

# Rare earth elements research conducted at Mintek

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The importance of rare earth elements (REEs) in the transition to a green economy is gaining momentum. Given the vast primary and secondary resources of REEs in Southern Africa, there is potential for the region to contribute significantly to global REE production. Mintek is a player in the REE space and conducts REE research across several disciplines, including mining and mineral economics, chemical and mineralogical characterisation, minerals processing, extractive metallurgy and advanced materials. This paper provides a summary of research and development of REEs conducted at Mintek.

**Key words:** Rare earths, REEs extraction, REEs recycling, REEs characterisation

## INTRODUCTION

Given the monopolised global supply of REEs by China, there is an urgent need to source REEs from other regions. Studies have reported geopolitical issues surrounding REEs and potential supply risks (Binnemans *et al.*, 2018; Seaman, 2019; Shen *et al.*, 2020). As a result, numerous studies have explored alternative sources of REEs in different countries and devised efficient extraction methods (Binnemans *et al.*, 2013; Dutta, *et al.*, 2016; Jyothi, *et al.*, 2020); Eterigho-Ikelegbe *et al.*, 2021). Southern Africa has considerable primary and secondary REEs resources which are currently underexploited. Mintek is a world leader in the specialisation of minerals processing, extractive metallurgy and related fields. A summary of Mintek's research and development (R&D) in REEs across the technical disciplines is presented in this paper.

## REEs chemical characterisation at Mintek

### *Sample preparation for REE-bearing samples*

It is critical that analytical results obtained in a laboratory are highly accurate and reflect the sample being analysed. Despite substantial progress in sample preparation over the previous three decades, it remains one of the biggest challenges with limiting variables in geochemical research. Due to challenges associated with dissolution of REE-bearing monazite during sample preparation for analyses by inductively coupled plasma optical emission spectroscopy (ICP-OES) and inductively coupled plasma mass spectroscopy (ICP-MS), the harsh conditions such as the use of corrosive mineral acids or flux fusion fluxes at elevated temperatures are required. The conventional method for decomposition of monazite includes the fuming in sulphuric acid (H<sub>2</sub>SO<sub>4</sub>) for about two to three hours, and subsequent fusion of residue using phosphate and fluoride salts.

The shortcomings of the aforementioned method are that REE-bearing minerals often host minor quantities of associated minerals such as zircon, ilmenite, rutile and sillimanite, to name a few, which do not completely decompose during the sulfuric acid fuming stage. H<sub>2</sub>SO<sub>4</sub> introduces sulphur-bearing molecular interference to ICP-MS spectra which can lower the REE recovery. Additionally, the large ratio of light REEs (LREEs) to heavy REEs (HREEs) in monazites makes it difficult to accurately determine very low HREE concentrations, and the heavy thorium matrix in monazites interferes with ICP-OES. Sample preparation can be a limiting factor quantification of REEs, particularly the HREEs which are developed within the refractory minerals such as garnet, zircon and sphene phases which may not be completely decomposed using traditional open vessel multi-acid decomposition. Flux fusion and sintering processes are employed for refractory mineral samples, such as monazite, to enable complete sample dissolution and accurate reactive element detection. These procedures are required for geochemical laboratories to efficiently digest hundreds of samples daily. Microwave-assisted acid digestion for dissolution of REE-bearing minerals has been widely studied. Microwave acid-assisted digestion is a sample preparation technique in analytical chemistry that is particularly useful for recovering REEs from a variety of matrices such as ores, rocks, soils, sediments, and industrial products. Microwave heating enables substantially faster digestion than traditional methods. The high-frequency electromagnetic radiation penetrates the sample and generates heat within, resulting in quick and homogenous heating. This dramatically decreases digestion periods from hours to minutes, enhancing sample throughput and overall laboratory efficiency.

#### ***Analytical quantification for REEs***

The utilisation of analytical techniques is crucial in all disciplines related to REEs, during which every step: the ore, rock, and minerals have to be analysed for REEs concentration and mineralogical concentration using the various techniques. This section focuses on chemical characterisation of REEs. The most effective analytical techniques for quantitative analysis of REE were instrumental analytical neutron activation and isotopic dilution mass spectrometric analyses; however, these analytical techniques are time-consuming and require sophisticated and expensive equipment which is not readily available in laboratories (Navarro, 2002). ICP-OES has been recognised as the most efficient multi-element analytical technique for quantitative analysis of major and trace elements in most geological materials including REEs (Navarro, 2002). Research has been based on the analysis of REEs in different matrices including coal and coal fly ash, using various analytical techniques including ICP-OES, laser-induced breakdown spectroscopy, ICP-MS (Sandeep, *et al.*, 2023). Among these techniques, ICP-MS is rapidly taking the lead in the quantitative analysis of REEs in a variety of samples. This is due to its ability to perform multi-elemental analysis, lower detection limits at ppm or even ppb levels, and commercial availability in typical chemical analysis laboratories (Zhu, 2022; Bandura *et al.*, 2006).

