Temperature		
Alcohol thermometer (K)	0.05^b	Rectangular
Temperature measurement repeatability (K)	0.7^a	Rectangular

Notes: (a) Estimated - treated as a type A distribution
(b) Estimated - treated as a type B distribution

Results and discussion

The composition of the waste powders is important to make a comparison of results. Table 4 presents the results of the characterisation of WPM powders in comparison with literature data. It can be observed that, in comparison with the literature, samples of magnets used in this study contain higher wt% of iron and lower wt% of neodymium. The average standard deviations from the analyses are included in the table. The results are based on the average wt% of 3 experiments using 75-100 µm, 100 – 150 µm, and 425-500 µm particle size WPM powder fractions.

For the leaching experiments using 2.2M, 6.7M and 12.3M HNO_3, the results presented in Table 5, show the transfer of metals from WPM powder to pregnant leach solution was above 80% for all studied parameters combinations. The effect of different particle sizes on the leaching efficiencies of NdFeB magnets from HDDs has not been reported using HNO_3 as the leaching reagent. The results obtained from leaching with varying nitric acid concentrations indicate increased solid recoveries from 89.4% to 99.66% when nitric acid concentrations increased from 2.2M to 6.7M. However, the solid recovery decreased to 97% when 12.3M nitric acid was used. Hence, the 6.7M nitric acid solution is an enhanced oxidizing ability and maintains the stability of metal ions in the solution. On the other hand, a 12.3M nitric acid solution has the highest oxidizing ability and the lowest pH. However, a decrease in the recovery indicates that the solubility of metal ions was less favourable in such acidic conditions. A similar trend was obtained by Erust et al. (2021), whereby the recoveries increased with increasing nitric acid concentrations.

Control measurements in this study were conducted with a particle size of 425-500 µm, an acid concentration of 2.2M HNO_3, a temperature of 298.15 K and a 30-minute leaching time for each experiment. The solid-to-liquid ratio was maintained at 0.02 based on the recommendations of Lee et al. (2013) and Erust et al. (2021). The operating parameters and conditions adopted in this leaching study are summarized in Table 6. Parameters were established based on a factorial design. Particle size was fixed and the change of acid concentration, temperature and time intervals were used to establish optimal leaching conditions.

Table 4: The average wt.% of the elements in waste permanent magnet powder.

Source	Fe^{3+}	Nd^{3+}	Dy^{3+}	Pr^{3+}	B^{3+}	Sm^{3+}	Reference
NdFeB magnet powder (75-100 µm particle size)	68.45	24.48	2.74	1.24	2.44	0.65	This work
NdFeB magnet powder (100-150 µm particle size)	67.70	23.85	2.47	3.08	2.27	0.63	This work
NdFeB magnet powder (425-500 µm particle size)	67.80	22.58	1.50	4.50	2.00	1.62	This work
NdFeB scrap magnet	59.62	31.27	-	-	1.26	-	(Lee et al., 2013)
NdFeB powder without roasting	58.50	32.36	1.00	4.38	-	-	(Reisdörfer et al., 2019)
NdFeB powder with roasting	66.69	25.19	0.72	2.96	-	-	(Reisdörfer et al., 2019)
PC HDD (before 2005)	59.40	24.44	1.39	1.85	-	-	(Gruber et al., 2020)
PC HDD (2010-2015)	61.33	25.94	2.14	0.81	-	-	(Gruber et al., 2020)
Servomotors	64.86	19.54	4.63	5.92	-	-	(Gruber et al., 2020)
Traction engine	61.15	18.76	4.05	5.72	-	-	(Gruber et al., 2020)
Magnetic separator	62.70	23.80	1.25	6.66	-	-	(Gruber et al., 2020)

Notes: (a) Results determined via ICP-OES analyses.
(b) The average standard deviation of wt.% are 1.35%, 0.68%, 0.08%, 1.73%, 0.07% and 0.02% for 75-100 µm particle size powder, 0.34%, 0.32%, 0.03%, 0.05%, 0.12%, 0.01% for 100-150 µm particle size powder and 0.67%, 0.83%, 0.04%, 0.07%, 0.06%, and 0.15% for 425-500 µm particle size powder, respectively.
(c)The results are based on the average wt% of 3 experiments using particle sizes 75-100 µm, 100-150 µm and 425-500 µm, respectively.

