



**TOPIC 21: URBAN MINING OF RARE EARTH ELEMENTS FROM  
RARE EARTH MAGNETS – HYDROMETALLURGICAL PROCESSING**

**ENCH4LA**

**LABORATORY PROJECT**

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## Statement of Authorship

I, Riyolin Govender, declare that:

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- (ii) This report has not been submitted for any degree or examination at any other university.
- (iii) This report does not contain other persons' data, pictures, graphs or other information, unless specifically acknowledged as being sourced from other persons.
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## ABSTRACT

A laboratory-scale leaching experiment was conducted to aid in the development of urban mining technologies to extract rare earth elements from neodymium-iron-boron magnets. In this work, neodymium and iron were the two elements investigated. The optimum leaching conditions had to be determined, to ensure a feasible commercial recycling process, which could help mitigate the accumulation of electronic waste to landfill sites. Nitric acid (aqueous solution at 55 wt%) was used as the leaching agent. The physical process of the experiment started with the demagnetization of the magnets in an oven, followed by the crushing, sieving and the screen analysis of the particles. The effect of particle size on the leaching process was investigated to determine the size to which the rare earth magnets must be comminuted prior to extraction. Other factors were guided by literature, such as the base measurements, to produce valuable results, due to the time constraints and a limited budget of this project. The conditions at which the base parameters were evaluated included a temperature of 25°C, particle size of 425-500µm, a leaching time of 30 minutes, and nitric acid (10 wt%), and the measurements were duplicated to determine the repeatability, reproducibility, and uncertainty in measurements. To investigate the effect of temperature and time, measurements were conducted at 45°C, 60°C, 50 minutes and 60 minutes, respectively. The chemical process was initiated by the leaching process, where 50ml of nitric acid (10 wt%) and approximately 1g of crushed sample was added to a beaker, and placed on a magnetic stirrer for each test. The effectiveness of the leaching process was monitored using a mass balance to determine the amount of magnet dissolved, as well as through the analysis of the leach liquor using ICP- OES analysis to determine the concentration of iron and neodymium. All leaching recoveries were calculated to be above 80%. Approximately 55.40% of the crushed magnets consisted of the particle size  $\geq 600\mu\text{m}$ , and a high leaching recovery of this particle size was calculated to be 91.14%, indicating that further comminution is not necessary for future projects. Upon analysis of the ICP results, the leaching efficiencies of the neodymium and iron could not be calculated, as the exact composition of the metals was not determined prior to leaching. Using an assumption of the weight percentages from literature, created an unrealistic result which resulted in the initial concentrations of neodymium and iron to be lower than the results provided by ICP analysis. Hence, a rate-based approach was used for a more realistic analysis. Furthermore, by adopting this method, the mass fractions of iron and neodymium in the beaker was found to

decrease over time. Future experiments are necessary to determine the exact compositions of neodymium and iron present in the initial sample, in order to plot the efficiency graphs and determine the optimal conditions.

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## NOMENCLATURE

<u>Symbol</u>	<u>Description</u>	<u>Unit</u>
m	Mass	g
s	Standard Deviation	-
T	Temperature	°C or K

<u>Subscript</u>	<u>Description</u>
aq	Aqueous
g	Gas

<u>Abbreviation</u>	<u>Description</u>
Al	Aluminium
B	Boron
Co	Cobalt
Dy	Dysprosium
e-waste	Electrical waste
Fe	Iron
HDDs	Hard disk drives
ICP-OES	Inductively Coupled Plasma Mass Spectrometry
ml	Millilitres
Nd	Neodymium
NdFeB	Neodymium-iron-boron magnets
Ni	Nickel
Pr	Praseodymium
WEEE	Waste Electrical and Electronic Equipment
wt.%	Weight percent



# CHAPTER 1

## INTRODUCTION

### 1.1. Background and rationale

With the rapid development of electronic technology, the demand for electronic devices has increased significantly (De Froberville, 2019). This has led to more electrical waste (e-waste) and the accumulation of this type of waste is a globally growing problem (De Froberville, 2019). A significant amount of waste electrical and electronic equipment (WEEE) are sent to landfills or exported, rather than recycled (Erust et al., 2019). It is estimated that approximately 50 million tons of WEEE are generated globally per year (Erust et al., 2019). There is a very small number of large companies that focus on the recovery of metals from waste, through the smelting and refining process (Erust et al., 2019). However, there are a large number of companies that have focused on the dismantling and pre-processing techniques, especially for the collection of e-waste (Erust et al., 2019). The average recycling rate globally for REEs, is less than 1% (Karal et al., 2020). According to Tsamis and Coyne (2015), there are limited industrial operations for the recycling of e-waste.

The mishandling and improper disposal of e-waste pose environmental health risks (De Froberville, 2019). The environment and community are adversely affected due to the exposure to toxic fumes and the leaching of hazardous chemicals which contaminate the water, soil, and vegetation which serve as a source of food (Faurie, 2020). South Africa is estimated to produce 2 million tons of e-waste annually (Faurie, 2020). Hence, there is currently an increased demand for economically feasible commercial processes to recover and recycle rare earth elements (REEs) from e-waste, which reduces the dependence on mining first generation REEs for these supplies (Matsumoto et al., 2020). This is due to the implementation of the national ban on the disposal of waste electrical and electronic equipment to landfill sites, effective from August 2021 in South Africa (Faurie, 2020).

The process of recycling e-waste for REE recovery is termed “urban mining” and is an essential alternative to the highly environmentally impactful mining process of these elements (Williams-Wynn et al., 2020). NdFeB magnets in hard drive disks have been identified as an important secondary resource of the REEs (Erust et al., 2019). The physical separation processes such as



demagnetization, crushing, grinding, and screening, are important to provide feasible methods for further recycling steps (Erust et al., 2019). Erust et al. (2019) reported that for an experimental batch process involving the treatment of NdFeB magnets, the economic analysis of the process is focused on optimizing system parameters, thus allowing it to be implemented on a commercial scale.

## **1.2. Aim and objectives**

According to Lee et al. (2017), batch experiments have to be conducted to optimize the leaching conditions with factors such as a solid/liquid ratio, leaching contact time, the concentration of reagents used, and the leaching temperatures. Sahin et al. (2016) also reported that particle size has a significant effect on the leaching process.

The present study is aimed to optimize the extraction of rare earth metals from rare earth magnets, through the crushing and leaching processes. The experiment was performed at a laboratory-scale and leaching tests of the REEs from rare earth magnets were conducted. This involved testing the effect of particle size, pH, temperature, and time on the extraction process. The particle size effect on the leaching process had to be investigated to determine the size to which the magnets had to be comminuted, before the extraction process. The effectiveness of the leaching process was monitored from the analysis of the leach liquor using ICP-OES (Inductively Coupled Plasma Mass Spectrometry) analysis. Nitric acid (55 wt.%) was used as the reagent for the leaching process.

To achieve the aim, two objectives were proposed and these include:

1. To validate the results of the novel experimental leaching procedure developed in this work with experimental data found in literature sources using different methods. ✓
2. To perform laboratory-scale testing of the leaching process by:
  - i) Determining the effect of particle size of the rare earth magnets.
  - ii) Assessing the effect of pH by varying the nitric acid concentration.
  - iii) Observing the effect of temperature of the mixtures.
  - iv) Quantifying the effect of contact time on the leaching of NdFeB powders in solution. ✓

Two students performed the investigation with one student (Kavisha Kalicharan) who focused on the effect of particle size and nitric acid concentration on the leaching process. In this report, the objectives of varying the temperature of the mixtures and measuring the effect of contact time on the leaching of NdFeB powders in solution were explained Chapter 2. For the Results and Discussion section of this report, the results from each student were combined and explained.

### 1.3. Background on Rare Earth elements

Rare earth elements comprise of seventeen elements such as scandium (Sc), yttrium (Y), and fifteen lanthanides (Sarfo, 2019). This is shown in Figure 1.1.

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La-Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac-Lr	Rf	Db	Sg	Bh	Hs	Mt									
lanthanide series		La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	
actinide series		Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	

Figure 1.1. The periodic table showing the rare earth elements (Sarfo, 2019)

REEs are categorized into two main groups, such as light rare earth elements (LREEs) and heavy rare earth elements (HREEs), according to their ionic diameters and geological differences (Erust et al., 2019). The light rare earth elements from Figure 1.1, range from lanthanum (La) to gadolinium (Gd), and the heavy rare earth elements from terbium (Tb) to lutetium (Lu), also including scandium and yttrium (Sarfo, 2019). ✓

### 1.4. Applications of rare earth elements

REEs have a variety of applications in consumer products and industry (Sarfo, 2019). In the metallurgical field, REEs are used as additives and in alloys (Sarfo, 2019). Permanent magnets are made from alloys of neodymium-iron-boron (NdFeB) and the demand for these magnets has

significantly increased, due to their high magnetic strength (Sarfo, 2019). They are widely used in computer hard drives, electric motors (in hybrid vehicles and wind turbines), actuators in aircraft, cellphones, etc. (Sarfo, 2019). However, certain REEs are unable to meet the industrial needs in the manufacturing sector, as they are identified as critical materials due to low availability (Sarfo, 2019). These materials have low collection and recycling rates, and can cause environmental issues (Sarfo, 2019).

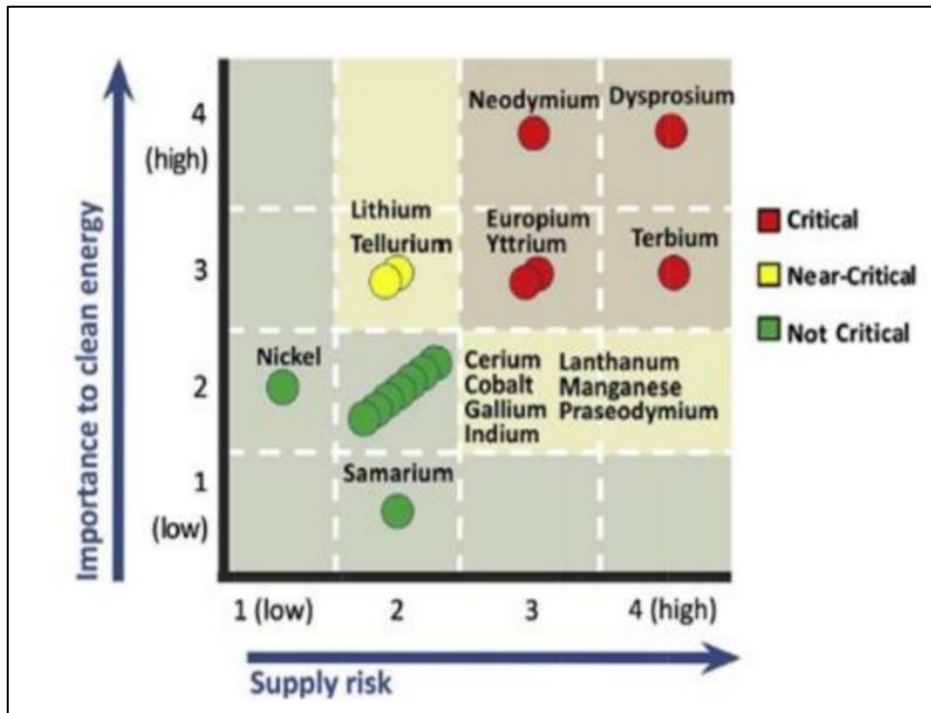


Figure 1.2. The five critical rare earth metals (Sarfo, 2019).