The analytical chemistry division (ACD) at Mintek has successfully established routine analyses of REEs in various ores, including sediment, coal, and coal-combustion by-products. Furthermore, the division engages in extensive research on the mineral association of REEs in various ores. Mintek's ACD has developed several certified reference materials and accredited methods for REE extraction and chemical analysis. The REEs research within the division contributes significantly to human capacity development and visibility. Staff and students involved in these projects often obtain university qualifications and skills transfer to analysts and technicians is enhanced. Additionally, REE-related research in the division opens opportunities for new collaborations and strengthens existing ones.

#### **Mineralogical characterisation for REEs flowsheet development and optimisation**

Since the boom in REE demand in the late 2000s, the scramble to develop hitherto unmined ore and waste repositories resulted in numerous feasibility projects appearing online. Given the complexity and variability, mineralogical investigation has played a significant role in the characterisation of numerous REE ores and secondary resources (e.g., Tailings; Balaram, 2019), and the consequent development of flowsheets for REE upgrading and extraction (Chetty and Clark, 2021).

In the REE industry, mineralogy plays a crucial role throughout the value chain, from exploration through to extraction of the REEs for:

- Geological understanding of ore bodies from drill cores and grab samples.

- Concentration methods like ore sorting, gravity, magnetic and flotation separation, hydrometallurgical gangue leaching, or high temperature treatment like calcining and smelting.
- REEs extraction methods, assessing pre-treated and REEs leach residues.
- REEs extraction from precursor mixtures for manufacturing purposes.

Key questions addressed by mineralogical studies include:

- What are the REE-bearing minerals or phases, and how are the REEs distributed among them? This immediately determines where the value lies, and what must be targeted as the main host from which the REEs must be recovered.
- What is the mode of occurrence of these REE-bearing minerals or phases? Here, the grain size distribution of the targeted REEs minerals for given particle size distributions must be established, and related to their liberation, which is the extent to which mineral grain size and particle size approach unity – a critical aspect for downstream processing.
- What are the gangue minerals? For REEs processing, gangue mineralogy can easily influence the economics of an operation, e.g., gangue acid consumers, like carbonate minerals, which feature strongly in carbonatitic ores, the most common REE deposits studied.

By using X-ray diffraction (bulk mineral proportions), scanning electron microscopy (SEM), imaging and qualitative mineral chemistry), automated SEM (quantitative mineralogy) and electron probe microanalysis (quantitative mineral chemistry) as the main mineralogical techniques, these questions can be comprehensively addressed, both in upfront ore assessment, as well as in trouble-shooting various stages of flowsheet development and optimisation.

Figure 1 represents an example of mineralogical outputs at each stage of a concentration and upgrading flowsheet to remove deleterious gangue minerals and reduce mass for REE leaching and extraction from a xenotime-bearing carbonatite feed. Following detailed automated SEM study of the feed, rapid and cost-effective quantitative X-ray diffraction was employed for quick troubleshooting purposes at each step in the proposed flowsheet. The mineral magnetic susceptibilities from the ore assemblage were assessed, thus leading to magnetic separation as a mechanism to remove as much albite as possible. The magnetic stream was subjected to flotation for more albite and calcite removal, and its concentrate leached to remove ankerite. Lastly, the residue from this was leached to remove Fe oxide in preparation for REE leaching of 8% of the initial material. Thus, guided by the mineralogy, 92% of the initial mass comprising mostly the deleterious gangue, was removed to substantially upgrade the REE content of the feed (Chetty and Clark, 2021).

