

A proposal to recover rare earth oxides from phosphogypsum

Lazenby, MM

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Matthew Michael Lazenby
16040954

Department of Chemical Engineering
University of Pretoria
South Africa

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Executive Summary

The global market for rare earths is dominated by traditional ore mining. More specifically, China has controlling majority in the production and market share for rare earths at 62 %. South Africa contributes minimally with less than 0.3 % of the global production. This is, similarly, achieved through traditional mining means (Steenkampskraal mine).

There is a demand for sustainable alternatives to traditional mining. Reprocessing a phosphogypsum waste stream to recover rare earths was found to be a strong alternative technique. Phosphogypsum is currently stored in landfills and pumped out to sea in Richards Bay. The cost of this disposal amounts to R490 000 per annum (Foskor, 2018). This phosphogypsum contains critical rare earths, namely neodymium, europium, dysprosium, terbium and yttrium. The value of the rare earths is expected to grow with the emerging market in green technologies which relies heavily on rare earth use.

In light of the prospects of the rare earth market, a novel beneficiation process proposed by van Vuuren & Maree (2018) is investigated. The process contains *inter alia* carbothermal reduction of phosphogypsum to CaS. This CaS product is of interest to leach the rare earths using H_2S . The purpose of the recovery process is to increase the rare earth concentration in the phosphogypsum from 0.4 % to 4 % in the leached product. Experimental design to investigate the physical realisability and economic viability of the recovery process, is proposed.

Additionally, a financial study of the process estimated a revenue of R365 000 000 per annum, from the rare earth oxide mixture, when the plant operates at an annual full capacity of 3 240 000 tons of phosphogypsum.

Keywords: rare earth, leaching, feasible, phosphogypsum, recovery

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1 Introduction

Phosphogypsum is a byproduct of the wet process production of phosphoric acid. Phosphogypsum is produced as hydrated calcium sulphate $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. The plant of the Foskor acid-division is located in Richards Bay, Kwa-Zulu Natal. Foskor (2016) reported that at full capacity, a total of 720 000 tons per annum (tpa) of H_3PO_4 is produced — this results in a phosphogypsum production of 3 240 000 tpa. However, because H_3PO_4 is the desired commodity, the production of phosphogypsum is considered as waste. Phosphogypsum is currently pumped into the sea at Richards Bay. The ocean water has the ability to dissolve the phosphogypsum due to the salinity. Regardless, the pollution of ocean waters is increasing as the rate of pollution far exceeds the rate of degradation of phosphogypsum. Consequently, there is growing interest into developing alternative processing and utilisation of phosphogypsum.

The phosphogypsum is alleged to contain valuable rare earth oxides. Rare earths are a commodity which are increasing in demand as green technologies increase in production. Electric or hybrid cars, solar panels, and green energy generators are all products which rely on a stable resource of rare earths. Rare earths have various applications in electronic devices as certain rare earths form permanent magnets. Neodymium is one of the rare earths which forms a permanent magnet and which makes the rare earth valuable. A prime example of the value of rare earth materials is the introduction of the first colour television. This was made possible due to the availability of europium; which is a rare earth found in the phosphogypsum produced at Foskor, Richards Bay. China has proven to be the country to seize this expanding rare earth market opportunity. The Chinese rare earth production is responsible for 62 % of the global production.

There has been gained interest into developing innovative techniques to produce rare earths as a result of China's domination over the global market. Potential lies in the phosphogypsum byproduct. This byproduct is reported to contain 0.4 % rare earths (Rychkov *et al*, 2018). A novel process for rare earth oxide recovery from the byproduct phosphogypsum is proposed by van Vuuren & Maree (2018). The recovery process involves recovering a rare earth oxide mixture which is concentrated to a 4 % grade. The process includes producing elemental sulphur and high-grade calcium carbonate (CaCO_3). The recovery process involves carbothermal reduction of the dehydrated phosphogypsum (CaSO_4). This is then followed by acid leaching, where H_2S is used as the leaching agent to produce a rare earth oxide concentrate of 4 %.

This study serves to evaluate the rare earth market, the scale of global production, and competitive processes for rare earth production. This is in attempt to provide preliminary research which provides a foundation for the development of rare earth recovery processes.

The key question of the recovery process is whether it is possible to concentrate the rare earth oxide mixture. Additionally, this study documents a proposed technique to determine the success of the H₂S leaching process using a phased lab-scale testing model. No practical work has been done on whether the leaching process is realisable. However, evidence has been provided which indicates that the proposed recovery process is not unrealistic (Preston *et al*, 1996).

2 Market

Rare earth metals are one of the functional materials in the construction of renewable energy generation devices (Giurco *et al*, 2019). Renewable energy generation and use of clean energy is becoming evermore demanding as the importance of environmental awareness increases. Renewable energy relies, partly, on a steady supply of rare earths (Giurco *et al*, 2019). Along with the renewable energy reliance on rare earths, many other day to day technologies involve rare earth application in their physical make-up. Rare earths are widely used in electronic components found in cellular devices and computers. Less obvious application of rare earths can be found in a day-to-day or energy efficient fluorescent light bulbs (ChemicalBook, 2017; Uulu, 2018a).