From Figure 1.2., it is evident that neodymium and dysprosium are the most critical REEs. Erust et al. (2019) reported that approximately 95% of the rare earth raw materials are produced in China, making this country the largest commercial exporter of REEs. This has been beneficial to countries who rely greatly on these critical minerals to meet their demand (He, 2018).

## CHAPTER 2

### LITERATURE REVIEW

#### 2.1. NdFeB magnets and recycling routes

Hard disc drives (HDDs) consist of a significant amount of NdFeB magnets, which have been identified as a secondary resource for the magnets containing these rare earth elements (Munchen and Veit, 2017). Erust et al. (2019) reported that HDDs contains approximately 1 to 30g of NdFeB magnets. From an economical perspective, waste NdFeB magnets can be of great importance for countries aiming to make a profit from recycling processes (Schulze and Buchert, 2016). WEEE is increasing rapidly, hence the demand for these magnets is high and the supply is low, therefore making the recycling of spent NdFeB magnets very important (Lee et al., 2013). Electronic waste adversely affects the environment in terms of pollution and toxicity, which is caused by the mishandling and improper disposal of this type of waste (De Froberville, 2019). However, there are advantages to recovering, re-using, and recycling the waste, which will not only be beneficial to the economy but also the environment (Laurino et al., 2019). To meet the global demand of rare earth elements, non-traditional mining methods are being investigated (Laurino et al., 2019).

According to Erust et al. (2019), the recovery of REEs in scrap magnets can be accomplished using a variety of different recycling routes, such as electrometallurgy, chemical vapour transport, pyro-metallurgy, hydrogen decrepitation, and hydrometallurgy. In the hydrogen decrepitation method, a portion of the magnet coating must be removed to allow hydrogen to enter the magnet (Erust et al., 2019). This method is economically unfeasible, due to the high investment costs (Erust et al., 2019). Chemical vapour transport requires high temperatures and a long processing time, making this recycling route unfavourable (Erust et al., 2019). Furthermore, chemical vapour transport has limitations on the thermodynamic information available, relating to the intermetallic compounds in Nd-Fe binary systems (Erust et al., 2019). Pyro-metallurgical processes are also disadvantageous, due to the intensive energy requirements, high environmental load, and limited processing space (Erust et al., 2019). A direct or combined hydrometallurgical process is more advantageous for the separation of rare earth elements (Erust et al., 2019).

To reduce the pressure on the environment and satisfy the demand, innovative techniques have been developed (Cardoso et al., 2019). The leaching of solid materials with a variety of acids,

forms the major steps in hydrometallurgical processing (Karal et al., 2020). The leaching process is an extractive metallurgical technique, where metals are converted into soluble salts in aqueous media (Lee et al., 2017). This process is more advantageous over pyro-metallurgical operations, as it is easier to operate, there is no gaseous pollution and there is low toxicity (Lee et al., 2017). However, large volumes of wastes are produced in practical operations, due to the high consumptions of acid (Gruber and Carsky, 2020). More intensive recycling routes for REEs provide many advantages, such as a smaller environmental footprint and a cheaper source of material, compared to primary production (Cardoso et al., 2019). ✓

## 2.2. The extraction process of REEs from NdFeB magnets.

Yang and Honaker (2020) reported that studies were focused on developing REE extraction processes from secondary resources such as magnet recycling industries, industrial wastes, and mine waste streams. Erust et al. (2019) reported on the batch process of the NdFeB magnets. This is shown in Figure 2.1.

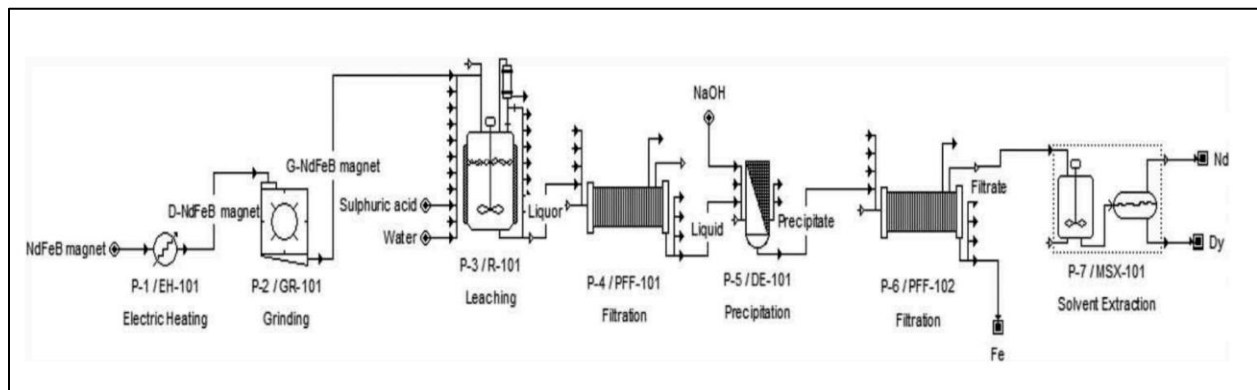


Figure 2.1. Flowsheet showing the process of NdFeB magnets (Erust et al., 2019). ✓

The physical process such as the demagnetization, crushing and grinding steps to obtain a sample of magnetic powders, is the first stage of operation in the extraction of REEs from waste NdFeB magnets (Erust et al., 2019).

The demagnetization of magnets can be accomplished by the heating method, ✓ used by Erust et al. (2019), Karal et al. (2020) and Lee et al. (2013). This involves placing the magnets in an oven at



a certain temperature above its Curie temperature for a certain amount of time. The Curie temperature is the temperature at which magnets lose their magnetic properties (Gruber and Carsky, 2020).

The alternate method relates to using liquid nitrogen to super-cool the magnets. The immersion of the magnets in liquid nitrogen at  $-196^{\circ}\text{C}$  doesn't cause damage to the magnets, however the adhesive force of the magnets will increase as the temperature is reduced (Supermagnete, 2021). Furthermore, when the magnets are at temperatures below  $-125^{\circ}\text{C}$ , the adhesive forces will decrease steadily, however the original adhesive force will return to normal once the magnet is brought back to room temperature (Supermagnete, 2021). This super-cooling method is not feasible as the magnets will regain its magnetism, which is not desirable for this experiment.

For the heating method, Erust et al. (2019) removed the pieces of the NdFeB magnets from the hard drive disks, to be used in the investigation. The magnets were placed in a furnace at  $350^{\circ}\text{C}$ , for 30 minutes. This method was also used by Karal et al. (2020). However, Lee et al. (2013) used the same temperature, but the magnets were placed in the oven for 15 minutes. This is summarized in Table 2.2. Karal et al. (2020) reported that magnets lose their magnetic properties at  $350^{\circ}\text{C}$ .

Table 2.2. Operating parameters applied in the demagnetization of NdFeB magnets from HDDs

<u>Parameter</u>	<u>Erust et al.(2019)</u>	<u>Karal et al.(2020)</u>	<u>Lee et al.(2013)</u>
Temperature ( $^{\circ}\text{C}$ )	350	350	350
Time (min)	30	30	15

The step which follows demagnetization involves the crushing and grinding of the magnets. Erust et al. (2019) crushed the pieces of magnets using a cutting mill and ground the material to a size of  $500\mu\text{m}$  using a centrifugal mill. Lee et al. (2013) used ceramic balls (2 inches in diameter) to crush the magnetic material in a self-designed grinding equipment. Furthermore, it was reported by Lee et al. (2013) that the crushing procedure was a problematic process, and the optimal grinding conditions had to be investigated. Karal et al. (2020) used a hammer mill for the comminution process.

Once the magnets are demagnetized and crushed, the chemical process is applied which begins with leaching the prepared samples with various acids (Erust et al., 2019). Erust et al. (2019) used inorganic acids (sulphuric acid (H<sub>2</sub>SO<sub>4</sub>), nitric acid (HNO<sub>3</sub>), hydrochloric acid (HCl)) and organic acids (acetic acid (CH<sub>3</sub>COOH)), oxalic acid (C<sub>2</sub>H<sub>2</sub>O<sub>2</sub>) to test for the extraction of REEs from the magnets. Table 2.3 summarizes the parameters and operating conditions assessed in the leaching process by Erust et al. (2019).

Table 2.3. Parameters and operating conditions assessed for the leaching process

Parameter	Erust et al. (2019)
Particle Size (µm)	<500
Time (minutes)	30 – inorganic acids 420- organic acids
Temperature (°C)	27
Concentration of acid (M)	1-3



The leaching recoveries of the metals can be justified using the following equation (Erust et al., 2019) :

$$\text{Leach recovery (\%)} = \frac{w_1}{w_t} 100\% \quad (1)$$

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

The results of the extraction of metals, using inorganic and organic reagents are provided in Figure 2.4.