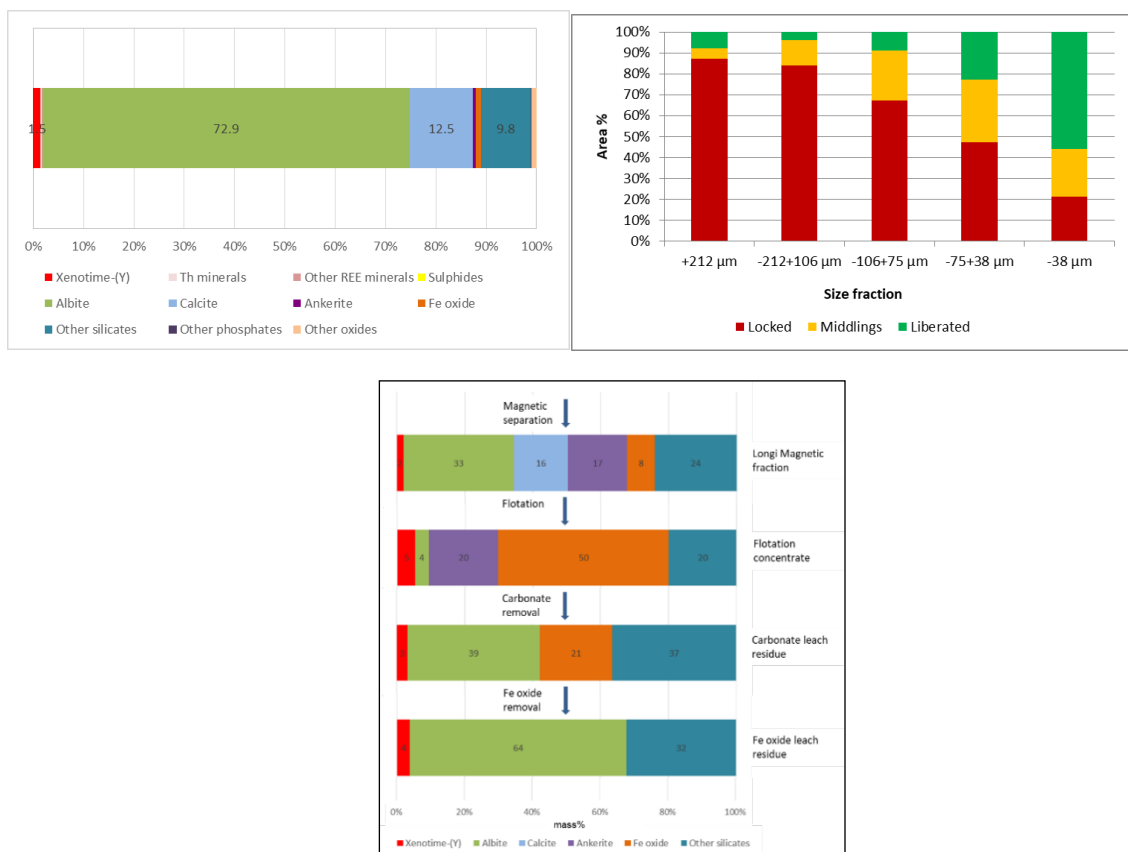


Figure 1. Top: Modal mineralogy and xenotime liberation as a function of particle size distribution in a carbonatite-derived process feed; bottom: Change in mineral proportions from the magnetic fraction (albite, calcite rich) to flotation concentrate (reduced albite, calcite; increased Fe oxide, ankerite), to carbonate leach residue (ankerite removal) and Fe oxide leach residue (Fe oxide removal), to produce a product that is 8% of the original feed mass.

In addition to acid leaching for gangue removal, alkaline or acid cracking may be applied to break down refractory matrices, e.g., REE phosphates, to release REEs and make them amenable to leaching. In this instance, SEM studies prove effective in quickly assessing the extent of cracking, commensurate with REE extraction. In a similar manner, SEM studies have proved useful for determining REE phases and mode of occurrence for their extraction from such wastes as phosphogypsum (Yahorava *et al.*, 2018).

In a world first, Mintek developed and has commercialised the PyEarth process as a concentration method to treat highly ferruginous, lateritised carbonatite ore (Bisaka *et al.*, 2017). It can be said that innovation came about following mineralogical investigation, which indicated that textures in the ore were too complex to treat by conventional means. PyEarth thus ‘reconfigured’ the ore with a smelting process to neatly concentrate the Fe (and Mn) into an alloy, and the REE into a slag. Mineralogy was again required, however, to determine just what this slag looked like, and how the REEs occurred, so that further steps could be taken to upgrade the REE slag phases and leach them (Chetty *et al.*, 2017; Chetty and Clark, 2021).

On the manufacturing side, REE magnet research has involved SEM work to characterise Nd batteries and the phases present in seed mixtures, in ongoing research.

Emerging techniques such as micro-XRF imaging (centimetre-scale element and mineral mapping) and 3D scanning (3D mineral distribution images), complement traditional techniques in mineralogical characterisation. These, together with the wide range of disciplines served by mineralogical work, have ensured that hitherto unprocessed repositories have become technically feasible entities for extraction and use of REEs.

## **Minerals processing-based research of REEs at Mintek**

### ***Extraction of REEs from low-grade ores via flotation***

Flotation, typically designed to target sulphide mineral surfaces, has also shown promise in upgrading REE oxide minerals since Choi and Wang (1963) proposed a mechanism for collector adsorption on monazite. The REEs, particularly those hosted within phosphate rocks, are oxidic in nature and thus are prime candidates for testing Mintek's novel flotation methodologies. The most successful method of concentrating rare earth minerals, particularly those of low grade, involves using hybrid circuits. These integrated circuits exploit both the physical (magnetic, density, and conductivity) and surface (mineralogical, flotation) properties of the ore. This approach was adopted in a recent study by Singh *et al.* (2024), who developed a flowsheet to recover monazite from a lean-grade ore body in Odisha, India.