Linking to the topic of renewable energy, is rechargeable batteries. The rare earths are key components in the manufacturing of these batteries. The rare earths function as a storage facility for hydrogen, with the ability to absorb and de-absorb the hydrogen (Lucas *et al*, 2015). There is an ever expanding global demand for the implementation of hybrid and electric vehicles. Rechargeable batteries are used in hybrid technology, thus a steady supply of rare earths (in a cost effective manner) is required in order to make the production of hybrid technologies further feasible and desirable (Chemicool.com, 2012d).

Additional to the common use applications of rare earths are more specific applications. Rare earths can be used as a catalyst in catalytic reactions (Stanford Advanced Materials, 2018). These catalysts are used to reduce the air pollution (Hanaoka, 1976). Therefore, furthering the contribution from rare earths in reducing the environmental impact. Furthermore, specific applications of rare earths can be found in national defence equipment (night-vision goggles, precision guided weapons, laser range finders, guidance systems, fluorescence and communications) and medical equipment (X-ray machines and MRI scanners) (Batalu *et al*, 2015; Grasso, 2013). The unique applications are owed to rare earths optical enhancing properties. The above points illustrate the potential strength that lies in the rare earth market with rare earths having a wide variety of applications.

According to Hatch Ltd (2020), the compound average growth rate (CAGR) of the rare earth market is at 5 % and for the critical rare earths is at 8 %. This providing further evidence as to how the rare earth market will continue to grow in strength. It is noted that, the main market application for rare earths is the application of a permanent magnet. Permanent magnets are the strongest types of magnets that are available and contribute to the production of green energy generators (Chemicool.com, 2012c). According to Jellicoe (2019), “the permanent magnets represent more than 90 % by value and 20 % by mass.”

The overall demand for rare earths has grown over time as a result of the development of the technological age, specifically an increase in the introduction of nanotechnology. Therefore, where an unstable supply of rare earths are encountered in the need of rare earths features, innovators have developed substitutions for rare earths. Rare earths may be replaced with the use of other substances that serve the same purpose (Stegen, 2015). However, these substitutes are not as effective as the rare earths and as a result, become furthermore cost intensive to use. These substitutes make the final product (perhaps a renewable energy product) more expensive to the consumer. Thus, less appealing for retailers to promote a ‘greener’ lifestyle to the consumers.

According to a study conducted by Jellicoe (2019), which discussed the relevance of rare earths to South Africa, a topic of issue was the inability to be able to manipulate the mined ore into a valuable consumer product. The ability to separate the rare earths from the mined ore is the most important part of the process, yet this rare earth extraction and separation from the ore is difficult and costly to design, construct and operate. This however, does not dispute the fact that the rare earths cannot be separated (Preston *et al*, 1996), as China has achieved separation from the ore (Fan *et al*, 2016). Thus, separation from the phosphates and calcium sulphates will be possible. Another issue explored, was the battle between supply and demand. Figure 1 and Figure 2 taken from the research presented by Jellicoe (2019) which shows how the forecasted demand for rare earths will be far greater than the supply.



Figure 1: The comparison of the forecasted supply and demand of rare earths taken from Castelloux (2019)

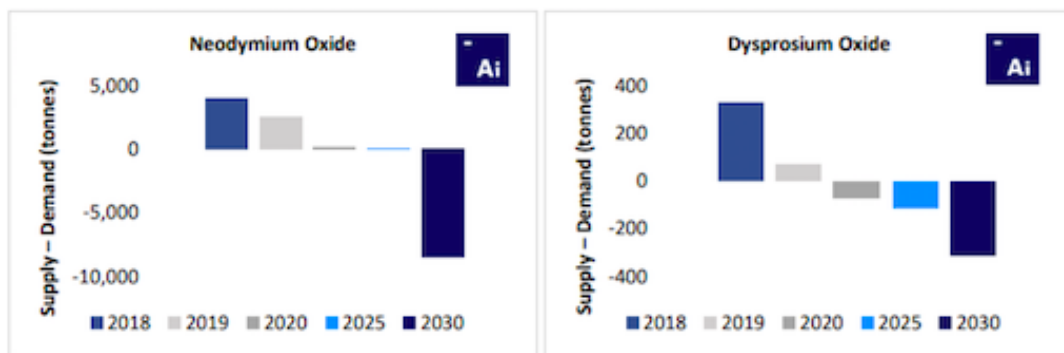


Figure 2: The comparison of the forecasted supply and demand of rare earths taken from Castelloux (2019)

Therefore, one might think, in 2030, the market for rare earth recovery is going to be extremely valuable. A shortage of rare earth supply with high demand will imply that rare earth prices will be of a high market or resale value. The high demand and low supply will mean a reduction of exports from rare earth producing countries. Implying, only China will have a source of rare earths available if an alternative is not found. Matching supply and demand curves implies excessive production amounts of the less frequently demanded yet more abundant rare earths. When the demand for a commodity is high with low supply, this implies high market value, the opposite is true for high supply and low demand.