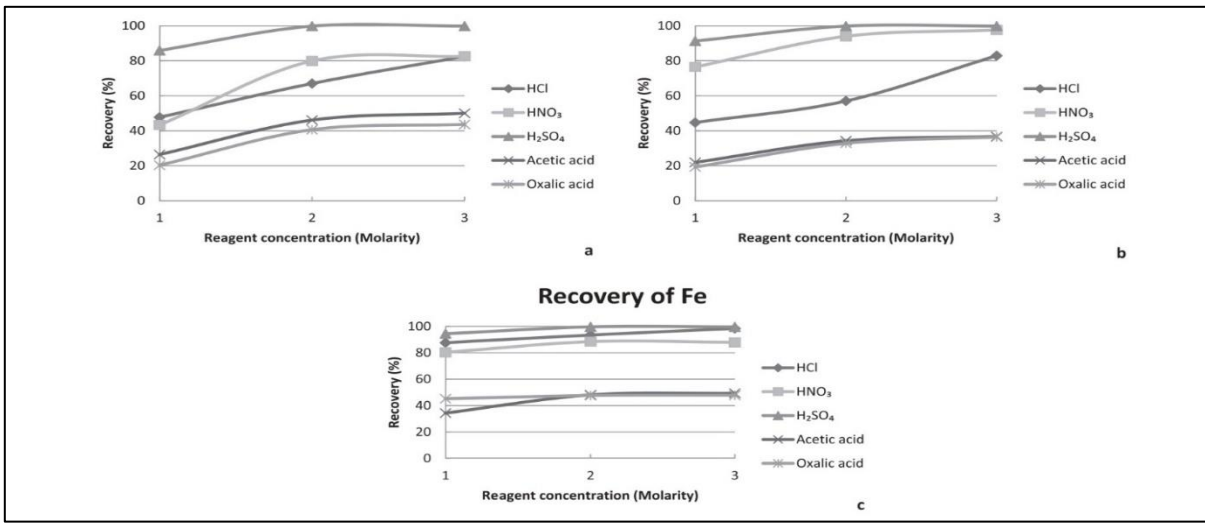
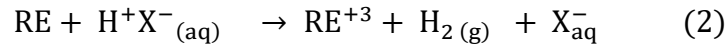


Figure 2.4. The recovery of REEs and Fe in organic and inorganic acids concentrations (a) neodymium, (b) dysprosium, and (c) iron. These results were conducted using the operating conditions in Table 2.3. (Taken from Erust et al., 2019).

The inorganic acids had higher recoveries than the organic acids (Erust et al., 2019). Erust et al. (2019) reported that the leaching of Nd (Figure 4a), Dy (Figure 4b), and Fe (Figure 4c), can be improved by increasing the concentration of inorganic acids from 1M to 2-3M. Sulphuric acid appeared to be the most effective inorganic acid (Erust et al., 2019). At 3M acid concentration, sulphuric acid achieved approximately a 17% higher recovery of neodymium, compared to the other inorganic acids (Erust et al., 2019). Lee et al. (2017) also reported sulphuric acid to be a more efficient reagent compared to HCl and HNO<sub>3</sub>. Nitric acid has a higher recovery for neodymium and dysprosium than hydrochloric acid, and a smaller recovery for iron, compared to sulphuric acid and nitric acid. This is evident in Figure 2.4.

A solid-liquid reaction occurs once the rare earth elements are added to the acidic solutions (Erust et al., 2019). Inorganic acids are strong acids and allow for ionization, provide a high recovery of metals found in the magnets and dissolve metals more easily compared to organic acids (Erust et al., 2019).

The solid rare earth metals (RE) in the magnets are converted to ions [RE<sup>+3</sup>] as follows (Erust et al., 2019):



The rare earth elements in the sulfuric acid, nitric acid, and hydrochloric acid change to hydrogen gas and ions containing the sulfate, nitrate, and chloride, respectively (Erust et al., 2019). Iron and boron form  $\text{Fe}^{+2}$  and  $\text{B}^{+3}$  ions, respectively with the release of hydrogen gas (Lee et al., 2013). X in the above formula represents the  $\text{SO}^{-2}$ ,  $\text{NO}_3^-$  and  $\text{Cl}^-$  ions in the solution, depending on which acid is used.



After the optimal leaching solution is obtained, a filtration step is followed (Erust et al., 2019). The filtration is used to separate solid and liquid fractions (Karal et al., 2020). According to Figure 2.1, the liquid fractions after filtration, are sent to the precipitation process. The obtained optimal leaching solution will contain Nd along with other metals (Lee et al., 2013). Neodymium is the target metal, and can be separated from the other metals using a precipitation method (Lee et al., 2013). The pH value of the optimal leaching solution can be adjusted by adding sodium hydroxide (Lee et al., 2013). After this process, a further filtration step and solvent extraction process is followed downstream (Erust et al., 2019).



## CHAPTER 3

### EQUIPMENT AND EXPERIMENTAL METHOD

#### 3.1. Material collection and chemicals.

The magnets were sourced from discarded hard drive disks available at UKZN, provided by the IT department (School of Engineering). The hard drives were not categorized by the different manufacturers, due to time constraints. Leaching reagents such as nitric acid (55 wt. %) and other chemicals such as phenolphthalein, ethanol (purity  $\geq 99.50\%$ ), sodium hydroxide pellets, deionized water and potassium hydrogen phthalate (purity  $\geq 99.95\%$ ) were available at UKZN's (Howard College) School of Chemical Engineering laboratory.

#### 3.2. The removal of magnets

The magnets were fixed onto an aluminium support and were manually removed using a screwdriver and a hammer. The tip of the screwdriver was placed on the magnet and the hammer was used to knock on the handle of the screwdriver, providing force for the magnet to be released from the support. This process was done for all the magnets. Magnets of different sizes and thicknesses were obtained.

#### 3.3. Demagnetization

Demagnetization was accomplished by the heating method. The magnets were placed in an oven for 30 minutes and set for 400°C.

#### 3.4. Comminution

The demagnetized magnets were comminuted using UKZN's roller mill (model 123032). Magnets of similar size were separated into batches. The roller mill settings were adjusted to ensure that the space between the rollers could allow for sufficient compression of the magnets. These were fed into the roller in batches of two to three magnets. It was necessary to perform this at a slow pace to avoid jamming the rollers. For safety concerns, a screen was used to cover the mill to prevent the sparks from exiting the mill.

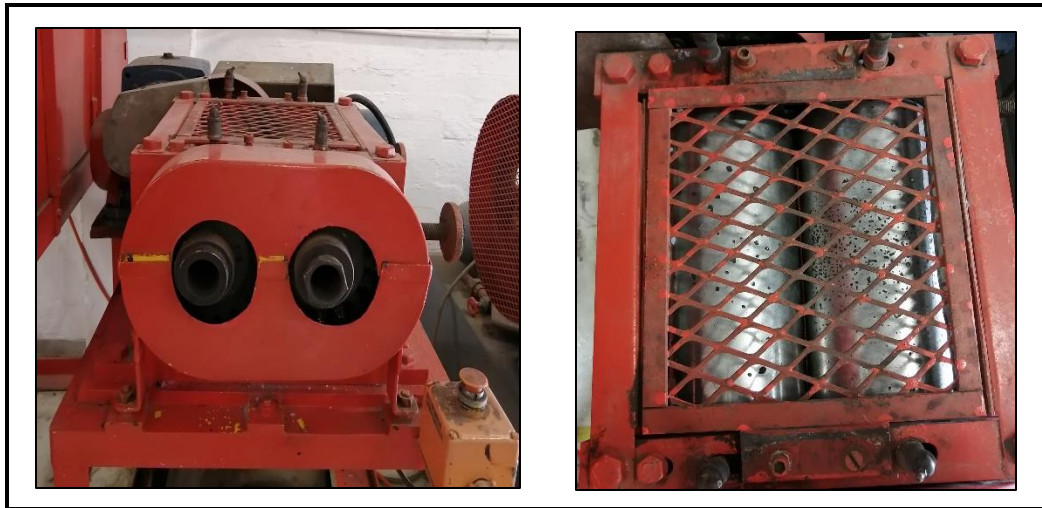


Figure 3.1. The roller mill used for the comminution of the magnets

### 3.5. Sieving Analysis

All crushed samples were sieved using trays with apertures of 600 $\mu$ m, 500 $\mu$ m, 425 $\mu$ m, 355 $\mu$ m, 300 $\mu$ m, 200 $\mu$ m, 150 $\mu$ m, and 100 $\mu$ m. The sieve trays were agitated for approximately 10 minutes. Thereafter, screening analysis was performed at sizes  $\geq$ 600 $\mu$ m, 500-600 $\mu$ m, 425-500 $\mu$ m, 355-425 $\mu$ m, 300-355 $\mu$ m, 200-300 $\mu$ m, 150-200 $\mu$ m, and 100-150 $\mu$ m. The mass of the sample at each tray was weighed using a mass balance (Ohaus Model PA423C, mass uncertainty=  $\pm$ 0.001 g) and placed in sample packets. These were labelled accordingly.

### 3.6. Baseline experiments

Table 3.2 shows the parameters tested in the leaching process. A trio of different particle sizes, concentrations of nitric acid, temperature, and time values were used. The highlighted cells indicate the base measurements.

Table 3.2. Parameters tested in the leaching process

Operating Parameters			
<u>Particle size (<math>\mu</math>m)</u>	<u>pH (% HNO<sub>3</sub>)</u>	<u>Temperature (<math>^{\circ}</math>C)</u>	<u>Time (minutes)</u>
100-150	<b>10</b>	<b>25</b>	<b>30</b>
<b>425-500</b>	30	45	50
$\geq$ 600	55	60	60

\*For the pH tests, the wt% of nitric acid was reported.

The solid to liquid ratio used in this experiment was 20 g/L (1g in 50ml of acid), as this was used by Erust et al. (2019). The optimum concentration of inorganic acids to use at these conditions must range from 2-3 M (Erust et al., 2019), hence 10% HNO<sub>3</sub> was used, which is approximately 2.24 M.

A factorial design could be implemented to determine the effect that several parameters have on the process (Mandal et al., 2015). In terms of the factorial design method, all parameters should have been done under all the conditions, where each combination of particle size is tested with each nitric acid concentration, temperature, and time value. The factorial design method can be disadvantageous as a large number of experiments will need to be performed when working with more than two or three parameters (Massart et al., 2003). Due to time constraints and a limited budget of this project, the factorial design method could not be applied. Instead, base measurements were selected as they were guided by literature, to produce the most valuable results. All base measurements are highlighted in Table 3.2 and these conditions were used by Erust et al. (2019). Thus, the base measurements were performed in duplicate to determine the repeatability and reproducibility of results, and evaluate the uncertainties in measurements.

### **3.7. Leaching tests**

Several borosilicate glass beakers were filled with 50 ml nitric acid and 1 g of sample. A stirrer was added. The beakers were placed on magnetic stirrer plates. The parameters of temperature and time are explained in this report, however, the Results and Discussion section of the report will have information of all parameters (including the results by Kalicharan (2021) ). From Table 3.2, the particle size of 425-500 $\mu$ m was selected as the base measurement, and this particle size was used in all temperature and time tests.