Mintek has been involved in both state-funded and commercial flotation activities over the past decade. The minerals processing division (MPD) has developed flowsheets for integrated circuits consisting of flotation cells, spirals, and magnetic separators for clients in Africa and abroad over the past two decades. In cases where flotation was unsuccessful, physical separation methods are preferred. A recent study on REE sovite-rich ore from Namibia investigated the feasibility of pre-concentration prior to direct smelting of the concentrate and/or blending of the concentrate with other iron-rich samples. Laboratory-scale gravity separation was conducted using a Wilfley shaking table followed by magnetic separation using the Eriez wet high intensity magnetic separators (WHIMS) on the gravity concentrates. In cases where such physical separation methods are sometimes challenging for the separation of monazite from other minerals owing to similar densities and magnetic character, flotation on its own is used. In one such case, flotation optimisation work was performed with the aim of evaluating different collectors, depressants, and other operating parameters such as pulp conditioning time, pH, and temperature. A fairly recent example of a successful study was where MPD used an oleic acid-sodium silicate reagent recipe at pH 10.5 to produce a bulk concentrate for downstream test work, which generated an overall product that met the specification of >90% monazite removal with less than 1% heavy minerals loss. MPD has been inundated with requests to develop such flowsheets for upgrading low-grade monazite to saleable leach grades. In this regard, a paper will be presented at the current rare earths conference detailing a comprehensive study on the laboratory-scale concentration of low-grade monazite beach sand through pH-dependent flotation techniques. This paper highlights the critical role of flotation chemistry in enhancing monazite recovery. In future, high-resolution froth images will be subjected to digital processing to extract information about froth stability characteristics and attachment-detachment behaviour between particles and bubbles. Despite this research being in its infancy (currently at TRL2), ultimately the aim is to integrate downstream hydrometallurgical leaching into the flowsheet. The success of this integrated flotation-leaching flowsheet will not only lead to the efficient upgrading of a low-grade monazite orebody but also pave the way for sustainable and environmentally responsible REE extraction. By selectively recovering monazite in the concentrate, the heavy minerals in the tailings can be subjected to further processing, thereby reducing the environmental footprint and economic losses associated with traditional methods.

### ***Typical physical separation pre-concentration of REE-bearing minerals***

The processing of lower grade material poses challenges in terms of a finer grind required to liberate valuable minerals from gangue. This then restricts the technology that can be employed to upgrade/pre-concentrate material. The industrial benefit of pre-concentration is evident in upfront gangue reduction and in its ability to improve production capacity.

### ***Magnetic separation***

Magnetic separation methods exploit the differences in magnetic susceptibility of minerals within a given ore. This technique uses magnetic susceptibility of different minerals to separate materials. The materials, which respond more strongly to a magnetic force, will be separated from materials that exhibit a weak response (Barry A. Wills, 2006). Typical magnetic separation procedures for REE minerals are both wet and dry magnetic separation techniques. The units used are Davis Tube, laboratory wet low intensity magnetic separator (WLIMS), Wet High Intensity Magnetic separators (WHIMS), and a dry laboratory high-intensity induced-roll lift type magnetic separator. Mintek has undertaken a wide range of investigations using of a number of magnetic separation processing units

at laboratory scales for REEs recovery; this includes Davis tube, LIMS, dry laboratory high-intensity induced-roll lift type magnetic separator and WHIMS.

#### *Gravity separation*

Gravity separation methods are the most commonly used beneficiation methods. They are employed to exploit the density differences between valuable minerals and the gangue of a given ore (Roy, 2009; Murthy & Tripathy, 2020). For a smaller sample testwork, the shaking is a suitable unit. Mintek is equipped with shaking tables, spirals, multi-gravity separator, and a falcon concentrator for REEs physical separation work, at scales varying from laboratory to pilot scale. The shaking table has been employed extensively on REEs separation flowsheets due to smaller feed mass requirements. With the availability of feed mass: spirals, multi-gravity separator and the falcon concentrator could be explored.

#### **Pyrometallurgical research, development and innovative work on REEs at Mintek**

In industrial REE operations, pyrometallurgy processes are typically applied on the production of REE metals from the hydrometallurgical separation process products. Examples of the feeds to pyrometallurgy processes are separate rare earth oxides (REOs) and RECl<sub>3</sub> (Krishnamurthy & Gupta, 2015). Mintek has undertaken metallothermic reduction for the production of crude REE metals.

Application of pyrometallurgical processes on upstream materials for pre-concentration and/or extraction of REEs is not prevalent in typical REE process flowsheets. The pyrometallurgy division of Mintek has been involved in several studies investigating the feasibility of oxidative and reductive roasting, including salt roasting of complex REE mineral ores as a pre-concentration stage for downstream hydrometallurgical processing. An innovative process called PyEarth was developed by Mintek for smelting iron-rich and complex REE mineral ore concentrates to pre-concentrate REOs in the slag and coproduction of pig iron for steelmaking (Bisaka & Thobadi, 2017; Bisaka, *et al.*, 2017; Bisaka, *et al.*, 2016). Another Mintek approach involves the selective extraction of REEs from complex REE mineral phases using the conventional sulfation roasting process (Maluleke, *et al.*, 2023; Maluleke, 2022; Maluleke, *et al.*, 2020; Maluleke, *et al.*, 2018). Mintek's pyrometallurgical research, development and innovation for extracting REEs from primary and secondary resources is discussed further in the following subsection.