There are 15 rare earths found in the phosphogypsum produced by Foskor. The specific applications and market value of specific rare earths have led researchers to categorise the rare earths according to their value and use. The critical or high demand rare earth oxides have been identified as neodymium, europium, dysprosium, terbium and yttrium (Lifton, 2020). Cerium oxide is used in the pharmaceutical industry. In the nanotechnology

market, cerium is used as an additive in fuel and as a catalyst. The dry powder form is used for grinding and as an abrasive, particularly to polish highly specialised glass surfaces. Cerium can furthermore be used as an alloy compound that is heat resistant in certain products (Stanford Advanced Materials, 2018). Cerium oxide is R24 150 per ton in the current market.

Neodymium oxide is used to produce permanent magnets. These magnets together with iron and boron, form a fundamental part of modern vehicle mechanisms. Neodymium is used in data storing components, loudspeakers and medical devices. In addition to this, neodymium oxide is used in optical apparatus (Chemicool.com, 2012c). This rare earth is the strongest and most affordable magnet at a price of R614 250 per ton rare earth oxide.

Lanthanum oxide is used in China, foremost in electronic manufacturing. Additionally, a more specialized form of lanthanum is used to make carbon arc-lights which are used for motion pictures in studio lighting. The lanthanum oxide is responsible for 25 % of misch metal. Lanthanum oxide is an important component for manufacturing camera glass lenses as well as image projection (Chemicool.com, 2012b). This rare earth can be bought for R24 600 per ton.

Praseodymium oxide is sold at R672 000 per ton. This can be utilized in combination with magnesium to create high-strength metals that are used in aircraft engines. It can be used as a dopant to amplify signals in optical cables. This rare earth is similar to lanthanum oxide as glass is coloured by praseodymium oxide used for protective equipment. In addition, it can be used in nickel metal hydride for rechargeable batteries for hybrid motors (Chemicool.com, 2012d).

Samarium oxide is used in cosmetics, ceramics, electronics, optics and bio-medicine. This is a strong absorber of neutrons and therefore serves in nuclear reactor control rods. When making ceramics, samarium oxide has a high permittivity which is used for dielectric resonators and substrates. Additionally, it is used when manufacturing gas sensors, capacitors as well as structural and shielding parts for nuclear piles (AZoNano, 2013c) (Panahi & Samadi, 2016). This rare earth is also used in solid oxide fuel cells and sold at R26 250 per ton.

Yttrium oxide can be found in colour televisions, energy-saving lamps and glasses. When used in material sciences, it produces phosphors necessary for conveying the red colour of pictures in television tubes. It can also be found in ultra-fast sensors that are used in x-rays and g-rays. Yttrium oxide is an important starting point in inorganic synthesis of compounds (AZoNano, 2013d). It is an additive in steels, non-ferrous alloys and iron. This rare earth is currently R42 000 per ton.

Gadolinium oxide is a rare earth with many uses. It can be used as a clarity enhancer for MRI scans as well as the contrast agent in these MRI scanners. It is used in magnetic resonance and florescent imaging, in doping modification of thermally treated nanocomposites and in magnetocaloric materials on a semi-commercial level. Gadolinium oxide can be utilized as a burnable poison as a part of the fresh fuel in reactors to control power and neutron flux (Uulu, 2018a). This rare earth is sold for R355 950 per ton.

Europium oxide, like many other rare earths, is used for colour televisions, x-rays, luminescent material, glass and phosphors in lamps. Europium oxide can be bought by the ton at a price of R441. Europium is frequently used in the cell phone manufacturing processes to provide coloured LCD screens (AZoNano, 2013b).

Terbium oxide is another rare earth that has similar uses to others. It is used in glass, optics and ceramic applications. Terbium oxide can be used in the preparation of other terbium compounds (Manufacturer, 2020b). Predominantly, this is used in phosphors, specifically in florescent lamps and in the high intensity green emitter in projection televisions. This is also utilized in magnetic materials as a permanent magnets (Zegen metals and chemicals limited, 2018). Terbium oxide can be purchased for R8663 per ton.

Dysprosium oxides main uses are in glass, optics and ceramics. Due to the wavelengths that can be emitted, dysprosium oxide is added to advanced optical formulations. This rare earth is a necessary additive in permanent (NdFeB) magnets (Manufacturer, 2020a). Dysprosium oxide is sold for R3833 per ton.

Holmium oxide has unique magnetic properties and is used in alloys for the production of magnets. Furthermore, as a flux concentrator for high magnetic fields. The yellow-red colour of holmium oxide is used for tinting glass as well as cubic zirconia (used in the jewellery industry). It can be found in nuclear reactor control rods and solid-state lasers, which are used for non-invasive medical practices such as: treating cancers and kidney stones (Chemicool.com, 2012a). Holmium oxide is sold at R299 000 per ton.

Erbium oxide is used for display purposes in glass and plastic monitors. Surface crystalline structures can be altered into aqueous and non-aqueous media for bio-imaging. Erbium oxide can also be used for high temperature corrosion-resistant coatings and dopants for laser materials and optical fibre (AZoNano, 2013a). This rare earth is sold for R330 750 per ton.

