UNIVERSITY OF
KWAZULU-NATAL

URBAN MINING OF RARE EARTH METALS FROM RARE EARTH MAGNETS

HYDROMETALLURGICAL PROCESSING

ENCH4LA

LABORATORY PROJECT

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Statement of Authorship

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Abstract

The recovery of rare earth metals from waste electrical and electronic equipment is essential in minimizing the global dependence on freshly mined rare earths. An increased demand of rare earths for modern technologies has created special workspaces for the management of associated solid wastes. This work investigated a hydrometallurgical leaching process with nitric acid for the recovery of neodymium from neodymium-iron-boron magnets of discarded hard disk drives. The hard disk drives were manually dismantled and the NdFeB magnets were removed, demagnetized and comminuted. Batch experiments were conducted to optimise the leaching operating conditions with respect to particle size, concentration of acid, temperature and time. The optimal leaching parameters were for a particle size of 100-150µm, 30% nitric acid concentration, temperature of 60 °C and leaching time of 60 minutes, with a neodymium and iron composition of 31.84% and 68.16% respectively.

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1. Introduction

1.1 Overview

Rare earths refer to 17 chemically similar elements, including scandium, yttrium, lanthanum, and the 14 lanthanides in the periodic table of elements (Binnemans et al., 2013). Alloys of rare earths and transition metals such as nickel, iron, and cobalt produce permanent magnets (Xie et al., 2014). Technological development has increased the demand for Neodymium-Iron-Boron (NdFeB) permanent magnets in electrical and electronic equipment. China gained global dominance in the rare earth industry during the 1990s, supplying approximately 90% of metal alloys and 75% NdFeB magnets (Alon et al., 2014). In 2006, rare earths prices increased worldwide (figure 1) as China began to restrict rare earth exports (Alon et al., 2014). Hence, businesses and governments consider rare earths strategic resources (Rademaker et al., 2013). Governments have provided funding and improved policies to address the import dependence of rare earths (Rademaker et al., 2013).

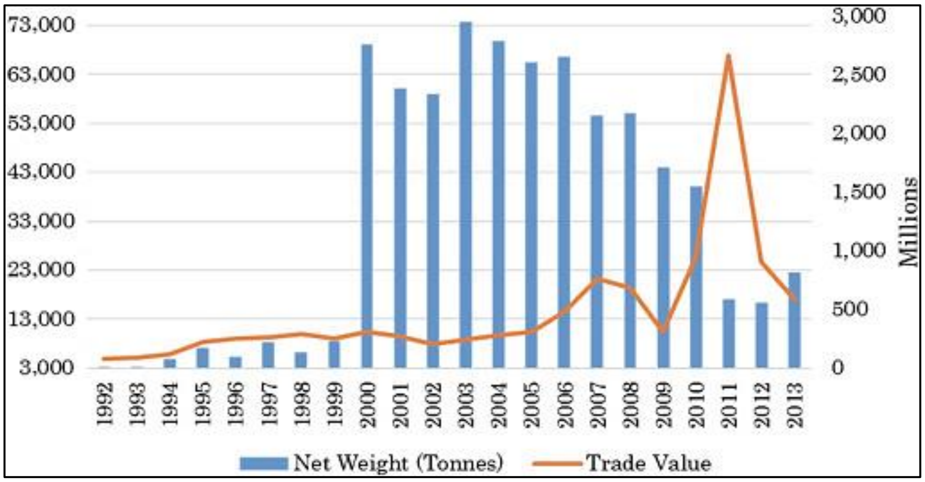

Figure 1: Chinese rare earth export restrictions (Mancheri, 2015) ✓

Rare earths occur at low concentrations in the Earth's crust (Xie et al., 2014). Hence, the exploitation of mineral deposits is economically intensive. Higher concentrations of rare earths are found in waste electrical and electronic waste (WEEE), making recycling an attractive sourcing alternative (Karal et al., 2021). Urban mining recycles valuable metals from WEEE through recovery processes such as hydrometallurgy (Lee et al., 2017), electrometallurgy (Venkatesan et al., 2018), chemical vapor transport (Firdaus et al., 2016), pyrometallurgy (Bian et al., 2015), and hydrogen decrepitation (Akhtar et al., 2010). The life cycle of NdFeB magnets ranges from 2-3 ✓

years in consumer electronics, such as hard disk drives, to 20-30 years in wind turbines (Tunsu, 2018). Hence, recycling NdFeB magnets from consumer electronics is essential to minimize global dependence on freshly mined ores (Yang et al., 2017). ✓

1.2 Problem identification

Rare earth elements have emerged as the most critical raw material group (Xie et al., 2014). Their increased use in electrical and electronic products has raised concerns about the responsible management of associated solid wastes. A national ban on WEEE to landfill sites, effective from August 2021, increases the demand for economically viable commercial processes to recycle rare earths (Sadan, 2019). There are no operational commercial processes to implement the recycling of rare earths (Gruber and Carsky, 2020). Hence, research is underway to optimize recycling techniques that are sustainable and have low environmental impacts (Reisdörfer et al., 2019).

1.3 Scope of project

1.3.1 Aim

This study aimed to optimise the extraction of neodymium from NdFeB magnets via hydrometallurgical leaching.

1.3.2 Objectives

The objectives of the study were to:

- Perform laboratory-scale testing of the leaching process by:
    - Varying the particle size of rare earth magnets.
    - Assessing the effect of varying concentrations of nitric acid.
    - Varying the temperature of the mixtures.
    - Measuring the effect of contact time on the leaching of NdFeB powders in solution.
    - Quantitatively analysing the chemical composition of the leachate by inductively coupled plasma - optical emission spectrometry (ICP-OES). ✓
- Assess and compare different extraction processes.

2. Literature review

2.1 Neodymium-Iron-Boron magnets

Neodymium-containing permanent magnets are tetragonal alloys of neodymium, iron, and boron, (Karal et al., 2021). The general composition of NdFeB permanent magnets vary based on the application of the magnets (Tunsu, 2018). Several elements may be added or removed to enhance specific properties. An electrochemical layer of nickel or plastics is often coated to the surface of magnets (Gruber and Carsky, 2020). Some iron may be replaced by cobalt (1-2%) to improve corrosion properties (Lee et al., 2017). Nd is partially substituted with praseodymium (Pr) and dysprosium (Dy) to improve Curie temperature and coercivity, respectively (Yang et al., 2017). NdFeB magnets are used more than samarium-cobalt magnets due to lower costs and higher magnetic field strengths (Xie et al., 2014). The United States Department of Energy reported that the five elements with the greatest supply risks are neodymium (Nd), europium (Eu), terbium (Tb), dysprosium (Dy), and yttrium (Y). Hence, the collection and recycling of NdFeB magnets are significant to meet the growing demand in the industry (Chu, 2011).

i. Applications

NdFeB magnets have applications in products requiring high strength, intensive energy, and high coercive forces (Xie et al., 2014). Such applications include electrical motor manufacture, renewable energy, technology, and medical science (Xie et al., 2014). The quantity of magnet materials used in different applications varies from milligrams in consumer electronics to kilogram ranges in electric vehicles and wind turbine generators (Tunsu, 2018). Hard disk drives (HDDs) are an important secondary source for rare earths since they contain significant amounts of NdFeB magnets. HDDs have 1-30 g of NdFeB magnet with a neodymium and dysprosium content of approximately 31% and 4-7%, respectively (Erust et al., 2019).