#### ***3.7.1. Effect of temperature***

Approximately 50 ml of nitric acid and approximately 1g of sample were added to borosilicate beakers. The beakers were placed on magnetic stirrers (FMH instruments model) and were operated at 25°C (room temperature) for 30 minutes. The temperature of 25°C was used for all particle size ranges. To assess the leaching kinetics, samples were collected at time intervals of 10,

20, and 30 minutes. Micro-filter plunger syringes (0.45 $\mu$ m) were used to collect the leachate from the beakers at the time intervals, and these were placed in ICP-vials and labelled. Micro-filter syringes were recommended by Yang and Honaker (2020), as they are used to effectively filter the solids from the leachate, hence terminating the solid-liquid reaction. Once the 30 minutes of leaching time had elapsed, the contents of the beaker were poured into a vacuum filter. Deionized water was added to the filter paper, once the sample from the beaker was added to the Büchner funnel, to stop the solid-liquid reaction. The mother liquor was collected after each experiment. The leachate samples and the mother liquor were sent to Pietermaritzburg for ICP-OES analysis, to determine the neodymium content, including the iron content.

The same procedure was carried out for the temperatures 45°C and 60°C, but using the particle size 425-500 $\mu$ m only. The magnetic stirrer apparatus also had a heater, which could be adjusted manually. The temperature of the acid was measured using an alcohol-based thermometer (standard uncertainty of  $\pm 0.5^\circ\text{C}$ ) until the desired temperature value was achieved. The temperature of the acid was maintained at a certain setting on the heater control knobs (no actual temperature values were provided but numbers were provided, ranging from 1 to 10, indicating an increase in the temperature).

The apparatus is shown in Figure 3.3. To assess the effect of temperature, the leaching time was set to 30 minutes and a sample of approximately 6ml was extracted every 10 minutes using the syringes. The leachate was placed in ICP vials and labelled. Once the leaching process was complete, the filtration step followed, and the mother liquor and leachate samples were sent for ICP-OES analysis.





Figure 3.3. The magnetic stirrer apparatus containing two dials. The dial on the left controls the magnetic stirrer speed, and the dial on the right controls temperature

### 3.7.2. Effect of time

To determine the effect of time on the leaching process, Lee et al. (2017) used time values of 30, 60, 90, and 120 minutes. However, due to time constraints, the time values used in this study were 30 minutes, with an intermediate time of 50 minutes and a maximum time of 60 minutes. Table 3.4 summarizes the conditions used for the time test:

Table 3.4. Table summarizing the conditions used for the time test

Particle size	425-500 $\mu\text{m}$ (~1.000 g)
Temperature	25°C
Time	30, 50 , 60 minutes

The micro-filter syringes were used to obtain the leachate at every time interval as listed in Table 3.4. These leachate (6ml) and mother liquor samples were placed in ICP vials and labelled for ICP-analysis.

Figure 3.5 provides an overview of the experimental procedure of the batch experiment.



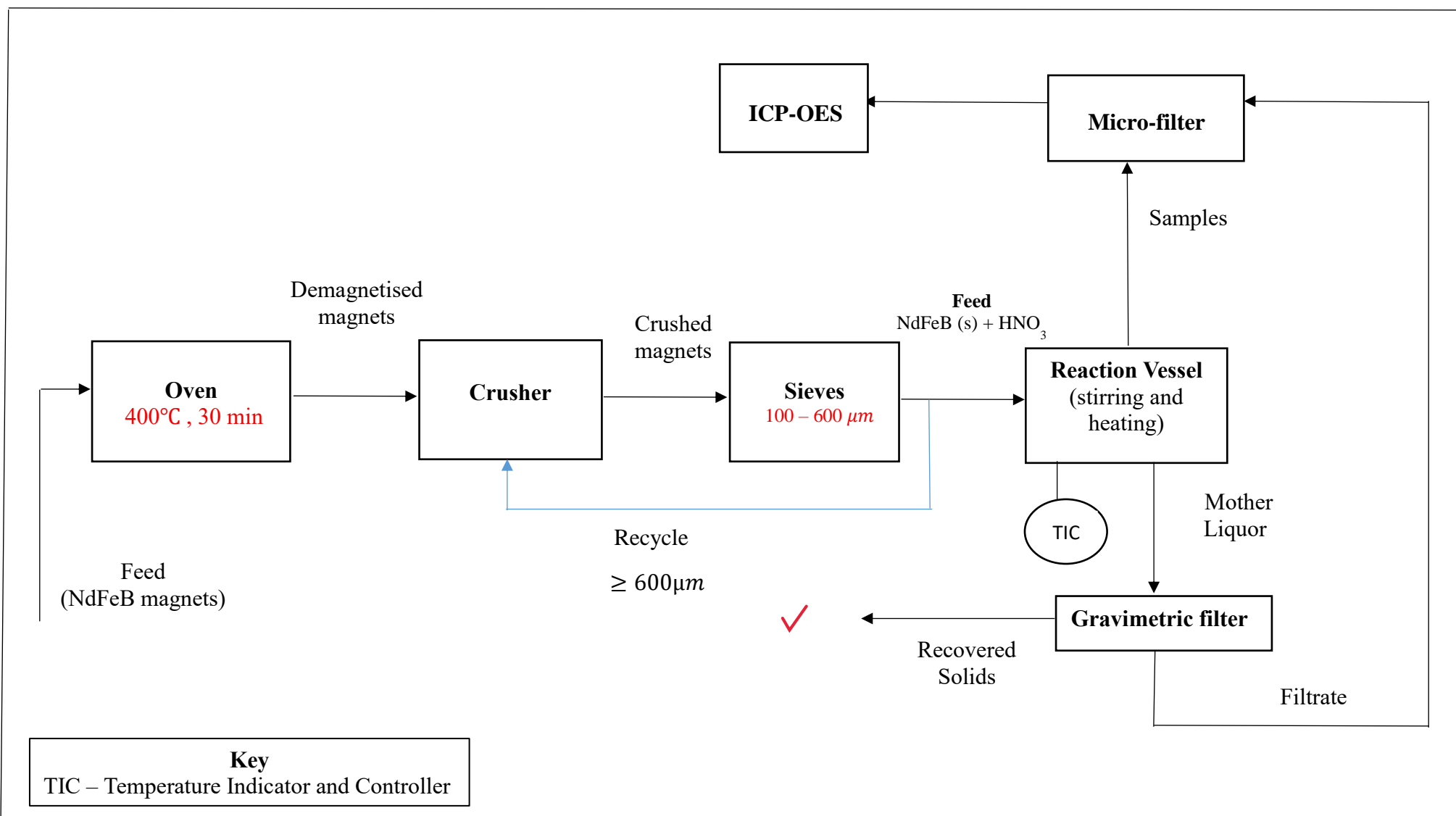


Figure 3.5. Overview of the batch experiment

### 3.8. Sample Analyses

The ICP calibration standards were prepared over a concentration range using neodymium and iron. These standards were prepared by Moodley (2021) and Bridgemohan (2021). These standards, along with the ICP samples, were sent to PMB's UKZN chemistry laboratory for ICP-OES analyses. ✓

### 3.9. Safety considerations

From Figure 3.5, the following factors must be carefully noted:

1. The NdFeB magnets are very strong and highly magnetic. It is therefore imperative that these magnets are handled carefully, especially before being placed in the oven. This could cause injury if the magnets are mishandled.
2. NdFeB dust is pyrophoric, and was handled carefully.
3. Exposure to strong nitric acid and hydrogen gas is toxic, hence the reaction vessel was placed in an extraction hood, due to the release of hydrogen gas, which is also flammable.
4. High oven temperatures are dangerous.
5. Chemicals were disposed carefully into hazard waste bottles and left in the extraction hood.
6. The MSDS for the neodymium, iron and nitric acid are provided in Appendix A.



## CHAPTER 4

### RESULTS AND DISCUSSION

#### 4.1 The demagnetization procedure

After the magnets and the support were separated, they were highly magnetic and became difficult to separate as they were attracted to each other. It is recommended that suitable material or padding is available to store these appropriately. The stacked magnets were placed in an oven at a temperature set at 400°C for 30 minutes.

After 30 minutes of heating, the magnets were cooled for another 20 minutes inside the oven after switching it off. It was observed that all the magnets had detached from one another, some became brittle and broke, releasing metallic dust into the oven and others lost their colour and coatings. The metallic coatings peeled off on some magnets and some surfaces did not peel. Most magnets retained their colour and others displayed a brown-orange colour and blue colour. Not all the small pieces of magnets and metallic dust could be removed from the oven, as they were in the perforations of the oven's surface. This contributed to a loss of sample. The magnets were non-magnetic and some were brittle. This method was effective.

An alternate method discussed with the supervisors considered the immersion of the magnets into liquid nitrogen after removal from the oven, to make them brittle and more efficient to work with. The hot-cold cycles would cause the magnetic performance to deteriorate and create a thermal shock, causing them to break and this will only be possible if the magnets are cooled below -130°C, to avoid the magnets from recovering its magnetism (First4Magnets, 2021). According to Flowe (2021), purchasing liquid nitrogen would not be convenient due to the high prices, and it would be more cost-effective to use commercially available equipment to generate nitrogen on the plant. Erust et al. (2019) reported that economical methods would need to be considered before implementing them on a commercial scale. Hence, the sustainability of this laboratory-scale experiment had to be considered. Thus, the use of liquid nitrogen would not be feasible for this experiment.

Since the heating method was effective, there was no need for liquid nitrogen to be used.

Figure 4.1 shows the magnets before and after heating.

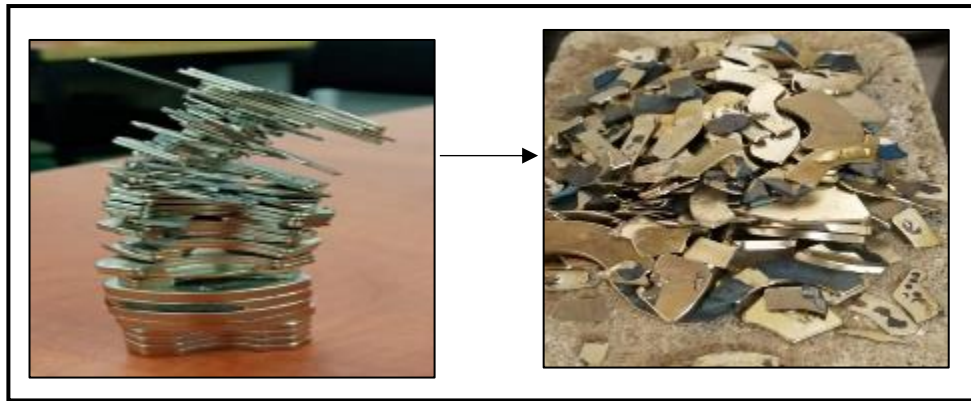


Figure 4.1. NdFeB magnets before and after heating

It is evident from Figure 4.1 that the demagnetization process was successful and all magnets detached from each other.