Thulium oxide is a pure metal and compound that is expensive with little to offer and therefore has few commercial uses. It can be used when producing lasers as well as having potential in ceramic magnetic materials (SkySpring Nanomaterials, Inc, 2020).

Ytterbium oxide is used for glass, ceramics and special alloys. Its main use is in carbon arc-lamps that produce a very bright light. Ytterbium oxide can be bought at R300 915 per ton. This rare earth is also a component of the misch metal used in lighters (ChemicalBook, 2017).

Lutetium oxide is used for glass, ceramics, phosphors and lasers. It is used as a cracking, alkylation, hydrogenation and polymerization agent. In addition, it is utilized in x-rays and starting materials for laser crystals (Uulu, 2018b).

The fore mentioned technologies involving rare earths are predicted to continue to rise in demand according to King (2020). It was estimated in 2019 that the total value of products, globally, that contain rare earths is around *US*\$1.5 trillion to *US*\$2 trillion (Jellicoe, 2019). This is roughly in the region between R21 trillion to R28 trillion (PoundSterling Live, 2019a). This strong market value of rare earths has one major beneficiary. China currently dominates the entire rare earth market, owing to a global share of approximately 62 % while the nearest to that is the USA owing to a global share of 12 %. South Africa sits at less than 0.28 % of the global share in production of rare earths (Garside, 2020).

Table 1 summarises the above market information about the rare earths available in the phosphogypsum. The price for the rare earths is taken from mineralprices.com (2019) and ISE (2020), reported on a per ton phosphogypsum basis. Exchange rates used were taken for 2019, as discussed in Section 6 (PoundSterling Live, 2019a; PoundSterling Live, 2019b).

Table 1: A rare earth oxide summary of the amount of the rare earth oxide present in 0.4 % of the phosphogypsum, price of the rare earth and application of each rare earth.

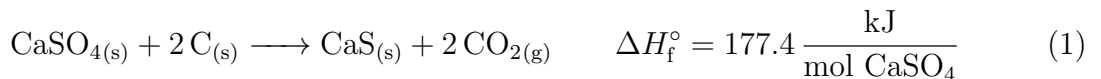
Rare Earth	wt fraction (%)	R per ton phospho-gypsum	Application
Cerium oxide	41.68	40	Pharmaceuticals, catalyst, abrasive for specialised glass surfaces
Neodymium oxide	23.15	569	Permanent magnets, electronic equipment
Lanthanum oxide	17.77	17	Electronic manufacturing, carbon-arc lights, 25 % of misch metal, camera lenses
Praseodymium oxide	5.36	145	High-strength metals used in aviation production, optical cables
Samarium oxide	3.89	4	Cosmetics, electronic ceramics, optics and bio-medicine
Gadolinium oxide	3.12	44	MRI scanners, magnetocaloric materials, fuel in reactors for control
Europium oxide	1.10	0.02	Colour TVs, LCD screens, x-rays, luminescent materials, glass and phosphors
Terbium oxide	0.18	0.06	Permanent magnets, glass, optics, ceramic applications
Dysprosium oxide	0.85	1.2	Glass, optics, electronic ceramics
Holmium oxide	0.08	1	Alloys for production of magnets, cubic zirconia, nuclear reactors
Erbium oxide	0.22	3	Display screens, bio-imaging, high-temperature corrosion-resistant coatings
Thulium oxide	0.01	-	Laser production and potential in ceramic magnetic materials
Ytterbium oxide	0.07	0.8	Carbon-arc lamps, glass, electronic ceramics, special alloys
Lutetium oxide	0.04	-	X-rays, glass, electronic ceramics, phosphors, lasers
Yttrium oxide	2.45	4	Colour TV, florescent lamps, energy-saving lamps, glasses
Total	100	828	

3 Proposed Process

According to Foskor (2016), the Richards Bay plant produces 720 000 tons of phosphorus pentoxide (P_2O_5) at full capacity per annum. van Vuuren & Maree (2018) state that: "the amount of gypsum produced is 4.5 tons per ton of phosphoric acid", supported with research done by Parreira, Kobayashi & Silvestre Jr (2003). It can then be calculated that approximately 3 240 000 tons of phosphogypsum is produced per year at the Richards Bay plant when operating at full capacity. The contents of this phosphogypsum does not have to be waste, having value and use in modern technology applications. An analysis of this phosphogypsum proved this true, reporting a total rare earth content of approximately 0.4 % (van Vuuren & Maree, 2018). Virolainen, Repo & Sainio (2019) supports that byproduct phosphogypsum has value, reporting the typical rare earth concentration in phosphogypsum as 0.4 %. Therefore, the phosphogypsum considered waste per year actually contains approximately 12 960 ton of rare earth oxide, at full capacity.

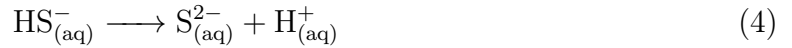
Thus, concentrating the rare earth oxide in the waste has raised attention. A rare earth oxide mixture of a 4 % grade, is allegedly attainable via the recovery process documented by van Vuuren & Maree (2018). This process increases the rare earth concentration and does not specifically isolate and separate rare earths. Preston *et al* (1996) reports to have achieved a mixed rare earth oxide containing approximately 2.8 % rare earths, therefore, providing insight into the proposed process by van Vuuren & Maree (2018) as being realisable.