2.2 Recycling techniques

Binnemans et al. (2013) reported three ways of maintaining the supply of rare earth elements (REEs): (1) re-establish old mines; however, considerable time would be necessary; (2) consider substituting the most critical REEs with cheaper REEs or by d-group metals and (3) recycle REEs from WEEE or production wastes, known as end-of-life (EoL) products. Recycling is a promising technique to mitigate the prospective risk of a shortage of REEs (Reisdörfer et al., 2019).

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Erust et al. (2019) characterized the recycling industry by a pyramid structure, with the most significant step of the pyramid constituting the collection, pre-treatment, and manual separation steps of WEEE. A small number of companies ultimately recover the REEs from WEEE through smelting and refinery (figure 2).

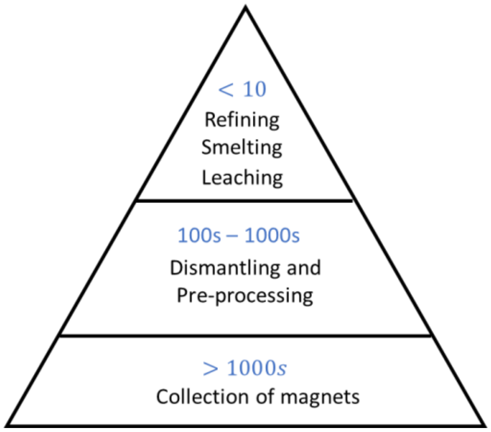


Figure 2: Number of companies in the WEEE recycling industry (interpreted from Erust et al. (2019))

2.2.1 Magnet-to-magnet approach

A magnet-to-magnet approach refers to the production of new magnets from spent magnets. It involves collecting spent NdFeB magnets, cleaning, pre-treatment such as comminution, and the addition of approximately 3% fresh REEs to create the NdFeB sintered block (Jin et al., 2016). Size reduction, coating, and re-magnetization processes are similar to primary production methods (Jin et al., 2016). This technique recovers approximately 90% of REEs with less than 5% feedstock from freshly mined rare earths (Jin et al., 2016). However, these methods have not produced magnets of the same quality. NdFeB from part of a wide range of applications, such as traction engines, wind turbines, servomotors, magnetic separators, and other devices (Nlebedim and King, 2018). Hence, direct mechanical methods are dissatisfactory due to the non-uniform composition.

2.2.2 Pyrometallurgy

Pyrometallurgical methods involve converting REE magnet alloys into oxides, chlorides, or fluorides, followed by reduction to metallic form (Binnemans et al., 2013). This technique is primarily used in the processing of high-grade ores (Tunsu, 2018). High processing temperatures create phase change, enabling the separation of REEs from the non-REE fraction (Yang et al., 2019). The concentrated REE fraction can be reduced to metallic form by metallothermic reduction or molten salt electrolysis (Yang et al., 2019). Pyrometallurgy has been used to recover precious metals and non-ferrous metals from WEEE (Cui and Zhang, 2008). However, significant drawbacks include high energy requirements, low selectivity, and significant environmental impacts (Tunsu, 2018).

2.2.3 Hydrometallurgy

Hydrometallurgical processing is a widely used technique for recovering REEs, and their compounds from NdFeB magnets scrap by acid dissolution (Gruber and Carsky, 2020). Leaching processes are favoured due to low energy consumption, waste generation, and gas emissions. The process is adaptable, enabling reagents with lower environmental impacts (Reisdörfer et al., 2019). The main disadvantages are high emissions of toxic gases and the generation of large volumes of acidic liquid effluents in an industrial-scale application (Gruber and Carsky, 2020). Hydrometallurgical processes are predominantly based on inorganic or mineral acids such as hydrochloric, nitric, and sulfuric acids since good leaching recoveries are obtained. The first stage operation in the extraction of REEs from waste NdFeB magnets includes the physical processes of demagnetization, crushing, and grinding to get magnet powders (Erust et al., 2019). The chemical process is initiated by leaching the NdFeB magnets with various acids (Erust et al., 2019). Leaching is affected by the particle size of magnets, concentration of acid, temperature of the solution, and contact time for leaching (Lee et al., 2017). A schematic of the process is depicted in figure 3.

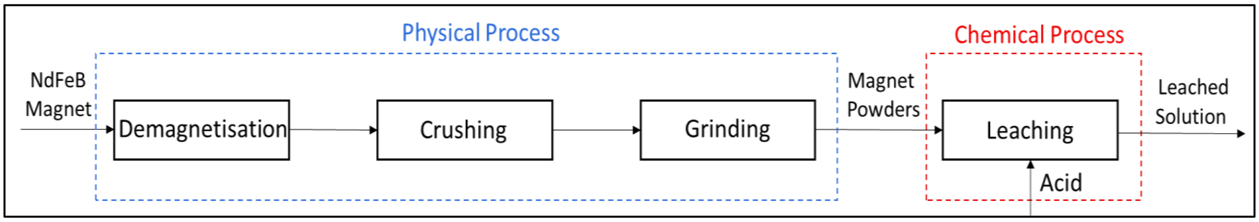
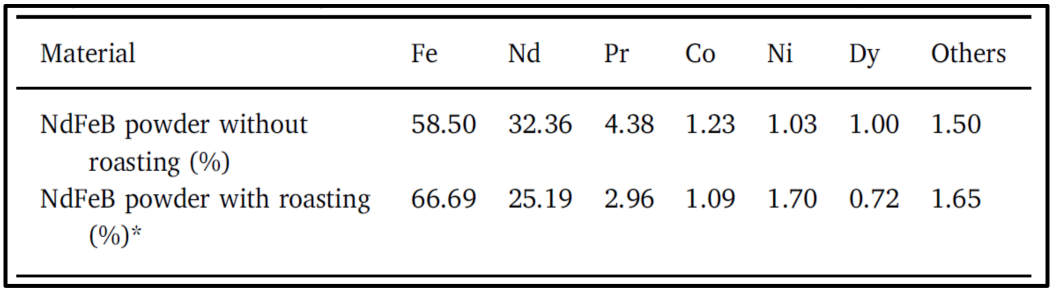


Figure 3: Flow diagram of physical and hydrometallurgical processing of NdFeB magnets (Erust et al., 2019).

2.2.3.1 Chemical characterization of NdFeB magnets

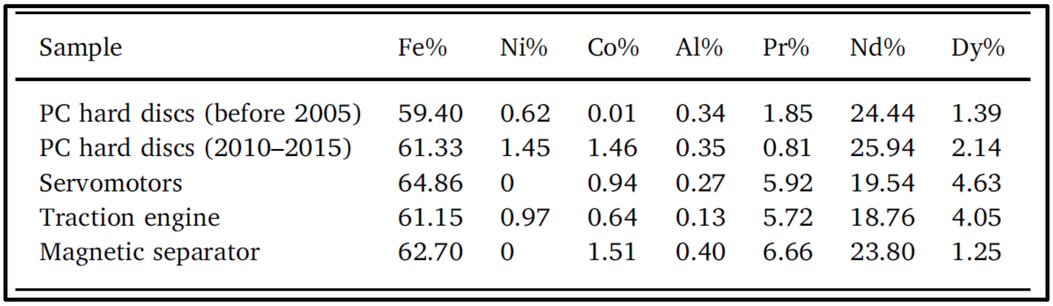
Reisdorfer et al. (2019) characterized roasted and unroasted NdFeB magnet powders sourced from hard disk drives (figure 4). Roasting is performed at high temperatures to convert the elements in the sample into oxides. This enhances the selectivity of Nd in the leaching procedure. Unroasted

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 mass spectrometry (ICP) (figure 5).