#### **4.2 Comminution of the NdFeB magnets**

For the crushing stage, the roller mill (model 123032) in the Chemical Engineering main laboratory was used to comminute the magnetic samples. This roller was mainly used to crush coal, therefore the efficiency of the roller had to be investigated during the comminution of the magnets.

There were approximately three different sizes of magnets, small, intermediate, and large magnets of varying thicknesses. The approximate thicknesses for the small, intermediate, and large magnets, were 0.1 cm, 0.2cm, and 0.4cm, respectively. The roller mill became problematic in the crushing process as the magnets had jammed the rollers. To allow for an efficient process, the distance between the rollers had to be adjusted for the different magnet thickness. To prevent the jamming of the rollers, two to three magnets were added at a time. This was very time-consuming.

### 4.3 Sieve Analysis

Smaller particles ( $< 300\mu\text{m}$ ) were difficult to remove from the pan and metal meshes. This led to dust and a loss of mass. This is also a safety factor to consider, as the NdFeB dust particles are pyrophoric. Table 4.2 shows the size distribution of the crushed magnets after sieving. It is evident that a reasonable amount of sample was present at each particle size range, proving that the roller mill was efficient at the expense of time.

Table 4.2. Size distribution of crushed magnet after sieving

Particle Size ( $\mu\text{m}$ )	Mass of sample (g)	Mass fraction (%)
$\geq 600$	339.273	55.40
500-600	40.878	6.70
425-500	37.242	6.10
355-425	32.685	5.30
300-355	30.386	5.00
200-300	57.498	9.40
150-200	28.789	4.70
100-150	33.857	5.50
$\leq 100$	11.694	1.90
<b>Total</b>	<b>612.302</b>	<b>100</b>

Standard uncertainties in mass are  $\pm 0.001\text{g}$ .

From Table 4.2, more than half of the total amount of sample contained the particle size  $\geq 600\mu\text{m}$ . Therefore, this size was used as part of the investigation to determine if further crushing is necessary. This is important, as energy in the comminution process can be reduced, if the larger particles can be dissolved well in the solution.



## 4.4 Leaching Tests

### 4.4.1 Type of acid used for leaching

From Figure 2.4, sulphuric acid (2M) had a 100% recovery for neodymium and dysprosium, compared to nitric acid and hydrochloric acid. Nitric acid had the second highest recovery for neodymium (80%), followed by hydrochloric acid (68%), which had a lower recovery for neodymium. Furthermore, sulphuric acid also had the highest recovery of 100% for iron, whereby nitric acid had a lower recovery for iron, of approximately 90% at a concentration of 2M. Erust et al. (2019) reported that high concentrations of iron in the leaching solution will create huge problems for further REEs separation ( Dupont and Binnemans, 2015), as 20-30 % of the rare earth elements obtained in the leaching process were lost due to the precipitation of iron (Rabatho et al., 2013). It would not be economical to use sulphuric acid due to this reason, rather it would be appropriate to use nitric acid due its low recovery of iron, preventing problems downstream in a commercial process. This justifies why nitric acid was used as an acid for the leaching process in this investigation.

Furthermore, sulphuric acid is highly toxic and hazardous (Martin, 2009). Therefore, the type of material of construction is important for the storage of this acid (Martin, 2009). The storage vessel must be well-fabricated with the correct metals to store this acid, leading to more fabrication costs (Martin, 2009). It cannot be stored in certain tanks, consisting of organic materials, as it may cause fires and explosions (Martin, 2009). Hence, there is a limitation in terms of the storage equipment. Nitric acid is not as toxic as sulphuric acid (Anon, 2020), hence the storage of this acid will be more convenient. Thus, by considering all these factors, nitric acid would be more convenient to use as a leaching agent.



Table 4.3. The leaching recoveries for the different parameters

Parameter	Leaching recoveries (%)
pH test 1 – 10%	87.44
pH test 2 – 10%	91.36
pH test – 30% nitric acid	99.66
pH test – 55% nitric acid	97.00
Particle Size 1 – (100 – 150 $\mu$ m)	91.04
Particle Size 2 Test 1– (425 – 500 $\mu$ m )	87.44
Particle Size Test 2 – (425 – 500 $\mu$ m)	91.36
Particle Size 3 – ( $\geq$ 600 $\mu$ m)	91.14
Temperature test 1 (45 $^{\circ}$ C)	95.20
Temperature test 2 (60 $^{\circ}$ C)	95.40
Time test -60 minutes	91.62

The standard deviation for base measurements (in blue):  $\pm 2.77\%$  for base measurements in blue.

\*For the pH tests, the wt% of nitric acid is reported.

Table 4.3 summarizes the leaching recoveries for the pH and particle size tests. All recoveries were above 80%. The leaching recovery of 91.14% for the particle size  $\geq 600\mu\text{m}$  is good, and is close to the leach recoveries of the other two particle sizes, indicating that further crushing is not necessary. Hence, this justifies that further comminution is not necessary to get the magnets to smaller sizes, due to the high leaching recovery.

It is noteworthy that when the leaching process was initiated, different colours and fumes were observable for each experiment. These observations are summarized in Table 4.6. It was also observable that once the metals were added to the chemical solution, the temperature had increased rapidly, indicating an exothermic reaction. After a few minutes, the temperature started to decrease until the temperature remained relatively constant for the duration of the leaching process. These can be seen in Figures 4.4 and 4.5.

Both Figures 4.4 and 4.5 of the base measurements (indicated in red) display a good trend and a good reproducibility, as it has a characteristic curve. It is also evident that the base measurements have peaked at approximately the same temperature and follow the same trend thereafter.

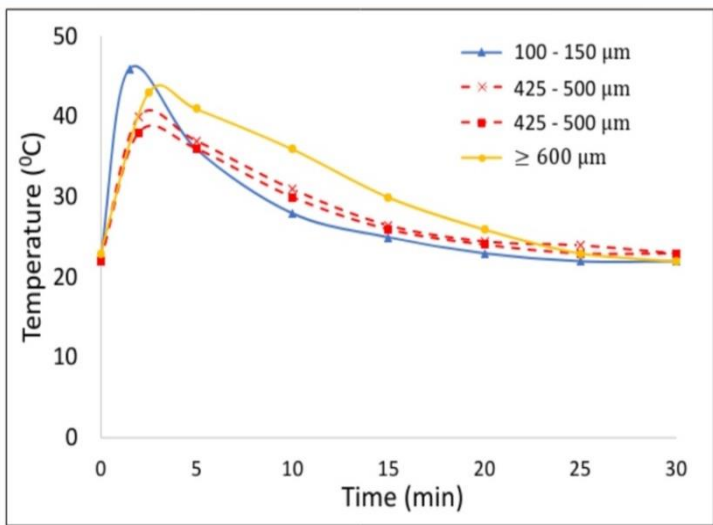


Figure 4.4. Reaction temperature variations in particle size tests (using 10wt% HNO<sub>3</sub>)

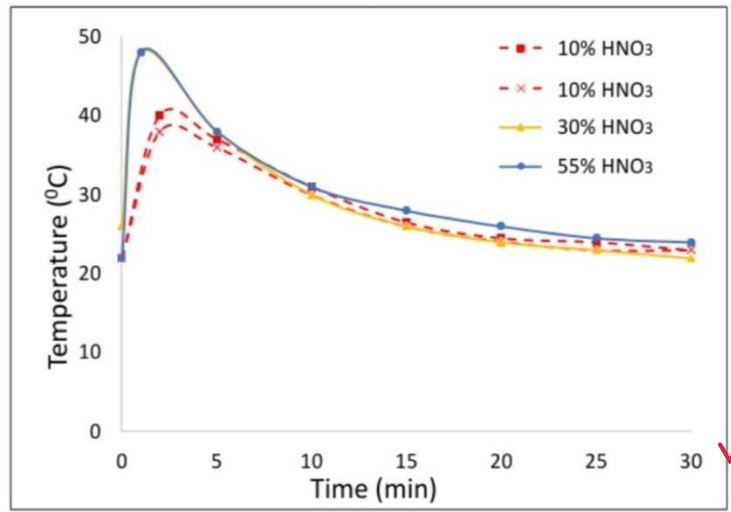


Figure 4.5. Reaction temperature variations in pH tests (425-500 μm)

For Figure 4.5, the pH of nitric acid was provided at different weight percentages.

Table 4.6. Colour observations from the leaching process

Operating Parameters	Observations
Particle Size 1: 100-150µm	When the sample was initially added, the solution had a black colour and started to froth. It gradually changed to a light brown colour. After 25 minutes, the solution displayed an almost clear colour.
Particle Size 2 : 425-500µm	The solution had a dark brown colour when the sample was initially added. The colour then gradually changed to light brown.
Particle Size 3: ≥ 600µm	No frothing and bubbling, when the sample was added to the solution. The solution was colourless.
pH test – (30% nitric acid)	When the sample was added to the solution, a yellow-green solution was displayed. Fumes were released. The solution gradually changed to a light yellow colour, eventually, it was close to colourless.
pH test – (55% nitric acid)	Red and yellow fumes were released once the sample was added to the solution. The solution displayed a red-brown colour. The solution gradually turned into a yellow-brown colour and released clear fumes.
Temperature - 45°C	Clear fumes, rapid bubbling, and a dark brown colour was displayed when sample was added to the solution. The solution gradually turned to a light brown colour.
Temperature- 60 °C	The solution started to bubble and fumes were released. The solution had a dark brown colour and gradually changed to light brown in colour.
Time Test -60 minutes	A black-brown colour was displayed, when the sample was added to the solution. The colour gradually changed to light brown, eventually turning colourless.

\*For the pH tests, the wt % of nitric acid was reported in Table 4.6.

#### ***4.4.2 Analysis of the ICP results.***

In order to determine the extraction efficiency of the metals, the concentrations of Nd and Fe in the initial sample had to be known for this. It was assumed to be 25.94 wt% neodymium and 61.33wt% iron. These values were obtained from Gruber and Carsky (2020).

From the ICP results received, it was observed that the Nd and Fe concentrations in the samples were in the range of 7100-8250 ppm and 12000-13500 ppm, respectively. When the calculations were performed, the recovery of the metals were found to have recoveries greater than 100%. These are unrealistic and too high, indicating that the assumptions of the weight percentages of Nd and Fe in the initial sample may be incorrect. It is not possible to extract more iron and neodymium than what was initially present in the solution. Hence, the concentration approach could not be used with the assumption from literature in this case.