Table 5: Summary of results of solid recoveries from leaching experiments.

Leaching Factor	Solid Recoveries/%
Particle Sizes (2.2M HNO_3, T = 298.15 K, t = 30 min)	
Particle Size (100 - 150 µm)	91.04
Particle Size (425 - 500 µm)	89.40
Particle Size (≥ 600 µm)	91.14
Concentrations of nitric acid (particle size 425-500µm, T = 298.15 K, t=30 min)	
2.2M HNO_3	89.40
6.7M HNO_3	99.66
12.3M HNO_3	97.00
Temperatures (particle size 425-500µm, 2.2M HNO_3, t = 30 min)	
T = 298.15 K	89.40
T = 318.15 K	95.20
T = 333.15 K	95.40
Time (particle size 425-500µm, 2.2M HNO_3, T = 298.15 K)	
t = 30 min	89.40
t = 60 min	91.62

The particle size ranges of the WPM powders samples varied from 100 – 150 µm, 425 – 500 µm, to ≥ 600 µm. Leaching experiments were performed with 2.2M nitric acid at 298.15 K and a leaching time of 30 minutes. The recovery decreased from 91.04% for (100 – 150 µm) to 89.4% for the range (425 – 500 µm). Hence, smaller particle sizes are favourable for leaching. Furthermore, as the particle size decreases, the active surface area of the particle increases, which enhances mass transfer during leaching allowing greater metal dissolution. These trends are consistent with particle size experiments performed by Behera et al. (2016) and Sahin et al. (2017), in which reported optimal particle sizes were 46-75 µm and 63-90 µm, respectively. In practical operations, further crushing would demand increased equipment to screen samples, thereby increasing the capital costs of the process and the workforce required. Additionally, an efficient crushing procedure is necessary to fast-track the leaching process.

Table 6: Leaching parameters studied

Particle Size (µm)	**HNO$_3$ Concentration (M)**	**Temperature (K)**	**Time (min)**
100-150	**2.2**	**298.15**	**30**
425-500	6.7	318.15	50
≥600	12.3	333.15	60

Note: (a) Control measurements are particle size of 425-500 µm, 2.2M nitric acid concentration, 25 ℃ and times of 30 min based on Erust et al. (Erust et al., 2021).

The influence of temperature was studied at 298.15, 318.15 and 333.15 K while keeping other factors constant, i.e., 2.2M nitric acid, particle sizes 425-500 µm and experimental time of 30 minutes. By increasing temperature from 298.15 K to 318.15 K and 333.15 K, increased solid recoveries from 89.4% to 95.20%, and to 95.40% are evident. Therefore, a leaching process of NdFeB magnets performed at 333.15 K is favourable. According to Ni'am et al. (2019), the optimal temperature for a similar leaching process is 338 K.

The influence of time was determined using 30- and 60-minute leaching times. The solid recovery increased from 89.4% to 91.62%. Therefore, longer times were more favourable for leaching since particles have more contact time to react in solution. The stirring speed was set to 333 rpm and kept constant during the experiments as its influence was not studied in this work. However, Ni'am et al. (2019) reported an effective stirring rate of 800 rpm as an optimal stirring speed, based on the data obtained for 600, 800 and 1000 rpm.

Figures 1 and 2 present the reaction temperature versus time for varying acid concentrations using particle size 425-500 µm and reaction temperature versus time for varying particle size in 2.2M nitric acid, respectively. It can be observed that a sharp increase in temperature occurs within five minutes for all reactions, indicating an exothermic reaction. In these experiments with varying nitric acid concentrations, the highest peak in temperature was observed at 12.3M nitric acid due to its high oxidizing ability.