Material	Fe	Nd	Pr	Co	Ni	Dy	Others
NdFeB powder without roasting (%)	58.50	32.36	4.38	1.23	1.03	1.00	1.50
NdFeB powder with roasting (%)*	66.69	25.19	2.96	1.09	1.70	0.72	1.65

Figure 4: Chemical characterization of roasted and unroasted NdFeB powders, extracted from (Reisdörfer et al., 2019)

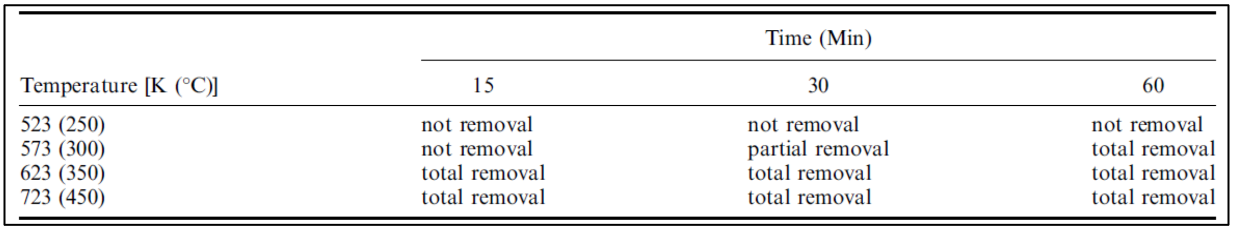


Sample	Fe%	Ni%	Co%	Al%	Pr%	Nd%	Dy%
PC hard discs (before 2005)	59.40	0.62	0.01	0.34	1.85	24.44	1.39
PC hard discs (2010–2015)	61.33	1.45	1.46	0.35	0.81	25.94	2.14
Servomotors	64.86	0	0.94	0.27	5.92	19.54	4.63
Traction engine	61.15	0.97	0.64	0.13	5.72	18.76	4.05
Magnetic separator	62.70	0	1.51	0.40	6.66	23.80	1.25

Figure 5: Chemical composition of NdFeB magnets, extracted from (Gruber and Carsky, 2020)

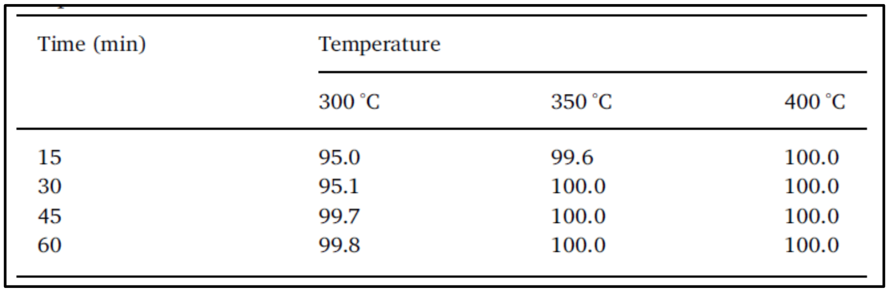
2.2.3.2 Demagnetization

Demagnetisation facilitates the handling of NdFeB magnets (Reisdörfer et al., 2019). The crushing of electrical waste generates creep magnets that bond to the surface of all ferrous particles (Bandara et al., 2015). They cannot be removed from the ferrous fraction in this state and are consequently lost. The magnet containing ferrous fraction must be heated beyond the curie temperature (loss of magnetic properties by heat) of NdFeB magnets (Bandara et al., 2015). The magnetic properties of NdFeB magnets are then lost and can be magnetically separated from iron. Hence, demagnetization must be conducted before comminution. Reisdorfer et al. (2019) and Lee et al. (2013) investigated the demagnetization of NdFeB magnets from hard disk drives and scrap, respectively. A heating method was adopted, using different temperatures and times. Lee et al. (2013) used a temperature range of 250-450 and 15, 30, and 60 minutes intervals (figure 6). The optimal temperature reported was 350 for 15 minutes. Reisdorfer et al. (2019) reported on the percentage removal of magnetism at temperatures between 300 and 400 for times 15, 30, 45, and 60 minutes (figure 7). At 350, a period of 15 minutes was insufficient for complete demagnetization, while total loss of magnetism occurred after 30 minutes. Dissimilarities in results are attributable to variations in the composition of NdFeB magnets of different applications. A gauss meter was used to evaluate the elimination of magnetism. Erust et al. (2019) and Karal et al. (2020) heated NdFeB magnets from hard disk drives for 30 minutes to ensure complete demagnetisation since optimization studies were not undertaken.



	Time (Min)		
Temperature [K (°C)]	15	30	60
523 (250)	not removal	not removal	not removal
573 (300)	not removal	partial removal	total removal
623 (350)	total removal	total removal	total removal
723 (450)	total removal	total removal	total removal

Figure 6: Time and temperature effect on demagnetization, extracted from (Lee et al., 2013)



Time (min)	Temperature		
	300 °C	350 °C	400 °C
15	95.0	99.6	100.0
30	95.1	100.0	100.0
45	99.7	100.0	100.0
60	99.8	100.0	100.0

Figure 7: Percentage removal of magnetism from NdFeB magnets at varying times and temperatures, extracted from (Reisdörfer et al., 2019)

2.2.3.3 Leaching

Leaching is a well-established extractive metallurgical technique that uses aqueous media to convert metals into soluble salts. Lee et al. (2013) conducted batch experiments to optimize leaching conditions with solid/liquid ratio, leaching temperature, the concentration of reagent, and leaching time. The study focused on recovering high purity Nd from NdFeB magnet scrap by varying the leaching conditions. Erust e al. (2019) investigated the leaching recovery of Nd and

Dy from NdFeB magnets sourced from hard disk drives, using inorganic and organic acids at different concentrations. Leaching recoveries were determined using the following equation:

$$\text{Leaching recovery (\%)} = \frac{w_1}{w_t} \times 100 \tag{1}$$

Where w_1 is the amount of metal leached by acids and w_t is the initial weight of metal available for leaching.

2.2.3.4 Effect of leaching variables

2.2.3.4.1 Time

Lee et al. (2013) studied the effect of time on the leaching of NdFeB magnet powders (297 at 27 with 6N HCl and H_2SO_4. Initially, sulfuric acid was observed to be the more effective leaching reagent. However, maximum recovery of metal ions was reported at 10 minutes for both reagents. Accordingly, 15 minutes was chosen as the best leaching time to ensure complete impregnation. The effect of 1-3 M nitric acid was investigated by Erust et al. (2019) with NdFeB particle sizes below 500 . The highest leaching efficiencies of Nd and Dy with nitric acid were approximately 85% and 97.6%, respectively, after 15 minutes. Leaching efficiencies with sulfuric acid were consistent with results reported by Lee et al. (2013). However, the maximum recovery obtained with HCl was about 85%. Parhi et al. (2016) performed a leaching time variation study with a time interval of 15 minutes to 360 minutes, using the following conditions: 0.15 M HCl, particle size of 76-105 and a temperature of 30. After 240 minutes, maximum recoveries of 94% Nd were obtained.