The recovery process is centralised around separating the rare earths from the sulphates and phosphates with attempt to make calcium compounds as soluble as possible. It is known that $CaSO_4$ has a very low solubility (Perry & Green, 2008). To recover and concentrate the rare earths, the $CaSO_4$ needs to be reduced and made into a soluble compound. The recovery process begins with the drying of the phosphogypsum to anhydrous $CaSO_4$. Drying temperatures vary greatly between previous studies conducted. It was established that a drying temperature above $100^\circ C$ but below $300^\circ C$ would achieve dehydration. This temperature range ensures evaporation of the water without degrading or changing the phosphogypsum. The dried phosphogypsum is then carbothermally reduced to CaS at around $900^\circ C$ shown in Reaction 1 (van Vuuren & Maree, 2018). In the recovery process, reduction to CaS enhances the ability to concentrate rare earth oxides. However, the CaS is still highly insoluble (Perry & Green, 2008), confirmed by experimentation done by De Beer *et al* (2015).



The CaS (which contains rare earths) is then reacted with a weak acid, H₂S, as shown in Reaction 7:

The H₂S is bubbled through H₂O and the resulting aqueous mixture is then reacted with the CaS. The chemistry displaying the reaction of H₂S bubbled through H₂O is broken down in Reaction 2 through Reaction 5.



The overall reaction of H₂S in H₂O can be written as follows:



The CaS is dissociated into its ions Ca²⁺ and S²⁻. Therefore, the total number of sulphide ions in solution is now increased to 2.



When Ca²⁺ reacts with two S²⁻ ions, the overall charge becomes 2-. Therefore, reaction with the two H⁺ ions results in the production of Ca(HS)₂.



The reaction of CaS with H₂S on the ion exchange level is depicted in Reaction 7, where soluble Ca(HS)₂ is formed (De Beer *et al*, 2015). Since the Ca(HS)₂ is soluble, it can be separated from non-soluble species which includes rare earth oxides. The H₂S is used as a leaching agent. In using H₂S implies that no wasted expenditure will be incurred for leaching agents as the recovery process enables the recycle of unused H₂S. Additionally, H₂S is desirable, since it has a similar molecular structure to water, implying the ability to strip H₂S using any gas. However, leaching agents used, can be any acid that display similar reaction properties to H₂S. Lokshin, Tareeva & Elizarov (2016), studied and proved that H₂SO₄ leaching was a poor economic leaching process. Additional to this, Virolainen *et al* (2019) showed that leaching efficiencies were low for H₃PO₄, HCl and H₂SO₄. The HNO₃ leaching was proved to be slightly more efficient than the H₂SO₄ leaching (Preston *et al*, 1996).

Following the leaching process the $\text{Ca}(\text{HS})_2$ is produced as a soluble product, having a solubility that is a function of the H_2S pressure and temperature. Thus, the solubility of $\text{Ca}(\text{HS})_2$ was calculated as $298 \frac{\text{g Ca}(\text{HS})_2}{\text{L}}$ (Kotowski, 1957). The $\text{Ca}(\text{HS})_2$ solution is able to be filtered to produce a filter cake of rare earth residue. The filtrate, $\text{Ca}(\text{HS})_2$, can now be processed. Since the $\text{Ca}(\text{HS})_2$ is not used directly in the recovery process, yet contains valuable H_2S . Means to recover the H_2S in the $\text{Ca}(\text{HS})_2$ is required. To remove the H_2S , $\text{Ca}(\text{HS})_2$ can be reacted with any acid, that is stronger than H_2S . Some of these acids are: nitric acid, hydrochloric acid, sulphuric acid, carbonic acid and acetic acid. However, it is essential to ensure that the calcium compound formed is of use to the process. The importance of the calcium compound being resalable is highlighted in studies done by Preston *et al* (1996), where the economic viability of the rare earth recovery depends largely on the cost of $\text{Ca}(\text{NO}_3)_2$ and on the facilities of disposal for nitrates formed. Table 2 depicts the reaction of the acid with $\text{Ca}(\text{HS})_2$ and the effective use of the calcium compound products that form.

Table 2: A table that summarises different possible H_2S recovery reactions with their associated calcium compound product uses.