Hence, the initial concentration of neodymium and iron may likely be lower and further tests are required to determine this, either via ICP-OES analysis or alternate methods. Furthermore, the concentrations may differ per screening size. These details need to be investigated further. ✓

According to Gruber and Carsky (2020), NdFeB magnets have the same structure of  $\text{Nd}_2\text{Fe}_{14}\text{B}$ . However, there may be variations from this general composition, depending on the manufacturing process of the magnets, or the properties of the magnets (Gruber and Carsky, 2020). These magnets can be made based on a specific purpose, hence other elements could have been added to displace the basic elements in the magnet structure (Gruber and Carsky, 2020). Iron can also be substituted by 1-2% of cobalt, to improve the corrosion properties of the magnets (Gruber and Carsky, 2020). Thus, in order to determine the chemical composition of the different NdFeB magnets, the magnets can be dissolved in a weak sulphuric acid solution and the time of the reaction needs to be sufficient, to ensure that complete dissolution of the magnets are achieved (Gruber and Carsky, 2020). The results can then be sent for ICP-OES analysis.

In order to get a broad perspective and analyze the ICP results, a rate-based approach using the initial time of 10 minutes, as the starting point was used. This approach was based on the assumption that the beaker was well-mixed. The sample calculations are available in Appendix E, and this approach gave more realistic results. From table E.2, after the calculations were performed, it was evident that the iron and neodymium mass fractions decrease in the solution.

## CHAPTER 5

### CONCLUSIONS

The magnetic removal of the magnets from the aluminium support was successful. Demagnetization was successful at 400°C for 30 minutes, as the magnets lost their magnetic properties. The heating method proved to be successful, hence there was no need to use liquid nitrogen.

The comminution process was effective with the use of the roller mill. The only drawback to this method was the reduced efficiency due to the smaller quantities to be crushed and the jamming of the rollers.

The pyrophoricity of the magnets was noted, hence the magnets samples were handled with care.

The sieving and screening process was successful, and a significant amount of sample was present at each size range. The amount of sample was sufficient to perform all the experiments, and the particle sizes  $\geq 600\mu\text{m}$  contributed approximately 55.40% to the total sample, whereas the sample sizes  $\leq 100\mu\text{m}$  contributed the least, of approximately 1.90%. All the physical observations of the solutions were recorded once the leaching process was initiated (colour, fumes, etc.). The leach recoveries were calculated successfully after vacuum filtration. The particle sizes  $\geq 600\mu\text{m}$  were calculated to have a high leaching recovery of 91.14%, hence further comminution to smaller particle sizes were not necessary.

All leaching tests were completed, where the effect of particle size, temperature, the concentration of nitric acid, and time on the process were assessed. Colour changes in the leaching process were noted and the solid-liquid reaction was highly exothermic.

The leaching efficiencies could not be determined due to lack of information on the concentration of the elements at the start of the experiments.

ICP calculations could not be performed on a concentration basis, by using an assumption of the initial composition of iron and neodymium reported in literature. Hence, a rate-based approach was used in calculations to get an overview of the leaching trends.

Future work is needed on the characterization of the magnetic powders. Furthermore, longer extraction times should be tested to determine the maximum extraction achieved.

## RECOMMENDATIONS

### The comminution process

A jaw crusher, which crushes metal can be used to improve the crushing efficiencies and ensure a higher sample output at each size interval. The performance of the jaw crusher can be performed with the performance of the roller mill.

### The sieving process

A bench top agitator can be used for an efficient and steady agitation, ensuring that the sample is evenly distributed across the mesh, allowing for an improved passing of particles into the sieve plates below it.

### The leaching process

The particle size 425-500 $\mu\text{m}$  is safer to use.

The particle size  $\geq 600\mu\text{m}$ , had a high leach recovery of 91.14 %, hence further comminution will not be required for future projects. This will save on time.

The factorial design method can be implemented in triplicate.

The leaching efficiencies of other constituents of the magnets can be determined, such as B, Dy, Pr, Ni, Al and Co using ICP – OES analysis.

The exothermic reaction releases hydrogen gas, and the amount of hydrogen gas can be determined if it was collected. The composition of this gas can be determined using gas chromatography.

### Composition of magnets

For future experiments, the composition of magnets will need to be determined first, before starting the leaching experiment. This will be achieved by dissolving the magnets in a weak sulphuric acid solution, and analysed by ICP-OES analysis. This will improve the accuracy of the experiment and the leaching efficiencies can be determined and plotted for iron and neodymium. Hence, the optimal conditions can be determined, satisfying the aim of this experiment. ✓

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# Appendix

## Appendix A: Material and Safety Data Sheets (MSDS)

The material and safety data sheets highlight the main components used in the investigation, such as the magnetic powders, neodymium powder, iron powder and nitric acid.



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### 3. Composition / Information on Ingredients

Chemical Name: Sintered Neodymium-Iron-Boron (NdFeB) Permanent Magnet

Material	Weight %	CAS #:	ACGIH TLV (mg/m <sup>3</sup> )	Notes
Neodymium	approx. 33%	7440-00-8	Not established	
Iron	approx. 65%	7439-89-6	10 (oxide)	
Boron	approx. 1.3%	7440-42-8	10	
Nickel	0.01-0.4%	7440-02-0	1(dust)/0.1(fume)	plating
Copper	0.01-0.2%	7440-50-8	1(dust)/0.1(fume)	plating
Dysprosium	0-4%	7429-91-6	Not established	hi-temp grades
Cobalt	0-5%	7440-48-4	0.02	hi-temp grades

### 4. First-Aid Measures

**Eye Contact:**  
Small pieces, chips or dust from magnet material may cause irritation. Wash eyes gently under running water for 15 minutes or more to remove. If symptoms persist, seek medical attention.

**Skin Contact:**  
Prolonged skin contact may cause irritation or allergic dermatitis, especially for individuals with nickel allergy. In the case of contact with chips or dust from a broken magnet, brush off powders and wash well with soap and water.

**Inhalation:**  
Rare. If vapors or dusts have been inhaled, move individual to fresh air and seek medical attention.

**Ingestion:**  
If a magnet is swallowed, seek medical attention immediately. If multiple magnets are ingested, magnets can stick together through intestinal walls, causing serious infections and death. Seek immediate medical attention.

**Information for Doctors:**  
Ingestion of multiple magnets can pose a serious risk. Consider consulting the algorithm presented in, "Management of Ingested Magnets in Children," (Hussain et al., 2012).  
Strong magnetic fields found near neodymium magnets can interfere with the operation of implanted medical devices such as pacemakers and ICDs.

Figure A.1. MSDS for hard drive disk magnets (MPI, 2018)





### 5. Fire-fighting Measures

**Flammable Properties:**

Dry powders of neodymium magnets will oxidize, smolder, and burn rapidly in the presence of air or oxygen. Maintain powders in water slurry or in inert atmospheres of nitrogen or argon to prevent spontaneous combustion. Magnets may spark on impact. Handle carefully in explosive atmospheres.

**Extinguishing media:**

Suitable: Sand or dry chemicals without oxygen compounds  
Unsuitable: Do not use Halon agents or water on smoldering or burning powder.

### 6. Accidental Release Measures

**Personal precautions, protective equipment and emergency procedures:**

No special measures required. See Section 7 for information on safe handling.

**Environmental precautions:**

Not applicable.

**Methods and Material for containment and cleaning up:**

No special measures required. Pick up mechanically.

**Reference to other sections:**

See Section 7 for information on safe handling.

### 7. Handling and Storage

Large magnets can attract to one another. Strong attractive forces can cause injury. Impacts of magnets can eject chips or bits of magnet material at speed – eye protection should be used.

Strong magnetic fields may affect the operation of implanted medical devices such as pacemakers and ICDs.

If magnetic dust is formed, sweep up dust and store in water slurry or sealed containers utilizing inert atmosphere such as argon or nitrogen to prevent spontaneous combustion.

### 8. Exposure Controls / Personal Protection

This product is considered to be an article which does not release or otherwise result in exposure to a hazardous chemical under normal use conditions. No engineering controls are necessary.

**Protection of hands:**

Avoid repeated and prolonged contact with the skin, especially if user has known nickel allergies. Protective gloves may be used.

**Eye protection:**

Safety goggles should be worn when handling magnetized magnets.

Figure A.2. MSDS for hard drive disk magnets (MPI, 2018)



# SDS

Safety Data Sheet  
per 29 CFR 1910.1200



THE Ames Laboratory  
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## Neodymium

### SAFETY DATA SHEET

#### **1 PRODUCT AND SUPPLIER IDENTIFICATION**

**Product Name:** Neodymium - pieces, ingot, rod, foil, sheet, target  
**Formula:** Nd

**Supplier:** Ames Laboratory, US DOE  
Materials Preparation Center  
121 Metals Development  
Ames, IA 50010 USA

**Telephone:** 515-294-5236

**Fax:** 515-294-8727

**Email:** [mpc@ameslab.gov](mailto:mpc@ameslab.gov)

**Emergency:** 515-294-3483 (24 hour)

**Recommended Uses:** Scientific Research

#### **2 HAZARDS IDENTIFICATION**

**GHS Classification (29 CFR 1910.1200):** Not classified as hazardous

**GHS Label Elements:**

**Signal Word:** N/A

**Hazard Statements:** N/A

**Precautionary Statements:** N/A

#### **3 COMPOSITION/INFORMATION ON INGREDIENTS**

**Ingredient:** Neodymium

**CAS#:** 7440-00-8

**%:** 100

**EC#:** 231-109-3

#### **4 FIRST AID MEASURES**

**General Measures:** Under normal handling and use, exposure to solid forms of this material present few health hazards. Subsequent operations such as grinding, melting or welding may create dusts or fumes which could be inhaled or contact skin or eyes.

**INHALATION:** Remove to fresh air, keep warm and quiet, give oxygen if breathing is difficult. Seek medical attention.

**INGESTION:** Rinse mouth with water. Do not induce vomiting. Seek medical attention. Never induce vomiting or give anything by mouth to an unconscious person.

**SKIN:** Remove contaminated clothing, brush material off skin, wash affected area with soap and water. Seek medical attention if symptoms persist.

**EYES:** Flush eyes with lukewarm water, including under upper and lower eyelids, for at least 15 minutes. Seek medical attention if symptoms persist.