2.2.3.4.2 Particle size

Parhi et al. (2016) reported an increase in Nd extraction from 83.74% to 99.9% with a particle size decrease from 151-180 to 25-45 after 240 minutes. However, the extraction of iron decreased from 62.91% to 60.24%. Sahin et al. (2017) performed ionic liquid leaching of nickel-metal hydride batteries, with two particle size fractions, 63-90 and 90-125. Slag powders contained rare earths such as neodymium, lanthanum, cerium, and yttrium with a total composition of 22.5 wt%. Small particles (63-90) had more efficient dissolution of neodymium with a maximum efficiency of 15% at 65 after 2 hours. The effect of different particle sizes on the leaching efficiencies of

NdFeB magnets from hard disk drives has not been reported, using nitric acid as the leaching reagent.

2.2.3.4.3. Concentration of acid

Erust et al. (2019) leached NdFeB alloy powders by inorganic and organic reagents in the range of 1-3 M with a pulp density of 20g/L at 27. Inorganic acids had a shorter leaching time of 15 minutes, while organic acids had a leaching time of 300 minutes. A similar leaching efficiency of Nd was obtained with sulfuric acid and nitric acid at concentrations of 2 and 3M. However, sulfuric acid was the most effective inorganic acid for the leaching of Nd at all acid concentrations tested. Lee et al. (2013) determined the leaching recovery using 6N sodium hydroxide and inorganic acids at 27. Sodium hydroxide was ineffective in recovery the metals present. All inorganic acids recovered 100 % of Nd and Fe. However, further investigations of time and acid concentration were performed using sulfuric acid and hydrochloric acid. Organic acids are promising alternatives to inorganic reagents. The most common green solvents used for hydrometallurgical processes include acetic, citric, and oxalic acids. Organic acids are environmentally friendly since they readily degrade and have low toxic gas emissions. Acetic acid has been recognized as the most effective reagent for leaching rare earths and metals from secondary sources.

2.2.3.4.4. Temperature

Leaching recoveries of NdFeB magnet powders were determined by Lee et al. (2013) at 27 and 70. A maximum recovery of 100% Nd and Fe were achieved at both temperatures. Other studies by Parhi et al. (2016) and Behera et al. (2016) reported that Nd recovery efficiencies increased from 92.12% to 99.99% when the temperature changed from 35 to 80 with 0.4 M acetic acid after 6 hours.

2.2.3.5 Leaching reaction mechanisms

Neodymium metal readily dissolves in dilute acids and forms Nd(III) with the liberation of hydrogen gas. Similar reactions occur with iron and boron.

$$Nd_{(s)} \quad + \quad H^{+}_{(aq)} \qquad Nd^{3+}_{(aq)} \quad + \quad H_{2(g)} \quad + \quad _{(aq)} \qquad (2)$$

$$Fe_{(s)} \quad + \quad H^{+}_{(aq)} \qquad Fe^{2+}_{(aq)} \quad + \quad H_{2(g)} \quad + \quad _{(aq)} \qquad (3)$$

$$B_{(s)} \quad + \quad H^{+}_{(aq)} \qquad B^{3+}_{(aq)} \quad + \quad H_{2(g)} \quad + \quad _{(aq)} \qquad (4)$$

3. Experimental

a. Materials

Hard disk drives of various brands and models were sourced from computers at the University of KwaZulu-Natal. The chemical characterisation of NdFeB magnets reported by Gruber & Carsky was used in this work. Table 1 shows the purities and chemical suppliers of the solutes and solvents used. Nitric acid (55% AR) and de-ionized water were used to prepare 30% and 10% nitric acid solutions for the leaching process. A potassium hydrogen phthalate primary standard was prepared to standardise sodium hydroxide. The concentrations of the nitric acid solutions were validated by titrating against standardised sodium hydroxide.

Table 1: Material purities and Suppliers

Component	**Chemical Formula**	**Molecular Weight (g/mol)**	**CAS number**	**Supplier**	**Mass fraction purity**
Nitric acid	HNO_3	63.01	7697-37-2	Merck	0.55
Sodium hydroxide	$NaOH$	40	1310-73-2	Merck	0.98
Potassium hydrogen phthalate (KHP)	$C_8H_5O_4K$	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
De-ionized water	H_2O	18.02	7732-18-5	-	0.99

i. Preparation of 30% and 10% nitric acid solution

Nitric acid solution (12.33 M, 55%) was used to prepare 1000 ml of 6.73 M (30%) and 2.24 M (10%) nitric acid solution. First, approximately 546 ml of 12.33 M nitric acid solution was added to a 1000 ml volumetric flask using pipettes of different sizes (500 ml, 20 ml, and 2 ml). Then, the solution was diluted up to the graduation mark of the flask using de-ionized water. Similarly, 182 ml of 12.33 M nitric acid solution was used to prepare 1000 ml of 2.24 M nitric acid solution.

3.1.2 Standardization of sodium hydroxide using potassium hydrogen phthalate

An Ohaus Pioneer analytical mass balance (mass readability = 0.001 g) was used to weigh approximately 5.105g of potassium hydrogen phthalate powder. The mass was transferred to a 50 ml volumetric flask using a funnel. The flask was filled to the graduation mark using de-ionized water to obtain 0.5 M solution. Approximately 10 g of sodium hydroxide pellets were added into a 250 ml volumetric flask. The flask was filled with de-ionized water to the graduation mark to prepare 1 M sodium hydroxide solution. Three conical flasks were cleaned and rinsed with de-ionized water. Thereafter, 15 ml aliquots of primary standard KHP solution were pipetted into each of three Erlenmeyer flasks. About four drops of phenolphthalein indicator were added to each flask. Next, a 50 ml burette was rinsed and prepared with the 1 M NaOH solution. Each aliquot of KHP was titrated against NaOH until the solution turned pink. The volume of NaOH dispensed was recorded to 0.02 ml. An average of three volume measurements was used to calculate the concentration of the NaOH solution. ✓

3.1.3 Determination of the pH of 55%, 30%, and 10% nitric acid solution

A burette was rinsed and prepared with the NaOH solution. Three conical flasks were prepared with 2 ml of 2.24 M nitric acid solution. Approximately four drops of phenolphthalein indicator were added to each flask. Each aliquot of nitric acid was titrated against sodium hydroxide until the solution maintained a permanent pink colour. The volume of NaOH dispensed was recorded to 0.02 ml. An average of three volume measurements was used to calculate the concentration of the nitric acid solution. Similarly, the concentration of 6.73 M and 12.33 M nitric acid solution was calculated. The concentrations of each nitric acid solution were used to obtain the pH of each solution. ✓

3.2 Equipment and procedure

3.1.1 Manual dismantling

HDDs were manually dismantled to remove the NdFeB magnets attached to aluminium support. Next, a heavy-duty IRWIN Record Bench Vice was used to clamp the magnets in position. Finally, a Ball Peen hammer and chisel were used to remove the aluminium supports. The remaining components were dispatched for waste treatment. ✓

3.1.2 Demagnetisation

Demagnetisation was performed by the heating method. The magnets were fed into a preheated furnace (Scientific 909) at 400. After 30 minutes, the furnace was turned off and left to cool for 20 minutes. The magnets were then removed using safety gloves and placed on sand lime bricks to cool at 25. The elimination of magnetism was evaluated by bringing the NdFeB magnet sample into close contact with magnetic material. ✓

3.1.3 Comminution

The demagnetised NdFeB permanent magnets were comminuted batch-wise in a roller mill (model 123032). Magnets were separated according to different sizes. The distance between rollers was adjusted to accommodate magnets of different sizes. Two to three magnets were loaded into the roller at a time. The crushed sample was screened by laboratory test sieves (apertures 100 , 150, 200, 300, 355 , 425, 500 and 600) to investigate the grinding efficiency. Magnets greater than 600 were further crushed until adequate amounts of the desired particle size ranges (100 -150, 425-500) were obtained.