Reaction	Uses of product
$\text{Ca}(\text{HS})_2 + \text{H}_2\text{CO}_3 \longrightarrow \text{CaCO}_3 + \text{H}_2\text{S}$	CaCO_3 is widely used in the paper and construction industry
$\text{Ca}(\text{HS})_2 + \text{H}_2\text{SO}_4 \longrightarrow \text{CaSO}_4 + \text{H}_2\text{S}$	CaSO_4 is the dehydrated gypsum that is the feed to the recovery process
$\text{Ca}(\text{HS})_2 + \text{HNO}_3 \longrightarrow \text{Ca}(\text{NO}_3)_2 + 2 \text{H}_2\text{S}$	$\text{Ca}(\text{NO}_3)_2$ has a main use in fertiliser
$\text{Ca}(\text{HS})_2 + \text{HCl} \longrightarrow \text{CaCl}_2 + \text{H}_2\text{S}$	CaCl_2 has similar uses to NaCl and uses in swimming pool chemicals
$\text{CaS} + 2 \text{CH}_3\text{CO}_2\text{H} \longrightarrow \text{Ca}(\text{CH}_3\text{CO}_2)_2 + \text{H}_2\text{S}$	$\text{Ca}(\text{CH}_3\text{CO}_2)_2$ applications in the dietary industry

The reaction of CaS with H_2S to produce highly soluble $\text{Ca}(\text{HS})_2$ and then reacting the $\text{Ca}(\text{HS})_2$ with CO_2 and H_2O is supported by findings made by Brooks & Lynn (1997) and De Beer *et al* (2015). This is the process responsible for producing high-grade CaCO_3 . Noting that the calcium carbonate is inert, implies it will not be of effect to the environment, if the CaCO_3 can't be sold and becomes waste (van Vuuren, 2020). CO_2 is bubbled through H_2O to form H_2CO_3 . The H_2CO_3 is then reacted with the $\text{Ca}(\text{HS})_2$ to recover H_2S shown in Reaction 8.



H_2S is used to produce S via existing known conversion processes while the remaining

H_2S is recycled to reduce leachate expenditure. The elemental sulphur production is advantageous to the phosphoric acid production. Figure 3 below, depicts the recovery process proposed in steady state operation adapted from van Vuuren & Maree (2018).

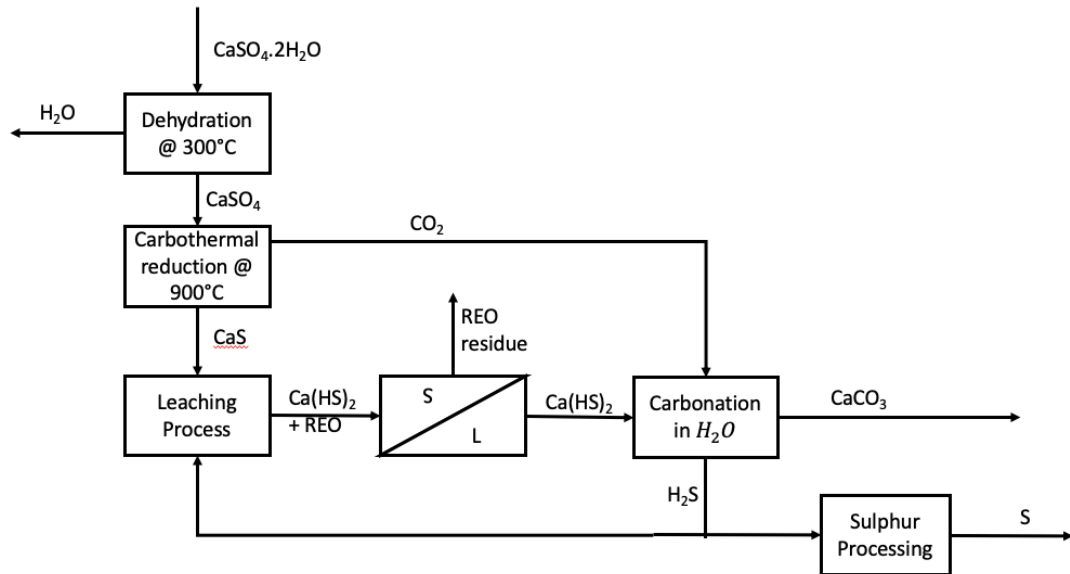


Figure 3: A process flow diagram to show the basic principles and flow of the recovery process proposed

van Vuuren & Maree (2018) propose the use of a tunnel kiln for the reduction of the CaS . Study on the use of a rotary kiln for waste gypsum treatment was done by Motaung *et al* (2015), in which the phosphogypsum was pelletized in order to increase conversion yields. Thus, using a tunnel kiln avoids the need to pelletize the phosphogypsum. The tunnel kiln must operate between 900°C and 1000°C . Figure 4 illustrates the operation of the tunnel kiln proposed for the recovery process reduction of CaS .

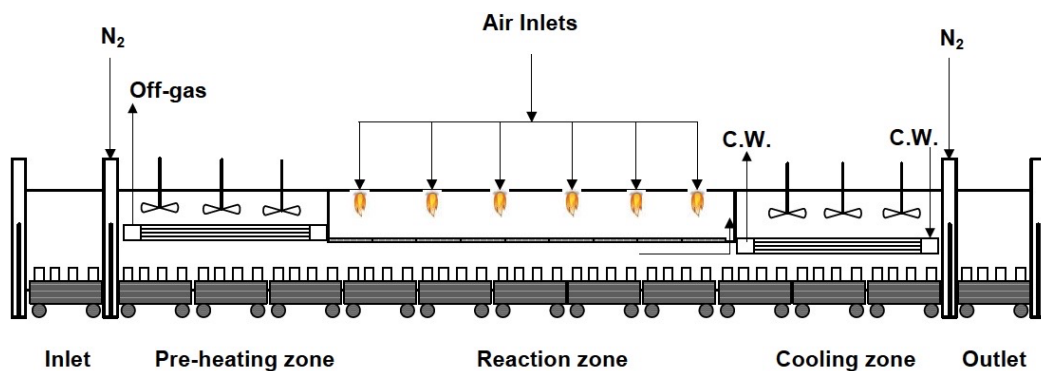


Figure 4: The proposed operation for the tunnel kiln used in the CaS reduction process (van Vuuren & Maree, 2018).