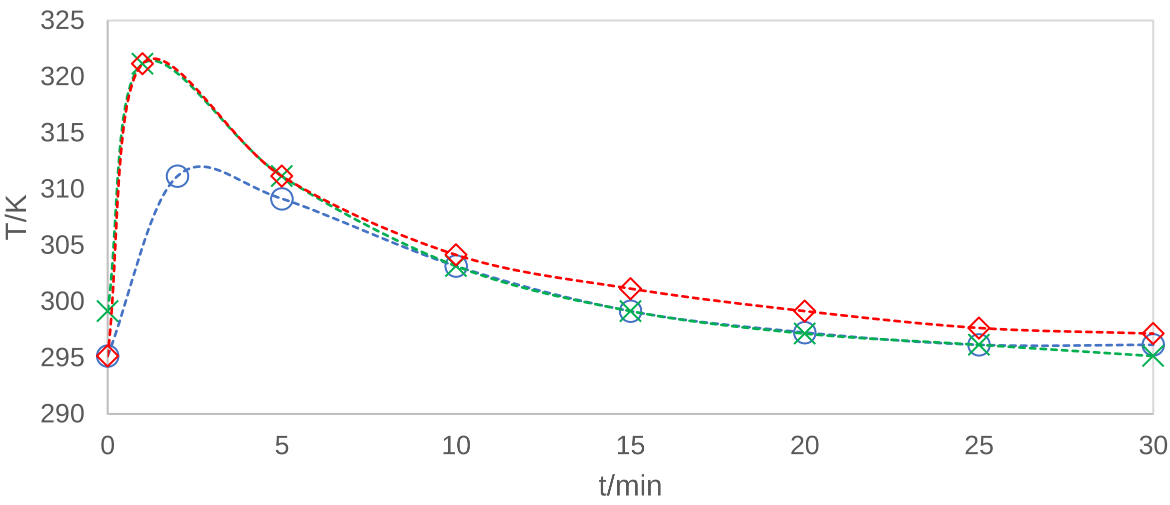

Figure 1: Reaction temperature versus time for varying acid concentrations using particle size 425-500µm (□ – 2.2M HNO_3, ▲ – 6.7M HNO_3, ×– 12.3M HNO_3).

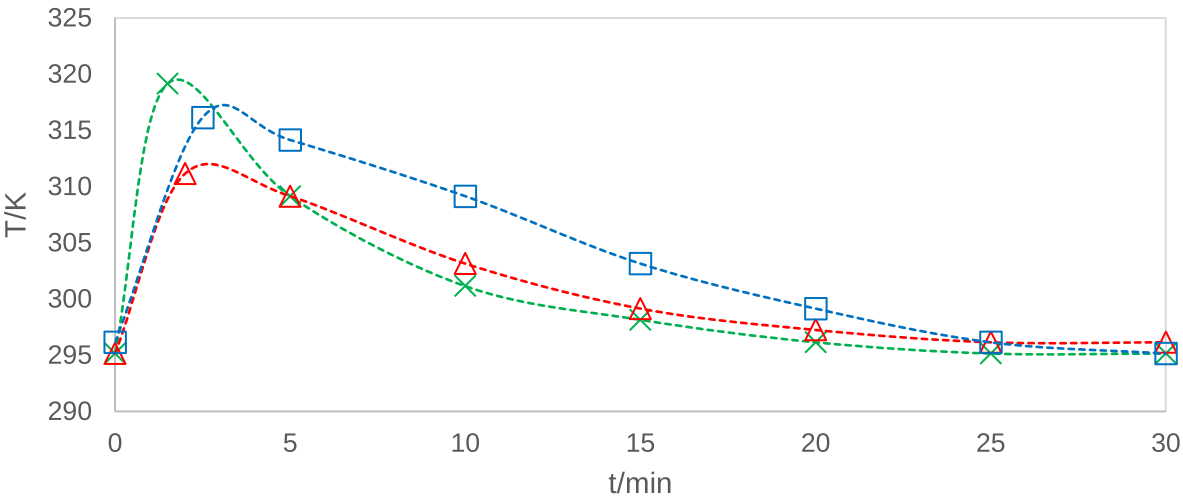

Figure 2: Reaction temperature versus time for varying particle size in 2.2M nitric acid (× – 100 - 150 µm, Δ– 425 – 500 µm, □ – ≥ 600 µm).