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3.3 Leaching

The extraction of rare earth metals from rare earth magnets were tested using nitric acid. Operating parameters and conditions adopted in this leaching study are summarized in Table 1.

Table 2: Leaching operating parameters and conditions

Leaching Reagent	**Particle Size (**	**Concentration (M)**	**Temperature ()**	**Time (min)**	**Solid/Liquid Ratio (g/ml)**
HNO3	100 – 150	2.24	25	30	0.02
	425 – 500	6.73			
		12.33			

✓

Control measurements are particle size = *425-500* , nitric acid concentration = *2.24 M*, temperature = *25* and time = *30 min* (Erust et al., 2019).

Several borosilicate glass beakers were prepared with 50 ml of 2.24 M nitric acid and approximately 1 g of crushed magnet sample of the desired particle size range. The temperature of the solution was monitored using an alcohol thermometer (temperature readability 0.1). A magnetic stirrer bar was placed inside the beakers and the beakers were placed on magnetic plates (FMH STR-MH140) operating at 333 rpm and room temperature (~25. Stirring was set at a moderate rate to ensure thorough mixing but prevent spilling of the solution. Approximately 6 ml of the leached solution was sampled at 10 - minute intervals using a syringe and, injected through a microfilter into sample vials. The leaching experiment was terminated after 30 minutes. A gravimetric filtration set-up was used to separate the mother liquor and unleached✓ solids, which were used to obtain leaching recoveries. Leaching experiments using control measurements were performed in duplicate to determine the repeatability and reproducibility of results and, evaluate the errors and uncertainty in measurements. The concentration of Nd and Fe in the leached samples and mother liquor were analysed by ICP-OES.

3.4 Calibrations and Uncertainties

The standard uncertainties of composition and temperature in table 2 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 level of confidence 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 *xi (xi)*	0.18[a]	Rectangular
Correlation of Nd calibration *(xi)*	3.5[a]	Rectangular
Correlation of Fe calibration *(xi)*	1.1[a]	Rectangular
Pipette uncertainty	0.05[b]	Rectangular
Burette uncertainty	0.03[b]	Rectangular
Temperature		
Alcohol thermometer ()	0.05[b]	Rectangular
Temperature measurement repeatability ()	0.7[a]	Rectangular

[a] Estimate treated as a type A distribution

[b] Estimate treated as a type B distribution

4. Results and Discussion

This work aimed to provide an early assessment of the hydrometallurgical leaching of NdFeB magnets from HDDs in aqueous inorganic media. Comprehensive leaching experiments involving NdFeB magnets were conducted in the literature, however limited studies were performed using nitric acid and HDDs. Hence it was chosen for this study. Optimisation of the leaching process will direct further development of the novel recycling technique and improve waste electrical and electronic equipment management. In this study, the key parameters evaluated in the leaching step were particle size, acid concentration, temperature and contact time.

4.1 Demagnetisation

Demagnetisation was performed to facilitate the handling of NdFeB magnets and favour the comminution step. The use of a temperature of 400℃ resulted in complete loss of magnetism after 30 minutes and is consistent with results obtained in literature. Lee et al. (2013) reported that total demagnetization occurred at 350℃ after 15 minutes, while Reisdorfer et al. (2019) found that these conditions were insufficient for full demagnetization. Optimal temperature and time conditions reported by Reisdorfer et al. (2019) were 350℃ and 30 minutes. Therefore, to ensure complete demagnetization, temperature and time conditions of 400℃ and 30 minutes were adopted. After heating, a small quantity of magnets had disintegrated, forming fragments and fine dust. Smaller magnet sizes were observed to be more susceptible to cracking. The surface of most magnets remained metallic silver while the coating of others were removed, exposing blue and grey interior surfaces. The blue powders were indicative of the cobalt present in the magnets to improve corrosion properties.

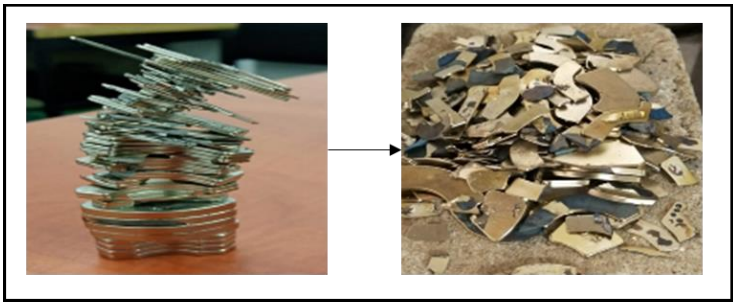

Figure 8: NdFeB magnets before and after demagnetization by the heating method.

4.2 Comminution

The NdFeB magnets obtained were too large to effectively digest in nitric acid, therefore the samples were crushed and screened down to three different particle size ranges. Comminution of the demagnetized magnets were performed using a readily available roller mill (model 123032) to obtain various particle sizes for efficient leaching. This was achieved by feeding the magnets into the roller mill batchwise. Roller mills or crushers are secondary crushing devices commonly used for soft ores and coal. Neodymium magnets are known for being strong magnets with a Vickers hardness value of 343 MPa. Due to strong physical properties of neodymium magnets, the comminution method presented numerous challenges. Firstly, the magnets caused jamming within the mill due to its stability and rigidity. The distance between rollers had to be adjusted to accommodate differences in magnet sizes after demagnetisation. The process overall milling process was time-consuming since the batch feed size was limited to 2 to 3 magnets per run. Particle sizes greater than 600 µm was fed back into the crusher until adequate amounts of the desired particle sizes were achieved.

The physical properties of the magnets, specifically hardness, were affirmed the largest sieve size (600 µm) retained more than 50% of the sample mass. The size distribution of crushed magnets are shown in Table 3. As observed in table 3, the mass fraction of crushed magnets decreased with decreasing sieve sizes indicating that roller mills are more suitable for achieving larger particle sizes. In figure 9, a fairly linear trend of the cumulative mass passing though sieve sizes is observed. The particle sizes were grouped into 3 categories: 100 – 150 µm , 425 – 500 µm and ≥ 600 µm. The selection of particle size 100-150µm was guided by literature. However, disadvantages of small particle sizes includes airborne dust leading to health and safety concerns since NdFeB magnet dust is pyrophoric and toxic. Other health hazards identified, and safety protocols followed are shown in the appendix. A particle size range ≥ 600 µm was used to determine if additional crushing or grinding is required. In practical operations, further crushing would demand for increased equipment to screen down 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. The standard uncertainties for mass measurements were 0.03 g.