#### ***Roasting of REEs mineral ores***

Roasting is typically used for pre-conditioning the REE mineral ore concentrates before the leaching stage for extracting REEs into the aqueous system. Several studies have been completed, with the focus mainly on the use of different salts to facilitate the transformation of complex phases in the REE feed to readily leachable phases (Peiravi, *et al.*, 2020; Krishnamurthy & Gupta, 2015; Chi, *et al.*, 2004; Zhang, *et al.*, 2004; Wang, *et al.*, 2002; Chi, *et al.*, 2000; Merrit, 1990a; Merritt, 1990b; Harley & Wylie, 1950).

Following up on the background literature on the subject, Mintek has conducted several studies on the roasting of a monazite REE ore, particularly the Zandkopsdrift (ZKD) ore. Preliminary work conducted at Mintek involved oxidative roasting of this ore for the decomposition of the complex phase composition, with the focus on liberating REO from interlocked silicate phases. Roasting was followed by hydrochloric acid leaching to extract the REEs into the solution stream.

In a different study, the phosphate ore was subjected to roasting in the presence of Na<sub>2</sub>CO<sub>3</sub>, as a preferred low-cost reagent (Peiravi, *et al.*, 2020). In other work, this iron-rich phosphate ore was subjected to solid-state carbothermic reduction, followed by magnetic separation to produce a high-purity direct reduced iron product and a proxy slag with concentrated REO contents.

Some investigations completed at Mintek involved H<sub>2</sub>SO<sub>4</sub>-pasting of the ZKD ore to form REE sulfates that are readily soluble in water or weak acids, followed by selective calcination of gangue mineral sulfates to minimise the co-leaching of impurities.

Most of the completed work on the roasting of the South African ZKD ore is yet to be published, owing to further development and optimisation.

### ***PyEarth process***

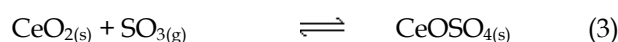
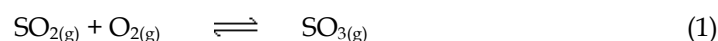
The PyEarth process entails direct-current (DC) arc furnace smelting of iron-rich and complex REE mineral ore concentrates for recovery of iron into a saleable iron-rich alloy and for concentrating REOs in the slag for downstream leaching to recover REEs. The slag is conditioned for favourable recovery of REEs in the leaching step. Mintek has successfully demonstrated the PyEarth process through smelting of various iron-rich REEs ores to produce pig iron and rare earth rich slag using DC arc furnace technology and subsequent leaching of the rare earth rich slags to recover REEs. Mintek carried out a conceptual study on possible flowsheets for the extraction of REEs from ashes and other residues using the PyEarth technology (Kekana *et al.*, 2021).

There is a knowledge gap in the properties of the REOs containing slags. With a lack of REOs slag properties (liquidus temperature, viscosity, density, and others) in the literature, there is thus an opportunity to improve the pyrometallurgical step of the PyEarth process by predicting the slag properties of REOs through computational molecular dynamics modelling. Research is ongoing to determine the thermodynamic and transport properties of REEs in various slags through computational modelling. The computational modelling results will be validated through experimental measurements. Knowledge of the slag properties could contribute significantly to estimating the performance of the slag in the furnace.

### ***Gas-based sulfation roasting for selective production of REEs***

Sulfation roasting is a process that involves the conversion of insoluble metal-bearing phases into readily leachable metal sulfates. This process is applicable to the treatment of minerals, which produce metal sulfates that can be leached in water or dilute mineral acids. H<sub>2</sub>SO<sub>4</sub>-pasting and calcination reported above and roasting in the presence of gases such as SO<sub>2</sub> and O<sub>2</sub> or direct oxidation of sulfidic ores using air are the typical sulfation roasting routes. Gas-based sulfation roasting using SO<sub>2</sub>/O<sub>2</sub> is typically used in the production of base metals from complex sulfidic ores. Roasting may be conducted in one of the following furnaces: fluidised bed reactor, multiple hearth furnace, or rotary kiln (Guntner & Hammerschmidt, 2011).

In view of the fact that most of the REE sulfates are readily soluble in water and weak mineral acids, Mintek investigated the technical feasibility of the gas-based sulfation roasting and leaching approach for the selective extraction of light REEs from primary and secondary resources. There is limited literature in the public domain on the proposed strategic process. Chemical thermodynamic calculations completed at Mintek using FactSage thermochemical simulation software showed that the sulfation of REEs can occur following the spontaneous chemical reactions [1] to [3], using Ce as an example.