The mole fraction of Fe^{3+} and Nd^{3+} ions obtained by the ICP-OES analysis was found to change slightly over the leaching period, as seen in Table 7. The maximum amounts of metal ions were obtained within the first 20 minutes of the leaching process. This is in accordance with the temperature-time graphs in Figures 1 and 2, which showed that the exothermic reaction occurs within the first 5 minutes of the leaching process, increasing the system temperature. At 10 minutes, the temperature of the pregnant leach solution is approximately 303.15 K and high solubility of both iron and neodymium were observed. After 10 minutes, the temperature of the solvent decreased and reached 298.15 K. Samples taken at the 30-minute time interval show a decrease in the mass of metal ions obtained. This suggests that the solubility of the metal ions increases when the solvent is at 303.15 K and decreases when the solvent reaches 298.15 K.

Table 7: Concentrations (g/L) and mole fractions (x) of Fe^{3+} and Nd^{3+} ions in the pregnant leach solution of particle size test. 2.2M HNO_3, T = 298.15 K, t = 30 min.

Time/min	C_{Fe} /g/L	C_{Nd} /g/L	x_{Fe}	x_{Nd}
Particle size 100-150 µm				
10	15.740	7.101	0.851	0.149
20	18.198	8.726	0.851	0.149
30	15.514	7.140	0.853	0.147
Particle size 425-500 µm				
10	18.244	7.654	0.860	0.140
20	14.790	6.762	0.860	0.140
30	17.723	7.658	0.862	0.138
Particle size ≥600µm				
10	15.570	7.168	0.849	0.151
20	16.032	7.412	0.849	0.151
30	14.702	6.723	0.849	0.151

Behera et al. (2016) reported an increase in Nd^{3+} extraction from 83.74% to 99.9%, with a particle size decrease from 151-180µm to 25-45µm after 240 minutes in 0.15M HCl solution. However, the extraction of Fe decreased from 62.91% to 60.24%. Sahin et al. (2017) conducted leaching tests on slag powders of nickel-metal hydride batteries using the ionic liquid 1-methylimidazolium hydrogen sulfate [HMIM][HSO_4]. The sample was ground and sieved to obtain two particle-size fractions: 63-90µm and 90-125µm. The slag powders contained REEs such as Nd, La, Ce, and Y with a total composition of 22.5 wt%. Small particles (63-90µm) had more efficient dissolution of Nd with a maximum efficiency of 15 wt% at 338.15 K after 2 hours.

In this work, the highest leaching efficiencies of 0.151 mole fraction (31.4 wt%) of the Nd^{3+} ions for the particle size tests were obtained for particles ≥600 µm using 2.2M HNO_3 at 298.15 K for 30 minutes. It is therefore deduced that further crushing of WPM may not be required.

Table 8: Concentrations (g/L) and mole fractions (x) of Fe^{3+} and Nd^{3+} ions in the pregnant leach solution of acid concentration test. Particle size = 425-500 µm, T = 298.15 K, t = 30 min.

Time /min	C_{Fe} /g/L	C_{Nd} /g/L	x_{Fe}	x_{Nd}
2.2M HNO_3				
10	18.244	7.654	0.860	0.140
20	14.790	6.762	0.860	0.140
30	17.723	7.658	0.862	0.138
6.7M HNO_3				
10	15.663	7.289	0.847	0.153
20	14.453	6.641	0.847	0.153
30	15.276	7.048	0.847	0.153
12.3M HNO_3				
10	18.234	8.317	0.850	0.150
20	16.317	7.706	0.850	0.150
30	13.061	5.905	0.851	0.149

It can be observed from the results in Tables 7 and 8 that by increasing the nitric acid concentration, there was a negligible change in the mole fractions of ions leached into the solution. The neodymium ion mole fraction obtained at the 20- and 30-minute intervals were higher than those observed using 2.2M nitric acid. This further supports that increasing the nitric acid concentration makes the metal ions more stable in the solution at 298.15 K. However, the effect of temperature still holds since the mole fraction obtained at 10 minutes were higher than those seen at 20 at 30 minutes. Since the ratio of metals leached remains constant at every interval, the differences can be attributed to solubility effects due to temperature and acid concentration. The mole fraction observed for Nd^{3+} using a 12.3M nitric acid solution in Table 8 was higher than 2.2M nitric acid but lower than the 6.7M nitric acid concentration results. As a result of the exothermic reaction, an increase in temperature under 10 minutes favoured the solubility and leaching of metals because of the use of a concentrated acid solution. The use of concentrated acid generates toxic fumes and can be highly exothermic. Hence, leaching can be optimized using lower concentrations of acid at higher temperatures. This promotes greener leaching processing and is less hazardous to work with in laboratory and industrial workspaces. Therefore 6.7M nitric acid has been recognized as the optimal nitric acid concentration.