**Most Important Symptoms/Effects, Acute and Delayed:** See section 11 for more information.

**Indication of Immediate Medical Attention and Special Treatment:** No other relevant information available.

#### **5 FIREFIGHTING MEASURES**

**Extinguishing Media:** Use Class D dry powder extinguishing agent.

**Unsuitable Extinguishing Media:** Do not use water.

**Specific Hazards Arising from the Material:** Flammable in the form of dust when exposed to heat, spark or flame. May react with water under fire conditions liberating flammable hydrogen gas. May emit fumes of neodymium oxide under fire

Figure A.3. MSDS for Neodymium (The Ames Laboratory, 2016)



# SDS

## Safety Data Sheet

per 29 CFR 1910.1200



THE Ames Laboratory

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conditions.

**Special Protective Equipment and Precautions for Firefighters:** Full face, self-contained breathing apparatus and full protective clothing to prevent contact with skin and eyes.

### 6 ACCIDENTAL RELEASE MEASURES

**Personal Precautions, Protective Equipment, and Emergency Procedures:** Wear appropriate respiratory and protective equipment specified in section 8. Isolate spill area. Avoid dust formation. Avoid contact with skin and eyes. Avoid breathing dust or fume. Eliminate all sources of ignition.

**Methods and Materials for Containment and Cleaning Up:** Sweep or scoop spilled product and place in a closed container for further handling and disposal. Use only non-sparking tools and natural bristle brushes.

**Environmental Precautions:** Do not allow to enter drains or to be released to the environment.

### 7 HANDLING AND STORAGE

**Precautions for Safe Handling:** Handle in an enclosed, controlled process, under dry protective gas such as argon when possible. Air and moisture sensitive. Protect from sources of ignition. Avoid contact with skin and eyes. Wash thoroughly before eating or smoking. See section 8 for information on personal protection equipment.

**Conditions for Safe Storage, Including Any Incompatibilities:** Neodymium metal should be stored in tightly-closed containers under argon or mineral oil. Store in a cool, dry area. Protect from moisture. See section 10 for more information on incompatible materials.

### 8 EXPOSURE CONTROLS AND PERSONAL PROTECTION

**Exposure Limits:** Neodymium

**OSHA/PEL:** No exposure limit established

**ACGIH/TLV:** No exposure limit established

**Appropriate Engineering Controls:** Handle in a humidity controlled atmosphere. Handle in an enclosed, controlled process under dry argon when possible. Ensure adequate ventilation to maintain exposures below occupational limits. Whenever possible the use of local exhaust ventilation or other engineering controls is the preferred method of controlling exposure to airborne dust and fume to meet established occupational exposure limits. Use good housekeeping and sanitation practices. Do not use tobacco or food in work area. Wash thoroughly before eating or smoking. Do not blow dust off clothing or skin with compressed air.

**Individual Protection Measures, Such as Personal Protective Equipment:**

**Respiratory Protection:** If permissible levels are exceeded, use NIOSH approved dust respirator.

**Eye Protection:** Safety glasses

**Skin Protection:** Wear impermeable gloves, protective work clothing as necessary.

Figure A.4. MSDS for Neodymium (The Ames Laboratory, 2016)



According to European Directive 67/548/EEC as amended.

Hazard symbol(s)



R-phrase(s)

R11 Highly flammable.

S-phrase(s)

S16

Keep away from sources of ignition - No smoking.

S33

Take precautionary measures against static discharges.

**2.3 Other hazards - none**

### **3. COMPOSITION/INFORMATION ON INGREDIENTS**

#### **3.1 Substances**

Formula : Fe  
Molecular Weight : 55,85 g/mol

### **4. FIRST AID MEASURES**

#### **4.1 Description of first aid measures**

##### **General advice**

Consult a physician. Show this safety data sheet to the doctor in attendance.

##### **If inhaled**

If breathed in, move person into fresh air. If not breathing, give artificial respiration. Consult a physician.

##### **In case of skin contact**

Wash off with soap and plenty of water. Consult a physician.

##### **In case of eye contact**

Flush eyes with water as a precaution.

##### **If swallowed**

Do NOT induce vomiting. Never give anything by mouth to an unconscious person. Rinse mouth with water. Consult a physician.

#### **4.2 Most important symptoms and effects, both acute and delayed**

Overdose of iron compounds may have a corrosive effect on the gastrointestinal mucosa and be followed by necrosis, perforation, and stricture formation. Several hours may elapse before symptoms that can include epigastric pain, diarrhea, vomiting, nausea, and hematemesis occur. After apparent recovery a person may experience metabolic acidosis, convulsions, and coma hours or days later. Further complications may develop leading to acute liver necrosis that can result in death due to hepatic coma., Long term inhalation exposure to iron (oxide fume or dust) can cause siderosis. Siderosis is considered to be a benign pneumoconiosis and does not normally cause significant physiologic impairment. Siderosis can be observed on x-rays with the lungs having a mottled appearance.

Figure A.5. The MSDS for iron powder (CDH, 2008)

# Nitric Acid, 70% w/w

## Safety Data Sheet

according to Federal Register / Vol. 77, No. 58 / Monday, March 26, 2012 / Rules and Regulations

### SECTION 5: Fire-fighting measures

#### 5.1. Suitable (and unsuitable) extinguishing media

- Suitable extinguishing media : Adapt extinguishing media to the environment.  
Unsuitable extinguishing media : No unsuitable extinguishing media known.

#### 5.2. Specific hazards arising from the chemical

- Fire hazard : DIRECT FIRE HAZARD. Non combustible. INDIRECT FIRE HAZARD. Promotes combustion. Reactions involving a fire hazard: see "Reactivity Hazard".  
Explosion hazard : INDIRECT EXPLOSION HAZARD. Reactions with explosion hazards: see "Reactivity Hazard".  
Reactivity : Concentrated solution reacts exothermically with water (moisture). Decomposes on exposure to temperature rise: release of toxic and corrosive gases/vapours (nitrous vapours). Violent to explosive reaction with many compounds e.g.: with (strong) reducers, with (some) bases, with organic material and with combustible materials with risk of spontaneous ignition. Reacts violently with (some) metals. Decomposes slowly on exposure to light: release of toxic and corrosive gases/vapours (nitrous vapours). Violent to explosive reaction with (some) metal powders: release of highly flammable gases/vapours (hydrogen).

#### 5.3. Special protective equipment and precautions for fire-fighters

- Firefighting instructions : Cool tanks/drums with water spray/remove them into safety. Do not move the load if exposed to heat. Dilute toxic gases with water spray. Take account of toxic fire-fighting water. Use water moderately and if possible collect or contain it.  
Protection during firefighting : Use self-contained breathing apparatus and chemically protective clothing.

### SECTION 6: Accidental release measures

#### 6.1. Personal precautions, protective equipment and emergency procedures

- General measures : Dike and contain spill. Absorb spillage to prevent material-damage.

##### 6.1.1. For non-emergency personnel

- Protective equipment : Gas-tight suit. Corrosion-proof suit. See "Material-Handling" to select protective clothing.  
Emergency procedures : Keep upwind. Mark the danger area. Consider evacuation. Seal off low-lying areas. Close doors and windows of adjacent premises. No naked flames. Corrosion-proof appliances. Keep containers closed. Wash contaminated clothes.

##### 6.1.2. For emergency responders

- Protective equipment : Equip cleanup crew with proper protection. Avoid breathing mist, spray.  
Emergency procedures : Stop leak if safe to do so. Ventilate area.

#### 6.2. Environmental precautions

Prevent soil and water pollution. Prevent spreading in sewers.

#### 6.3. Methods and material for containment and cleaning up

- For containment : Contain released substance, pump into suitable containers. Consult "Material-handling" to select material of containers. Plug the leak, cut off the supply. Dam up the liquid spill. Try to reduce evaporation. Dilute toxic gases/vapours with water spray. Take account of toxic/corrosive precipitation water. Hazardous reaction: measure explosive gas-air mixture. Reaction: dilute combustible gas/vapour with water curtain.  
Methods for cleaning up : Take up liquid spill into inert absorbent material, e.g.: sand, earth, vermiculite or powdered limestone. Do not take up in combustible material such as: saw dust. Scoop absorbed substance into closing containers. See "Material-handling" for suitable container materials. Carefully collect the spill/leftovers. Spill must not return in its original container. Damaged/cooled tanks must be emptied. Clean contaminated surfaces with an excess of water. Take collected spill to manufacturer/competent authority. Wash clothing and equipment after handling.

#### 6.4. Reference to other sections

Figure A.6. MSDS for nitric acid (LabChem, 2012)



## Appendix B: Data for Leach recoveries

The data for the leach recoveries in Table 4.3.

Equation 1 of the report was used. These were calculated after the leaching process and after the filtration. The filter paper with the sample was left to dry and the mass was weighed using the mass balance.

-The weight of metal unleached by the acid = B-C =D

- The weight of metal leached by the acids =  $\frac{A-D}{A} \times 100 = E$

Table B. Data for leaching recoveries

	A.Mass used (g)	B.Mass of filter paper and sample (g)	C.Mass of filter paper (g)	D. Unleached sample (g)	E.Leach recovery (%)
pH-test 30%	1.003	0.863	0.860	0.003	99.70
pH-test 55%	1.007	0.900	0.878	0.022	97.00
Particle Size 1 (100-150µm)	1.007	0.904	0.844	0.09	94.04
Particle Size 2 (425-500µm) Test 1 using pH 10%	1.003	0.951	0.825	0.126	87.44
Particle Size 2 (425-500µm) Test 2 using pH 10%	1.008	0.918	0.831	0.085	91.36
Particle Size 3 (≥ 600 µm)	1.005	0.936	0.847	0.089	91.14
Temperature Test 1- 45°C	1.001	0.879	0.831	0.048	95.20
Temperature Test 2 - 60°C	1.000	0.894	0.848	0.046 ✓	95.40
Time test 1	1.002 ✓	0.935	0.851	0.084	91.62

The standard deviation from Table 4.3 can be calculated as (Castrup, 2004) :

$$s = \sqrt{\frac{1}{n-1} \sum_{i=1}^n (xi - \bar{x})^2} \quad (3)$$

$$\bar{x} = \frac{91.36+87.44}{2} = 89.40$$

$$s = \sqrt{\frac{1}{2-1} ((91.36 - 89.40)^2 + (87.44 - 89.40)^2)} = 2.77$$

## Appendix C: Data for the exothermic reaction

Data for Figures 4.4 and 4.5, respectively.