In reaction (1), SO<sub>2</sub> reacts with oxygen to form SO<sub>3</sub>. This reaction is known to be very sluggish, but is catalysed by Ce oxide, which is an established catalyst. Hence, the rate of the reaction is enhanced. Reaction (2) shows the reaction of CeO<sub>2</sub>, a REO, with SO<sub>3</sub> produced in reaction (1) to form a Ce(III) sulfate. As seen in reaction (3), CeO<sub>2</sub> may react with SO<sub>3</sub> to form CeOSO<sub>4</sub>. Predominance phase diagrams indicated that both sulfate and oxy-sulfate can be produced, depending on the operational conditions. Of great importance is that there is a critical mass ratio of SO<sub>2</sub> to O<sub>2</sub> in the sulfation roasting reactor that should be maintained.

Experimental work completed at Mintek on ZKD ore and REO-rich slag produced by the PyEarth process has shown that indeed the gas-based sulfation roasting process results in selective and high extraction of LREEs. Further work is underway to improve the overall kinetics of the sulfation process for the extraction of REEs. The Mintek work demonstrating the technical feasibility of using sulfation roasting for selective and high extraction of REEs from different resources has been published in local and international conference and journal papers (Maluleke, *et al.*, 2023; Maluleke, *et al.*, 2020; Maluleke, *et al.*, 2018). As part of human capital development, Maluleke (2022) also published a dissertation in

fulfilment of an MSc Eng. (Metallurgy), on the subject of sulfation roasting for selective and high extractions of REEs from primary and secondary resources.

### **Hydrometallurgical-based research of REEs purification and separation**

#### ***Extraction of REEs***

The two most common methods for extracting REEs from minerals like monazite and bastnaesite are sulfuric acid baking and alkaline cracking (Demol *et al.*, 2019; Gupta & Krishnamurthy, 2005). Alkaline cracking, using NaOH, is utilised in the industry for REE extraction as it removes sulfates and phosphates, simplifying the thorium purification step for monazite-thorium concentrates (Ghahreman *et al.*, 2017). In this method, finely ground monazite concentrate is treated with a 50%-70% NaOH solution at 140°C, enhancing mineral liberation (Gupta & Krishnamurthy, 2005; Nawab *et al.*, 2022). Post conversion to REE hydroxides, the solids are treated with mild HCl to selectively dissolve REEs. Alternatively, monazite can be decomposed using concentrated sulfuric acid and baking at 200 - 220°C, where the sulfate ion acts as a ligand reacting with phosphate minerals. The baked solids are then leached with water at 60°C to dissolve REEs, thorium, and other impurities (Demol *et al.*, 2019; Gupta & Krishnamurthy, 2005; Kumari *et al.*, 2019; Kuppasamy & Holuszko, 2022).

#### ***Current purification techniques at Mintek***

Chemical precipitation, ion exchange (IX), and solvent extraction (SX) are the common methods for removing impurities from REEs rich liquor at Mintek.

#### ***Precipitation***

Several precipitation procedures are commonly used to selectively remove high levels of impurities or precipitate REEs (Han, 2020; Kotze *et al.*, 2013; Nawab *et al.*, 2022; Zhang *et al.*, 2022). Impurities in leach liquor vary based on ore composition and the leaching method employed (Kumari *et al.*, 2019; Sarker *et al.*, 2024).

Critical impurities such as Al, Zr, Th, Zn, and Fe leach together with REEs and can contaminate the final product during separation steps. These impurities are removed using neutralising agents as solutions or slurries, precipitating base metal impurities as hydroxides or sulphides, precipitating Th, U, and Zr as phosphates, and removing excessive alkaline earth metals as sulfates (Kotze *et al.*, 2013; Kumari *et al.*, 2019; Lapidus & Doyle, 2015). In an investigation of impurity rejection from crude REECl<sub>3</sub> solutions, Fe is effectively precipitated with hydroxides at pH below 4 (Sarker *et al.*, 2024). Operating at pH 5 rejected over 90% of Al but may co-precipitate 20% of heavy metals. Al can potentially be removed by precipitating with REEs, then selectively redissolving REEs at pH 3 - 4. In a separate study, bulk precipitation was performed by adjusting the pH to 8.5 - 9.0 using calcium hydroxide (Ca(OH)<sub>2</sub>), co-precipitating REEs with Fe and Al. Selective dissolution of REEs is achieved by treating the precipitate with HCl, leaving Fe, Al, and some Ce(IV) in the solid residue. When cerium is in solution, it can be separated by exploiting solubility differences between its tetravalent and trivalent forms; tetravalent cerium compounds precipitate out during oxidation (Chi *et al.*, 2006; McNeice *et al.*, 2019). Despite efficient impurity removal, elements like Cu, Fe, Th, Zn, P, and Si may persist and are challenging to remove with precipitation alone, requiring alternative methods like IX and/or solvent extraction (Bisaka *et al.*, 2017; Judge & Azimi, 2020).