4 Competitive Process Analysis

Mining and recovery processes are two very different operations that aim to achieve the same end goal; a commercially useful and profitable rare earth product. Therefore, these two processes can be considered competitive processes. The recovery process is far less common than the mining process and almost all of the global production of rare earths is from the mining sector. In fact there are no reports of commercial recovery processes in operation. The recovery branch is a relatively new branch of rare earth production. Specifically, in South Africa, there are currently no known fully operational recovery sites and little to non production from mining sites.

4.1 Mining Processes

Currently the mining processes are the main sources, worldwide, for rare earth element production. China is the leading mining producer of rare earth oxides, producing 132 000 tons per year with the USA lying second with a mining production of 26 000 tons per year (Garside, 2020; U.S. Geological Survey, 2020). South Africa's biggest producer of rare earth oxides is currently Steenkampskraal mine (Western Cape), which has a total confirmed resource of 86 900 tons of rare earth oxides available. It is important to analyse the production of rare earths locally, as well as internationally, as it is rumoured to be so, that as soon as competition rises, China floods the market and shuts down the possibility of competitors. Additionally, hints and trade tips can be picked up from how international producers, specifically China, achieve their success.

4.1.1 Local Processes

This section will evaluate the mining processes that are currently active in South Africa. South Africa has a few rare earth production sites, namely: Steenkampskraal mine (Western Cape), Palabora complex (Limpopo), Glenover (Limpopo) and Zandkopsdrift (Northern Cape). Mining the rare earths means that the rare earths exists naturally in ore. The grade of rare earths, apparent in the ore, differs from ore to ore. Thus, in some instances, mining could operate on an ore with a very low rare earth grade, expending large amounts of money on small returns of product mined. The Steenkampskraal mine has a rare earth grade of 14.4 % which has been proven to be the world's richest grade. This rich grade implies that the mining cost will be far lower than mines that have a lower grade. High grade ore implies low operating costs. The Steenkampskraal mine will have a throughput of around 35 000 tons of ore per year to produce 2 700 tons of rare

earths. A resource of 605 000 tons of ore yielding a total of 86 900 tons of total rare earth oxides, implies a total operating mine life of approximately 25 years. The mine operates under three main activities (Steenkampskraal, 2020):

- Drilling, blasting, hauling and hoisting ore to the surface
- Production of monazite concentrate using crushing and sizing, milling, gravity and magnetic separation, flotation and secondary milling
- Chemical treatment of the monazite concentrate using the caustic crack process

However, even after the above process, the product produced is a mixed rare earth carbonate that needs further separation to be sold on the rare earth market. Cerium is the only rare earth that is separated at the mine and available to be sold immediately. This additional separation will be an added cost to the production process. Added to the cost is the fact that this separation is off-site, as the mine currently does not house infrastructure to facilitate this final separation stage. This change of location comes at a cost of increased production time and increased expenditure.

The second leading prospect for rare earth production in South Africa is the Zandkopsdrift site. The project is headed by international company Frontier Rare Earths. Zandkopsdrift was South Africa's leading frontier rare earth project, set to be one of the major global rare earth producers outside of China by 2015 with a rare earth ore grade of 2.3 %. A pre-feasibility study was conducted on the Zandkopsdrift mining site, with a positive outcome that the mining operations and rare earth production processes proposed were considered to be feasible. The Zandkopsdrift mine has an estimated mine life of 20 years, with an indicated available, 739 000 tons of total rare earth oxide. Production is aimed at 10 000 tpa initially, phased into 20 000 tpa, where sulphuric acid is used as the leaching agent. The mine will produce waste from operations which will result in three separate tailings deposits. This is a downside to the mining processes, that increase environmental impact and result in unnecessary costs incurred - in order to dispose of the waste in orderly manner. The complete separation of the rare earths can't be carried out on-site at this mine. The rare earth mixture has to be transported 300 km to an external treatment plant which involves transportation costs (Frontier Rare Earths Limited, 2015). The capital expenditure for the rare earths separation plant was estimated to be at around R3.3 billion (Cornish, 2015a; PoundSterling Live, 2019a). Despite these positive leads and feasibility studies, one is led to believe that the mining operations never took place due to an absence in publications of the progress made by Frontier Rare Earths on the project. It is speculated that with a five year all time low price drop in rare earth prices around the time of project implementation, the funding for the project was not available

(Tassell, 2017). This provides evidence, that base focus on rare earth production, is heavily impacted by volatility in the rare earth market.