Table 3: Size distribution of crushed magnet

Sieve Size (µm)	**Mass retained (g)**	**Mass fraction**	**Cumulative Mass Passes (g)**	**Total Percent Passed (%)**
600	339.273	0.554	273.029	44.591
500	40.878	0.067	232.151	37.914
425	37.242	0.061	194.909	31.832
355	32.685	0.053	162.224	26.494
300	30.386	0.050	131.838	21.532
200	57.498	0.094	74.34	12.141
150	28.789	0.047	45.551	7.439
100	33.857	0.055	11.694	1.910
Pan	11.694	0.019	0	0
Total	**612.302**	**1**	**612.302**	**100**

[b]Standard uncertainties (u) are u (m) = 0.03 g

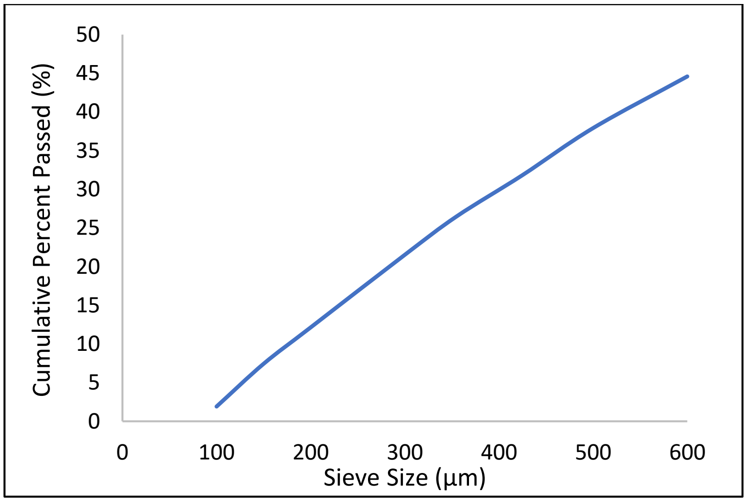

Figure 9: Grain Size distribution curve

4.3 Leaching

Leaching experiments were conducted batchwise with a solid to liquid ratio of 0.02g/ml, to enable accurate comparison to literature. Since the solid to liquid ratio was not an optimisation variable in this investigation, the results of Lee et al. (2013) and Erust et al. (2019) was used to establish an optimal solid to liquid ratio of 0.02 g/ml for the leaching process.

The mass retained in the particle size range of 100 – 150 µm and 425 – 500 µm were 33.857g and 37.242g respectively. Hence to ensure sufficient mass of sample for all experiments, a mass of 1 gram was used for each experiment with 50 ml of nitric acid. Leaching experiments using control measurements were performed in duplicate to quantify and evaluate the errors and uncertainty in measurement. Leaching recoveries were determined by measuring the difference in the mass of NdFeB sample before and after leaching, using equation one.

The leaching recovery results are summarised in table 4. The highest leaching recovery of 99.66% was obtained using a nitric acid concentration of 30%. The results obtained from leaching with varying concentrations of nitric acid indicated an increase in recoveries from 10% to 30% nitric acid with a recovery of 89.4% and 99.66%. However, the recovery decreased to 97% when 55% nitric acid was used. Hence, 30% nitric acid solution has an enhanced oxidising ability and maintains the stability of metal ions in solution. A 55% nitric acid solution has the highest oxidising ability and the lowest pH. However, a decrease in the recovery indicates that the solubility of metal ions were less favourable in such acidic conditions. A similar trend was obtained by Erust et al. (2019) whereby the recoveries increased with increasing concentrations of nitric acid. However, at 10% nitric acid concentration, a recovery of 100% was reported.

The particle size ranges of magnet sample was varied from 100 – 150 µm , 425 – 500 µm and ≥ 600 µm, whilst keeping the remaining control measurements constant. The recovery decreased from 91.04% for (100 – 150 µm) to 89.4% for the range (425 – 500 µm). Hence, lower particle sizes are favourable for leaching. As the particle size decreases, the active surface area of the particle increases, which enhances mass transfer during leaching directing more metal dissolution. These trends are consistent with particle size experiments performed by Parhi et al. (2016) and Sahin et al. (2017).

The influence of temperature was studied at 25°C, 45°C and 60°C, while keeping other factors constant: Concentration of nitric acid of 10%, particle sizes 425 – 500 µm and time of 30 minutes. Increasing temperature from 25°C to 45°C and 60°C increased the leaching recovery from 89.4% and 95.20% to 95.40%. Hence, this indicated an increased reaction rate as the temperature increased. Therefore, a higher temperature of 60°C was favourable for the leaching of NdFeB magnet. The influence of time was determined using 30 and 60 minutes. The leaching 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.

Table 4: Leaching recoveries for leaching tests.

Leaching Factor	Leaching Recoveries (%)
Concentration of HNO_3 – 10% and particle size (425-500)	91.36
Concentration of HNO_3 – 10% and particle size (425-500)	87.44
Concentration of HNO_3 – 30%	99.66
Concentration of HNO_3 – 55%	97.00
Particle Size (100 – 150)	91.04
Particle Size (≥ 600)	91.14
Temperature – 45	95.20
Temperature – 60	95.40
Time – 60 minutes	91.62

The temperature of the solution was monitored by placing an alcohol thermometer in solution for the duration of the experiment. As seen in figure 10, a sharp increase in temperature was observed within five minutes for all reactions, indicating an exothermic reaction. In experiments with varying concentrations of nitric acid, the highest peak in temperature was observed at 55% nitric acid due to its high oxidising ability

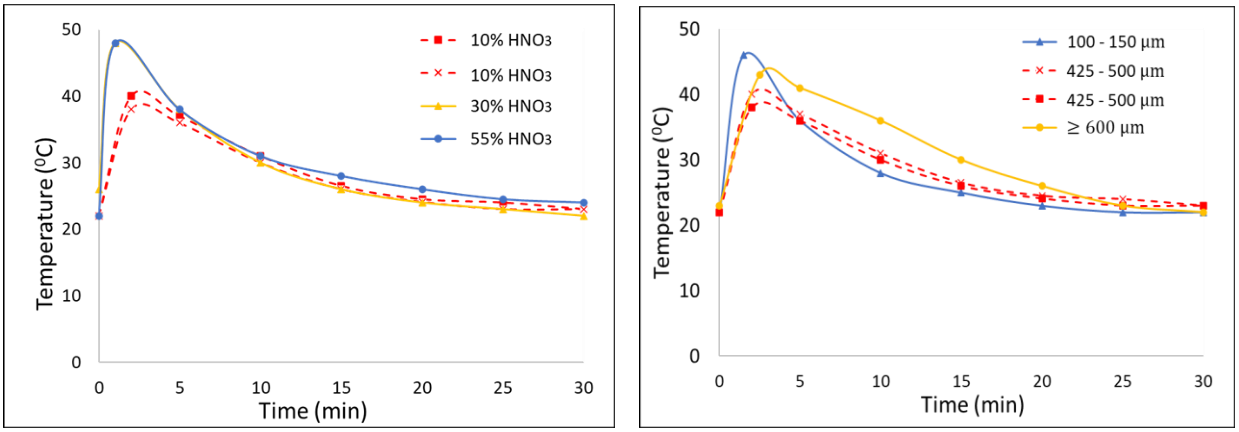

Figure 10: Reaction temperature variations in concentration and particle size experiments.

Inductively coupled plasma - optical emission spectrometry (ICP-OES) was employed for the quantification of metals after the leaching process. ICP - OES operates on the principle of emission spectroscopy. The liquid sample is aspirated and atomized when passed through a nebulizer and exposed to argon plasma. Metal atoms absorb and emit energy in the form of light. A spectrometer is used to isolate characteristic emission lines and wavelengths corresponding to metal oxidation states. A detector allows for the quantification of metals by measuring the intensities of the isolated photons of light. Calibration graphs are necessary for the quantification of metals and follows the principle of the Beer-Lambert's Law. This states that absorption or intensity is directly proportional to the concentration of a solution. Hence, a set of six standard solutions were prepared for Fe and Nd in 1 to 20 ppm. A calibration blank is used to eliminate interferences and matrix effects that may elevate sample concentrations. A blank solution of ultra-pure water was used for the calibration. The calibration graphs obtained had correlation co-efficients of 0.9956 and 0.9998 for Fe and Nd respectively. The R^2 values are closer to 1 indicating accurate standard preparation and a good correlation of x-y data for a linear directly proportional relationship. This is in accordance with the Beer-Lamberts Law. The equations obtained from the calibration were used to find the concentrations of Fe and Nd in the leachate samples.