The effect of temperature on leaching is further affirmed by tests conducted at 318.15 K and 333.15 K, shown in Table 9. Since the temperature of the mixture was maintained during experiments in the leaching process, the solubility of the metals remained constant over time. This shows that by using a low concentration of acid and increasing the temperature, the leaching process for Nd can be optimized to achieve higher efficiencies.

Table 9: Concentrations (g/L) and mole fractions (x) of Fe^{3+} and Nd^{3+} ions in the pregnant leach solution of temperature test. Particle size = 425-500 µm, 2.2M HNO_3, t = 30 min.

Time /min	C_{Fe} **/g/L**	C_{Nd} **/g/L**	x_{Fe}	x_{Nd}
T = 318.15 K				
10	16.284	7.654	0.846	0.154
20	14.087	6.762	0.846	0.154
30	15.950	7.658	0.846	0.154
T = 333.15 K				
10	15.913	7.455	0.846	0.154
20	15.926	7.453	0.846	0.154
30	16.929	7.864	0.846	0.154

It can be observed in Table 9 that leaching performed at 298.15 K for 60 minutes shows a higher Nd^{3+} recovery than those conducted for 30 minutes shown in Table 7. Leaching of Nd occurs at a lower rate after 30 minutes since the rate of reaction approaches zero. However, higher recoveries can be achieved at the end of the extended period. The decreasing trend of iron leaching can be attributable to its precipitation at increased leaching durations.

Table 10: Concentrations (g/L) and mole fractions (x) of Fe^{3+} and Nd^{3+} ions in the pregnant leach solution of contact time test. Particle size = 425-500 µm, 2.2M HNO_3, T = 298.15 K.

Time /min	C_{Fe} **/g/L**	C_{Nd} **/g/L**	x_{Fe}	x_{Nd}
30	14.972	6.893	0.849	0.151
50	15.114	6.987	0.849	0.151
60	15.883	7.436	0.849	0.151

Table 11 shows the leaching recoveries obtained over 5 hours. A trend was observed with Nd recoveries increasing over time and Fe decreasing over time. The enhanced leaching time favours the leaching of neodymium into solution. The result obtained for 300 minutes are not fitting the trend and can be recognized as an outlier.

Table 11: Concentrations (mg/L) and mole fractions (x) of Fe^{3+} and Nd^{3+} ions in the pregnant leach solution of contact time test. Particle size = 425-500 µm, 12.3M HNO_3, T = 298.15 K.

Time /min	**C_{Fe} /mg/L**	**C_{Nd} /mg/L**	**x_{Fe}**	**x_{Nd}**
60	22.827	19.527	0.751	0.249
120	17.101	10.649	0.751	0.249
180	13.646	4.861	0.746	0.254
240	11.276	5.408	0.735	0.265
300	19.495	14.838	0.726	0.274

CONCLUSIONS

The leaching conditions used in this study allowed for high recovery of Nd^{3+} from waste permanent magnet powder obtained from discarded desktop HDD NdFeB magnets, exceeding 99%. The demagnetization process was successfully performed at a temperature of 673.2 K over 30 minutes followed by crushing and particle size distribution.

Optimal leaching conditions were determined following a thorough analysis of the ICP-OES results based on the conditions and factors used in this experiment. The optimal leaching conditions for WMP powder were obtained using 6.7M nitric acid, a temperature of 333.15 K and a leaching time of 60 minutes with a solid recovery rate above 99%. In terms of Nd^{3+} ions, the highest mole fraction is reported at leaching conditions achieved using a particle size of 425-500µm, 12.3M nitric acid concentration, and a temperature of 298.15 K, and a leaching time of 240 minutes. Mole fractions of 0.735 and 0.265 of Fe^{3+} and Nd^{3+} are reported at these conditions, respectively.

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