Table C.1. Data for time and temperatures for the particle sizes

Time( min)	Temperature (°C) for Particle Size 100- 150µm	Temperature (°C) for Particle Size 425- 500µm	Temperature (°C) for Particle Size 425- 500µm	Temperature (°C) for Particle Size 600µm
0	22.0	22.0	22.0	23.0
1.5	46.0	40.0	38.0	43.0
5	36.0	37.0	36.0	41.0
10	28.0	31.0	30.0	36.0
15	25.0	26.5	26.0	30.0
20	23.0	24.5	24.1	26.0
25	22.0	24.0	23.0	23.0
30	22.0	23.0	23.0	22.0

Table C.2. Data for time and temperatures for the pH of nitric acid

Time( min)	Temperature (°C) for pH 10% HNO <sub>3</sub>	Temperature (°C) for pH 10% HNO <sub>3</sub>	Temperature (°C) for pH 30% HNO <sub>3</sub>	Temperature (°C) for pH 55% HNO <sub>3</sub>
0	22.0	22.0	26.0	22.0
2	40.0	38.0	48.0	48.0
5	37.0	36.0	38.0	38.0
10	31.0	30.0	30.0	31.0
15	26.5	26.0	26.0	28.0
20	24.5	24.1	24.0	26.0
25	24.0	23.0	23.0	24.5
30	23.0	23.0	22.0	24.0

## Appendix D: ICP-OES analysis results

ICP results received from UKZN's PMB Chemistry lab. The results highlighted in blue were used, as they gave the highest detections.

Table D. Data of ICP-OES results

<b>Sample Labels</b>	<b>Fe 259.940</b>	<b>Nd 401.224</b>	<b>Nd 406.108</b>	<b>Nd 410.945</b>
Test 1 (100-150µm) 10 min	15740	6365	7101	6344
20 min	18198	7809	8726	7824
30 min	15514	6286	7140	6316
Mother Liquor	12654	4928	5622	4961
Test 1 (425-500µm)10min	18244	6729	7654	6742
20 min	14790	5926	6762	5969
30 min	17723	6729	7658	6745
Mother Liquor	13606	5383	6152	5541
Test 2 (425-500µm)10min	14811	5944	6796	5969
20 min	15020	6053	6913	6084
30 min	14657	5851	6715	5873
Mother Liquor	12220	4743	5433	4795
Test 1 (≥600 µm) 10 min	15570	6254	7168	6280
20 min	16032	6460	7412	6485
30 min	14702	5856	6723	5937
Mother Liquor	13862	5470	6289	5486
pH test 30% HNO3 10 min	15663	6344	7289	6368
20 min	14453	5767	6641	5805
30 min	15276	6111	7048	6157
Mother Liquor	12755	4953	5719	4979
pH test 30% HNO3 10 min	18234	7243	8317	7283
20 min	16317	6676	7706	5177
30 min	13061	5119	5905	5177
Mother Liquor	8865	3273	3798	3301
Test 1 (425-500 µm) 30min	14972	5972	6893	6025
50 min	15114	6050	6987	6080
60 min	15883	6422	7436	6467
Mother Liquor	11384	4348	5038	4386
Test 1 @45°C 10 min	16284	6584	7608	6629
20 min	14087	5568	6437	5608
30 min	15950	6435	7432	6481
Mother Liquor	11986	4639	5378	4678
Test 2 @60°C 10 min	15913	6440	7455	6484
20 min	15926	6444	7453	6449
30 min	16929	6790	7864	6804
Mother Liquor	11009	4210	4893	4240



## Appendix E: Rate-based approach

Sample calculation for the rate-based approach using the data for the particle size 100-150 $\mu$ m from Table D :

Initially in the beaker, there is approximately 1.000g of crushed sample and 50ml of nitric acid. The beaker was assumed to be well-mixed.

Solvent (nitric acid density) =  $1\,413 \frac{\text{g}}{\text{L}}$  (Merck, 2021)

Solvent mass initially =  $1\,413 \frac{\text{g}}{\text{L}} \times 0.05 \text{ L} = 70.650 \text{ g}$

Initial crushed sample mass = 1.000 g

Total initial mass = 70.650 g + 1.000g = 71.650 g



Table E.1. Data for particle size test

Sample Labels	Fe 259.940 (mg/L)	Mass extracted (g)	Nd 406.108 (mg/L)	Mass extracted (g)	Total mass of solid extracted (g)	Solvent density (g/L)	Solvent mass (g)	Total solution mass (g)
Particle Size test 1 (100-150 $\mu$ m) 10 min	15740	0.0944	7101	0.0426	0.1370	1413	8.4780	8.6150
20 min	18198	0.1091	8726	0.0523	0.1614	1413	8.4780	8.6394
30min	15514	0.0930	7140	0.0428	0.1358	1413	8.4780	8.6138

### For the first row to Table E.1. :

Sample calculation of the rate-based method, to determine the mass fractions of the components in solution:

Volume extracted (using syringe) = 6ml = 0.006 L



$$\text{Mass of Fe extracted (mg)} = 15740 \frac{\text{mg}}{\text{L}} \times 0.006 \text{ L} = 95.440 \text{ mg} = 0.0944\text{g}$$

$$\text{Mass of Nd extracted (mg)} = 7101 \frac{\text{mg}}{\text{L}} \times 0.006 \text{ L} = 44.606 \text{ mg} = 0.0426\text{g}$$

$$\text{Total mass of solid extracted} = 0.0944\text{g} + 0.0426 \text{ g} = 0.1370\text{g}$$

$$\text{Solvent (nitric acid density)} = 1413 \frac{\text{g}}{\text{L}}$$

$$\text{Solvent mass} = 1413 \frac{\text{g}}{\text{L}} \times 0.006 \text{ L} = 8.4780 \text{ g}$$

$$\text{Total solution mass} = 8.4780\text{g} + 0.1370\text{g} = 8.6150\text{g}$$

Table E.2. Data for particle size test

	Mass Fraction Fe	Mass fraction Nd	Mass fraction solvent	Mass Fe in mother liquor (g)	Mass Nd in mother liquor (g)	Mass solvent in mother liquor (g)	Fe fraction in mother liquor	Nd fraction in mother liquor	Solvent fraction in mother liquor
10 minutes	0.0109	0.0049	0.9840	0.7809	0.3510	70.5036	0.010901	0.004899	0.9841
20 minutes	0.0126	0.0060	0.9813	0.6865	0.3084	62.0256	0.010893	0.004893	0.9842
30 minutes	0.0107	0.0049	0.9842	0.5774	0.2561	53.3862	0.010649	0.004723	0.9846
40 minutes				0.4844	0.2133	44.9082	0.010621	0.004677	0.9847



**For the first row of Table E.2 :**

$$\text{Mass fraction of Fe} = \frac{0.0944}{8.6150} = 0.0109$$

$$\text{Mass fraction of Nd} = \frac{0.0426}{8.6150} = 0.0049$$

$$\text{Mass fraction of the solvent} = \frac{8.4780}{8.6150} = 0.9840$$

**For the row, where time = 10 minutes (basis to what was present initially):**

$$\text{Mass of Fe in the mother liquor (original solution)} = 0.0109 \times 71.65\text{g (total mass)} = 0.7809\text{g}$$

$$\text{Mass of Nd in the mother liquor} = 0.0049 \times 71.65\text{g} = 0.3510\text{g}$$

$$\text{Mass of solvent in the mother liquor} = 0.9840 \times 71.65\text{g} = 70.5036\text{g}$$

$$\text{Fe fraction in mother liquor} = \frac{0.7809}{0.7809+0.3510+70.5036} = 0.0109$$

$$\text{Nd fraction in mother liquor} = \frac{0.3510}{0.7809+0.3510+70.5036} = 0.0048$$

$$\text{Solvent fraction in mother liquor} = \frac{70.5036}{0.7809+0.3510+70.5036} = 0.9841$$



**For the row, where time = 20 minutes (essentially what remained in solution after extraction at t = 10 minutes):**

$$\text{Mass of Fe in the mother liquor} = 0.7809\text{g (mass initially in beaker)} - 0.0944\text{g (mass extracted in Table E.1.)} = 0.6865\text{g}$$

$$\text{Mass of Nd in mother liquor} = 0.3510\text{g} - 0.0426\text{g} = 0.3084\text{g}$$

$$\text{Mass of solvent in mother liquor} = 70.5036 - 8.4780 = 62.0256\text{g}$$

$$\text{Fe fraction in mother liquor} = \frac{0.6865}{0.6865+0.3084+62.0256} = 0.0108$$



$$\text{Nd fraction in mother liquor} = \frac{0.3084}{0.6865+0.3084+62.0256} = 0.0048$$

$$\text{Solvent fraction in mother liquor} = \frac{62.0256}{0.6865+0.3084+62.0256} = 0.9842$$

**For the row, where time = 30 minutes (essentially what remained in solution after extraction at t = 20 minutes) :**

$$\text{Mass of Fe in the mother liquor} = 0.6865\text{g} - 0.1091\text{g (mass extracted in table E.1. )} = 0.5774\text{g}$$

$$\text{Mass of Nd in mother liquor} = 0.3084\text{g} - 0.0523 = 0.2561\text{g}$$

$$\text{Mass of solvent in mother liquor} = 62.0256 - 8.4780 = 53.5476\text{g}$$

$$\text{Fe fraction in mother liquor} = \frac{0.5774}{0.5774+0.2561+53.5476} = 0.0106$$

$$\text{Nd fraction in mother liquor} = \frac{0.2561}{0.5774+0.2561+53.5476} = 0.0047$$

$$\text{Solvent fraction in mother liquor} = \frac{53.5476}{0.5774+0.2561+53.5476} = 0.9846$$

**For the row, where time = 40 minutes (essentially what remained in solution after extraction at t = 30 minutes) :**

$$\text{Mass of Fe in the mother liquor} = 0.5774\text{g} - 0.0930\text{g (mass extracted in table E.1.)} = 0.4844\text{g}$$

$$\text{Mass of Nd in mother liquor} = 0.2561\text{g} - 0.0428\text{g} = 0.2133\text{g}$$

$$\text{Mass of solvent in mother liquor} = 53.3862\text{g} - 8.4780\text{g} = 44.9082\text{g}$$

$$\text{Fe fraction in mother liquor} = \frac{0.4844}{0.4844+0.2133+44.9082} = 0.010621$$

$$\text{Nd fraction in mother liquor} = \frac{0.2133}{0.4844+0.2133+44.9082} = 0.004677$$

$$\text{Solvent fraction in mother liquor} = \frac{44.9082}{0.4844+0.2133+44.9082} = 0.9847$$

This summarizes the rate-based approach for the first set of ICP results. The same method can be used for the other set of results.