Table 4: Composition of Fe and Nd in leachate of particle size test using 100-150 µm .

Particle Size (100-150 µm)				
Time	Mass Fe	Mass Nd	Fe (%)	Nd (%)
10	0.7854	0.3543	68.9112	31.0888
20	0.6910	0.3117	68.9112	310888
30	0.5818	0.2594	69.1648	30.8352
30	0.4887	0.2165	69.2964	30.7036

Table 5: Composition of Fe and Nd in leachate of particle size test using ≥600 µm .

Particle Size (≥600 µm)				
Time	Mass Fe	Mass Nd	Fe (%)	Nd (%)
10	0.7770	0.3577	68.4757	31.5243
20	0.6836	0.3147	68.4757	31.5243
30	0.5874	0.2702	68.4907	31.5093
30	0.4992	0.2299	68.4677	31.5323

Table 6: Composition of Fe and Nd in leachate of pH test using 10% nitric acid.

Nitric acid (10%)				
Time	Mass Fe	Mass Nd	Fe (%)	Nd (%)
10	0.9085	0.3811	70.4456	29.5544
20	0.7990	0.3352	70.4456	29.5544
30	0.7103	0.2946	70.6799	29.3201
30	0.6039	0.2487	70.8321	29.1679

Table 7: Composition of Fe and Nd in leachate of pH test using 10% nitric acid.

Nitric acid (10%)				
Time	Mass Fe	Mass Nd	Fe (%)	Nd (%)
10	0.7397	0.3394	68.5472	31.4528
20	0.6509	0.2986	68.5472	31.4528
30	0.5607	0.2571	68.5669	31.4331
30	0.4728	0.2168	68.5644	31.4356

Leaching of Nd was conducted using 50 mL of 10% nitric acid solution and 1g of crushed magnet with a particle size of 425 – 500 µm. The mass of Fe and Nd obtained was found to change over the leaching period. The maximum masses of metals were obtained within the first 10 minutes of the leaching process. This is in accordance with the temperature-time graphs which showed that the exothermic reaction occurs within the first 5 minutes of the leaching process and as a result increases the temperature of the solvent system. At 10 minutes, the temperature of the leachate is approximately 30℃ and a high solubility of both Fe and Nd was observed. After 10 minutes, the temperature of the solvent stabilized to room temperature. Samples taken at the 20 and 30 minute time intervals show a decrease in the mass of metals obtained. This suggests that the solubility of the metals increases when the solvent is at 30℃ and decreases when the solvent is cooled to room temperature. Sampling within the 10 minute interval can be done in future studies to understand the temperature effects of the reaction mixture at room temperature. The effect of temperature on leaching is further affirmed by tests conducted at 45 and 60℃. Since the mixture was heated through the leaching process, the solubility of the metals remained fairly constant over time. The percentage of Fe to Nd corresponds to that seen in literature. The percentage of Fe and Nd corresponds to the material characterization done by Gruber and Charsky.

Table 8: Composition of Fe and Nd in leachate of pH test using 30% nitric acid.

Nitric acid (30%)				
Time	Mass Fe	Mass Nd	Fe (%)	Nd (%)
10	0.7815	0.3637	68.2424	31.7576
20	0.6876	0.3200	68.2424	31.7576
30	0.6008	0.2801	68.2030	31.7970
30	0.5092	0.2378	68.1625	31.8375

It can be observed that by increasing the concentration of the nitric acid, there was a slight increase in the masses of metals that leached into solution. A 30% nitric acid has a higher oxidizing capacity in comparison to a 10% acid solution. This favours the leaching of the metals from the crushed magnet into the solution, forming stable nitrates. The observed percentages were still on accordance with literature. The masses of the metals found at the 20 and 30 minute interval were higher than those observed using 10% nitric acid. This further supports that by increasing the concentration of the nitric acid, the metals are more stable in solution at room temperature. However, the effect of temperature still holds since masses obtained at 10 minutes were higher than those seen at 20 at 30 minutes. Since the ratio of metals leached remain fairly constant at every time interval, the differences can be attributed to solubility effects due to temperature and acid concentration.

Table 9: Composition of Fe and Nd in leachate of pH test using 55% nitric acid.

Nitric acid (55%)				
Time	Mass Fe	Mass Nd	Fe (%)	Nd (%)
10	0.9076	0.4140	68.6754	31.3246
20	0.7981	0.3641	68.6754	31.3246
30	0.7002	0.3178	68.7820	31.2180
30	0.6219	0.2824	68.7715	31.2285

The masses observed for Fe using a 55% nitric acid solution were the highest compared to a 10% and 30% acid concentration. This can be attributed to the oxidizing ability of the nitric acid which increases with the concentration thus stabilizing the Fe in solution as nitrates. As a result of the exothermic reaction, an increase in temperature under 10 minutes favoured the solubility and leaching of the metals in addition to the use of a concentrated acid solution. Therefore, the highest leaching for Fe and Nd was observed using at 10 minutes using a 55% acid solution. The use of concentrated acid generates toxic fumes and can be highly exothermic as seen in Figure 10. Hence, leaching can be optimised using lower concentrations of acid at higher temperatures. This promotes greener leaching and is less hazardous to work with under laboratory and industrial workspaces.

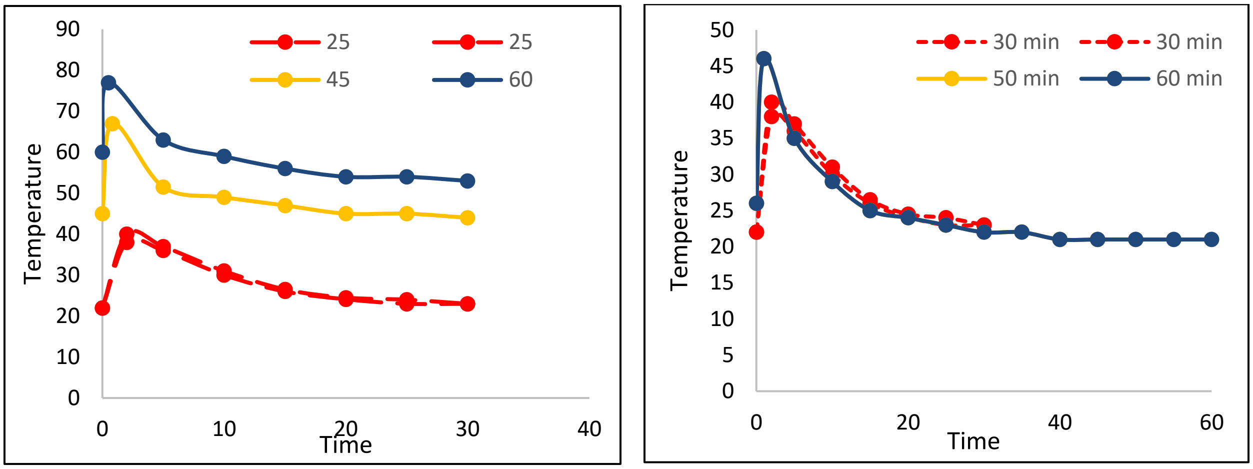

Figure 11: Reaction temperature variations in temperature and time experiments.