#### ***Ion exchange***

Mintek has tested various resins for commercial projects and R&D selection, based on public information and prior experience. Strong acid cation exchange resins were effective in recovering REEs from low-grade liquors and sparingly soluble REE precipitates with low calcium levels (Kotze *et al.*, 2013; Mottay *et al.*, 2014). Purolite C100 resin loaded ~14 g/L REE from a 2.9 g/L REE pregnant leach solution (PLS), with impurities of 16 g/L Al and 13 g/L Ca. Efficient eluting agents were 4 M HCl and acidified CaCl<sub>2</sub> (>1 M). The strong base resin's differing affinity for REEs and radioactive impurities allows for PLS purification via selective elution (Sanchez-Ocampo *et al.*, 1991). Uranium is eluted with 0.75 M H<sub>2</sub>SO<sub>4</sub>, REEs with 3 - 5 M HCl, and thorium with 10 M HCl, 3 M H<sub>2</sub>SO<sub>4</sub>, 5 M HNO<sub>3</sub>, and ammonium (i.e. oxalate carbonate, or sulfate) solutions. Weak acid cation exchangers, like Purolite C104, are suitable for bulk REE upgrade at pH >5. Mintek found it adsorbed ~24 g/L REE from 2.9 g/L PLS,



with REE elution using 0.5 M HCl. Iminodiacetic resins are more selective for base metals than REEs and can recover impurities from REE liquors. Bulk REE upgrade followed by split elution separates REEs from base metals. Solvent-impregnated resins extract thorium, uranium, zirconium, and iron from REE solutions (Judge & Azimi, 2020) or separate REEs from base metals (Hermassi *et al.*, 2021).

#### ***Solvent extraction***

Mintek has been actively advancing a comprehensive flowsheet aiming at producing high-purity individual REE products (Preston & Du Preez, 1996). The proposed flowsheet involves multiple solvent extraction (SX) circuits, strategically designed for extraction and separation (Preston & Du Preez, 1996). The initial SX circuit targets the selective extraction of middle REE (MREE) and heavy REE (HREE) from light REE (LREE). The chemistry of MREE and HREE enables their selective extraction using specific solvents and pH conditions, facilitating separate extraction from light REE (Jowitt *et al.*, 2017). PC-88A, selected as the organophosphorus extractant in Shellsol D70, showed no gel formation and easy stripping in varying HCL concentrations (Tavakkoli *et al.*, 2021). The optimal organic phase composition enabled better separation of LREEs from middle and heavy REEs. pH-dependent extraction led to S-curves construction to determine optimal pH, critical for Nd-Sm split, confirmed by batch tests. Another study explored neutral organophosphorus compounds' synergistic effects on Nd(III) and Er(III) extraction efficiency and pH behaviour from chloride and nitrate media. These compounds, combined with DIPSA in xylene, caused synergistic shifts in pH values required for extraction, with increasing effects in the order of  $(RO)_3PO < (RO)_2RPO < (RO)R_2PO < R_3PO$  (Preston & du Preez, 1995). Similar effects were observed in lanthanide extraction, with heavier lanthanides showing more pronounced effects than lighter ones. The addition of neutral organophosphorus compounds enhanced separation efficiency across the lanthanide series, evidenced by increased pH separation ( $\Delta pH$ ) from 0.17 units with 0.25 M DIPSA alone to 0.85 units with a mixture of 0.25 M DIPSA and 0.25 M TIBPO (Nadimi & Karazmoudeh, 2021). These results underscore the complexity of synergistic REE extraction, influenced by both chemical nature and extractant concentration. Mintek's systematic approach to REE solvent extraction has laid a strong foundation. Mixtures of DIPSA and TIBPO offer better separations at the Nd/Sm boundary than Versatic 10 and comparable separations for heavy lanthanides. Ongoing research aims to enhance extraction and separation for improved purity and recovery rates.

#### ***Individual REEs separation***

Mintek has been involved in research related to the recovery and separation of REO since the 1980s (Kotze *et al.*, 2013a; Mottay *et al.*, 2014; Preston & Du Preez, 1996). Initial lab trials successfully produced kilograms of REO, CeO<sub>2</sub> and magnetic grade Nd<sub>2</sub>O<sub>3</sub> from phosphoric acid sludges. Pilot plant trials, both at Mintek and on-site, scaled up production to hundreds of kilograms REO and CeO<sub>2</sub>, and tons of mixed REOs, respectively. Recent efforts have shifted towards the separation of individual REEs due to higher commercial returns. However, the similar chemical properties of REEs make separation using traditional techniques challenging (Aide & Aide, 2012; Pathapati *et al.*, 2023). Mintek's hydrometallurgy division is actively researching methods for more efficient REE separation. Two projects were initiated at Mintek. The first project focus on tailoring molecular organic frameworks to interact with specific REEs by modifying pore sizes, shapes, and functional groups. The other project targets the separation of samarium, europium, and terbium, exploiting their tendency to exhibit divalency.