The graphs obtained for the reaction temperature variations in tempertaure and time reveals that the leaching process is an exothermic reaction irrespective of external heating. A sudden spike in temperature is observed for all leaching process below 10 minutes. The solutions are found to stabilize to the external temperatures anf stabilize after 10 minutes indicating the comletion of the leaching reaction. The evolution of toxic nitrogen dioxide fumes were observed for all reactions as a result of the reaction of nitric acid with the crushed magnets. It can be observed for time variations that the leaching process done at room temperature for 50 and 60 minutes shows a higher reaction temperature than those conducted for 30 minutes. This is attributed to changes in the intial room temperature at the start of leaching. The room temperature for the 30 minute experiment was 20°C whilst 25°C was noted for the 50 and 60°C leaching experiments. For all experiments, the leaching process stabilizes after 20 minutes.

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Table 10 : Composition of Fe and Nd in leachate done over 60 minutes (Govender, 2021)

Time	Mass Fe (g)	Mass Nd (g)
30	0.089832	0.041358
50	0.090684	0.041382
60	0.095298	0.044616

It can be observed that by using a low concentration of nitric acid at room temperature over a longer period of time with adequate mixing, leaching occurs at a lower rate in comparison to sampling within 30 minutes. This shows that time does affect the leaching process and by extending the time period, leaching and solubility decreases.

Table 11 : Composition of Fe and Nd in leachate done at 45℃ for 30 minutes (Govender, 2021)

Time	Mass Fe (g)	Mass Nd (g)
10	0.097704	0.045648
20	0.084522	0.038622
30	0.0957	0.044592

Table 12 : Composition of Fe and Nd in leachate done at 60℃ for 30 minutes (Govender, 2021)

Time	Mass Fe (g)	Mass Nd (g)
10	0.095478	0.04473
20	0.095556	0.044718
30	0.101574	0.047184

Tables 11 and 12 show the results obtained for leaching at 45 and 60℃. This shows that by using a low concentration of acid and increasing the temperature, the leaching process for Nd can be optimised to achieved higher concentrations.

5. Conclusions

Leaching of neodymium magnets from NdFeB powder derived from desktop hard disk drives provided efficient recovery of neodymium. Demagnetisation was achieved at a temperature of 400℃ for 30 minutes. The optimal leaching parameters were for a particle size of 100-150μm, 30% nitric acid concentration, temperature of 60 ℃ and leaching time of 60 minutes, with a neodymium and iron composition of 31.84% and 68.16% respectively. The overall reaction was exothermic. Hence, it can be concluded that nitric acid is effective in the recovery of neodymium.

6. Recommendations

- To obtain higher mass fractions of lower particle sizes, tertiary crushing devices such as cone crushers can be employed.
- To investigate the effect of the rise in temperature due to the exothermic reaction, sampling can be done within the 10 minute interval.
- To increase the reliability of the results, many replicates can be done.
- Alternate sieving methods such as benchtop agitators can be used for efficient agitation.
- Use factorial design method in triplicate (72 samples)
- Determine the leaching efficiencies of B, Dy, Pr, Ni, Al and Co using ICP – OES analysis
- Apparatus to collect gaseous products
- Analyse concentration of gaseous products using Gas chromatography

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9. Appendix

9.1 Uncertainty analysis

Sample calculation

The instrument uncertainties reported for the pipettes used were:

Pipette : 2 ml = ± 0.01

10 ml = ± 0.03

50 ml = ± 0.08

The standard uncertainties were calculated using a rectangular distribution as follows:

$$\frac{0.01}{\sqrt{3}} = 0.006 \qquad \frac{0.03}{\sqrt{3}} = 0.017 \qquad \frac{0.08}{\sqrt{3}} = 0.046$$

The combined uncertainty was calculated as follows:

✓

$$\sqrt{0.006^2 + 0.017^2 + 0.046^2} = 0.05$$

Repeatability of data was determined by calculating the standard deviation of duplicate data measurements.

9.2 Crushing

Sample calculation

$$\text{Mass fraction} = \frac{Mass\ retained\ on\ sieve}{Total\ mass\ of\ sample} = \frac{339.273}{612.302} = 0.554$$

Cumulative mass fractions = Total mass of sample – mass retained on sieve

= 612.302 g – 339.273g

= 273.029 g

✓

9.3 Leaching recovery

Sample calculation

Sample of mass used = 1.007 g

Mass of unleached sample = 0.087 g

$$\text{Leaching recovery (\%)} = \frac{w_1}{w_t} \times 100 = \frac{1.007 - 0.087}{1.007} \times 100 = 91.36\%$$

9.4 ICP- OES analysis

Table 13: Concentration of neodymium and iron at various leaching times for particle size tests.

Sample Labels	**Fe 259.940 (mg/L)**	**Nd 406.108 (mg/L)** ✓
Particle Size Tests		
Test 1 (100-150 µm)10 min	15740	7101
20 min	18198	8726
30 min	15514	7140
Mother liquor	12654	5622
Test 2a (425-500 µm) 10 min	18244	7654
20 min	14790	6762
30 min	17723	7658
Mother liquor	13606	6152
Test 2b (425-500 µm) 10 min	14811	6796
20 min	15020	6931
30 min	14657	6715
Mother liquor	12220	5433
Test 3 (> 600) 10 min	15570	7168
20 min	16032	7412
30 min	14702	6723
Mother liquor	13862	6289

Table 14: Concentration of neodymium and iron at various leaching times for varying acid concentrations .

Sample Labels	**Fe 259.940 (mg/L)**	**Nd 406.108 (mg/L)**
pH Tests		
Test 1 30% HNO_3 10 min	15663	7289
20 min	14453	6641
30 min	15276	7048
Mother liquor	12755	5719
Test 2 55% HNO_3 10 min	18234	8317
20 min	16317	7706
30 min	13061	5905
Mother liquor	8865	3798

✓

Sample calculation of percentage compositions.

Mass of magnets (g)	1
Component one (Neodymoum) (29.94%) *	0,2594
Component two (Iron) (61.33%)*	0,6133
Initial sample mass (g)	71,65

Sample Labels	**Fe 259.940 (mg/L)**	mass (mg)	mass extracted (g)	**Nd 406.108 (mg/L)**	mass (mg)	mass extracted (g)	total mass solid extracted
Particle Size Tests							
Test 1 (100-150 µm)10 min	15740	94,44	0,094	7101	42,606	0,0426	0,137
20 min	18198	109,188	0,109	8726	52,356	0,052	0,161
30 min	15514	93,084	0,093	7140	42,84	0,042	0,135
Mother Liquor		0	0		0	0	0

✓

Solvent density g/L	Solvent mass (g)	Total solution mass	Mass fraction Fe	Mass fraction Nd	Mass fraction Solution	Mass Fe in solution	Mass Nd in solution
1413	8,478	8,61	0,010	0,005	0,984	0,785	0,354
1413	8,478	8,63	0,012	0,006	0,981	0,691	0,311
1413	8,478	8,613	0,010	0,0049	0,984	0,581	0,259
1413	8,478	8,478	0	0	1	0,489	0,2165

Mass solvent in solution	Fe fraction in solution	Nd fraction in solution	Solvent fraction in solution	Nd (%)	Fe(%)	Composition (%)
70,510	0,0109	0,026	0,913	31,09%	68,92%	1
62,032	0,0109	0,023	0,922	31,09%	68,92%	1
53,554	0,0106	0,020	0,934	30,84%	69,18%	1
45,076	0,0106	0,0170	0,944	30,70%	69,24%	1

✓