#### **Manufacturing of rare earth magnets: advanced materials-based research**

Currently, there are three types of commercial rare earth magnets, namely SmCo<sub>5</sub>, Sm<sub>2</sub>Co<sub>17</sub>, and Nd<sub>2</sub>Fe<sub>14</sub>B. The SmCo<sub>5</sub> and Sm<sub>2</sub>Co<sub>17</sub> were the first rare earth magnets developed. Rare earth magnets dominate the permanent magnet industry (First4magnets, 2018; Alliance LLC, 2018; Tanaka *et al.*, 2011). The drastic increase in demand for such magnets is attributed to their use in electric vehicles and renewable wind energy generation. Due to their strong magnetism and good thermal stability, their use has spread to other industries such as medical, military, aerospace, etc. The technologies for producing rare earth magnets are highly protected, providing an opportunity to develop methods at Mintek for South Africa to participate in the production and supply of these materials.

The objective of the research work was to develop a process in the advanced materials division for the production of rare earth magnets which are also used in renewable energy and clean energy technologies.

Firstly, computational methods were used to investigate the structural and elastic properties as well as the mechanical stability of the  $\text{Nd}_2\text{Fe}_{14}\text{B}$  i.e. the main phase of NdFeB magnets (Tanaka *et al.*, 2011). The DFT approach was used to study equilibrium lattice parameters and elastic properties of the  $\text{Nd}_2\text{Fe}_{14}\text{B}$  system (Tanaka *et al.*, 2011). The calculated equilibrium lattice parameters agree with the experimental results. It was found that  $\text{Nd}_2\text{Fe}_{14}\text{B}$  is mechanically stable according to the tetragonal criteria of mechanical stability.

Three rare earth alloys: NdFeB, FeDy, and FeGd were produced using a button arc furnace. The alloys were found to be very brittle due to the brittle nature of REEs. Although the NdFeB partially melted during production, the microstructure showed typical microstructural features of the NdFeB. The manufacturing process requires further refinement to avoid prevalent oxidation levels, which suppresses magnetic performance. As a result, alternative innovative ways to avoid reaction with oxygen are currently being explored at Mintek. The research work on the production of an REE magnet is still in its infancy; however, with the level of the team's expertise in powder metallurgy it has the potential to yield a novel manufacturing process that will produce an alloy with magnetic performance equivalent to the commercial RE-magnets. The alloy development work is ongoing and includes optimisation of the melting process to produce the main alloy (NdFeB) and sub (REE-rich) alloy using the recently acquired state-of-the-art AMAZEMET rePowder ultrasonic atomiser machine. This advanced technology enables Mintek to efficiently process a diverse range of materials into metal powder for various applications.

### **Mining and mineral economics of REE-based research at Mintek**

#### *Techno-economics analysis for the extraction of REEs*

The mining and mineral economic divisions undertake techno-economics analysis for various processes and flowsheets. Mintek's technical divisions collaborate with the mining and minerals economic division in analysing and undertaking techno-economics studies of interest; some of these techno-economics studies being processes aimed at the extraction of REEs from various feed materials.

#### *Legislation and best practice in the emerging Southern African REEs industry*

The mining and mineral economics division at Mintek was approached by the hydrometallurgy division to undertake an environmental legislation review of having an REEs refinery and waste disposal facility in the Saldanha Bay municipality, Western Cape.

The need for a new refinery and waste disposal facility arose because of the future development of mining development activities elsewhere in Africa where the REE ores will be brought to South Africa for processing. The processing of REE ores involves high material and energy use which is associated with significant environmental problems. The processing of REEs leads to the generation of hazardous waste streams, which consist of, but are not limited to tailings and other radioactive materials. The extent of exposure of risks to the environment might come through pathways involving tailings piles, wastewater ponds and disposing of other contaminated materials. Therefore, a thorough site selection process for an effective and safe site location proved to be essential for preventing the potential effects to the environment, particularly contamination of natural resources and populated areas. The study has offered a framework to ensure that the environmental legislation in the South African context supports the development of an REE refinery and waste disposal with acceptably low environmental impact and a negligible effect on human health.

The study applied a spatial multi-criteria decision-making and hazardous waste transport cost-benefit assessment to select the probable refinery and waste disposal within the Saldanha Bay municipality; factoring in the socio-economic parameters but more specifically looking at aspects relating to physical and economic infrastructure. The results indicate that having the refinery and the waste disposal in the same area would be preferable. This is anticipated to minimise the management cost and further environmental burdens while transporting the hazardous materials. Therefore, the area where mining

rights have already been granted will be the most suitable location for establishing the REEs refinery and waste disposal facility.

## CONCLUSIONS

Mintek is utilising its expertise in characterisation, minerals processing, extractive metallurgy and advanced materials to advance R&D of REEs across a number of disciplines including chemical and mineralogical characterisation, minerals processing, pyrometallurgy, hydrometallurgy, mining and mineral economics and advanced materials. Mintek leverages an interdisciplinary approach and has demonstrated robust flowsheet development for efficient extraction of REEs such as the PyEarth process.

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