The third site investigated is the Glenover rare earth project. The pre-feasibility study suggests that 5 500 tpa of rare earth oxides will be produced with an estimated capital expenditure of R3.3 billion (Glenover, 2020; PoundSterling Live, 2019a). A mine life of 24 years is estimated. Geo-Consult International (PTY) LTD (2012) conducted investigation which provided a result that indicated a rare earth grade of 2.17 % in the carbonatite mined at Glenover. The downside to this mining site, involves transportation costs for treatment of the rare earth mixture to produce a pure rare earth product (Glenover, 2020).

4.1.2 International Processes

China dominating the rare earth market implies it is important to obtain some insight into the production process. The main rare earth producing mine in China is the Bayan Obo mine, in the inner Mongolia region of China. This mine accounts for around 80 % of the Chinese rare earth production, with a rare earth ore grade of approximately 6 % (Fan *et al*, 2016). The Bayan Obo mine, produces rare earths as a byproduct of iron ore mining. With this mining operation, comes an environmental hazard and it has been reported that the surrounding villages have seen drastic pollution changes since the operation of this mine. Tailings ponds containing toxic chemicals harmful to the environment and human consumption and saturating the soils and groundwater with toxic chemicals. The mining of these rare earths takes place 120 km from where the rare earths are processed and separated. The Bayan Obo mine has a total rare earth resource of around 48 000 000 tons (Technology, 2014) and has been in operation for over 50 years.

Additional to the China domination, in a distant second is the United States. It is interesting to investigate into the Mountain Pass mine which is believed to have gone into bankruptcy as a result of the price of rare earths decreasing drastically in 2015. Another example of the inability of a mining process to maintain the cost of mining rare earths. Mountain pass had implemented innovative new technologies for extraction and separation. However, the revenues could not match the expenditure on these high-tech machinery. In 2018 the mine was re-opened under new management involving a Chinese firm, with an ore grade of 8 % rare earths and production of 26 000 tpa. It is currently the only operating rare earth mine in the US.

4.2 Summary Comparison

The production rates mentioned for the mines in Section 4.1.1 and Section 4.1.2 provide a good indication of what could be seen as a realisable production rate, despite the slow progress of certain projects. A common "rule-of-thumb" for new projects entering into a market is that, to be able to produce 20 % of the world market, is huge. Perhaps a more realisable value would be a production of between 5 % and 10 % of the world market production. Jellicoe (2019) suggests that in order to be competitive, an amount of 20 000 tpa of rare earth needs to be produced - this would be 10 % of the global market. Due to China's total market domination, 5 % of their production would amount to 6600 tpa. In comparison, 5 % of the US production would be 1 300 tpa. U.S. Geological Survey (2020), state a global rare earth production of "210 000 tons" for 2019. 5 % of this global market production would imply a production of around 10 000 tpa. Therefore, a ballpark, realisable value to work towards, would be the ability to initially produce a minimum of 10 000 tpa of rare earth oxide mixture. It is reported that the Chinese domination has fallen slightly over recent years (Castilloux, 2019), with China owing to approximately 90 % of the global production in 2013 (Technology, 2014).

Looking into the Steenkampskraal production methods in Section 4.1.1, we could argue that the recovery process cuts the costs of the first two phases and jumps straight into the chemical treatment phase of production. Important to take heed of, is the success of the Bayan Obo mine. This mine has a main focus on mining iron ore with the extraction and mining of rare earths as a secondary operation or byproduct production. In doing this, it is speculated that the revenue from the iron market covers mining operations and costs, which allows the revenue from the rare earth market to be an added profit. This implies the mine operation is not dependent on the so called "volatile" rare earth market and rather dependent on the more stable iron market. This adds justification for the recovery of rare earths from phosphogypsum as a "side operation", independent from the main production lines. If the market is to collapse, the effects won't be felt as hard as when the sole focus of the plant was rare earth production. It can be concluded that mining rare earths is an expensive process and in order to curb the mining operation cost and maintain success in operation, it is far more beneficial and financially sustainable for rare earth production to be carried out as a "side" or byproduct production. Therefore, a mirror image of the Bayan Obo mine would be the recovery of rare earths from phosphogypsum as a byproduct production to the main or central focus production of phosphoric acid.

5 Risk

5.1 Market Risk

The Chinese market domination results in this project involving inevitable risk when considering alternative commercial rare earth production means. Failure to produce competitive amounts of rare earth product at a competitive and economical price, will imply that China can swamp the rare earth market to nullify any competitive threat. Chinese producers have threatened first world countries to place a rare earth embargo on the competing countries. Therefore, added benefit, of being able to produce competitive amounts of rare earth oxide, is that the threat of an embargo would not raise concern as the local market for rare earth oxides would be self-sustainable. Mitigation of market risk involves attempt to employ the recovery of rare earths as a "side operation" or secondary source of income with the successful and well-established phosphoric acid producing plant as the base operation.

5.2 Technical Risk

A widely documented and ever more prevalent issue is the estimated demand and supply curve for the rare earths as addressed in Section 2. This causes consideration into the risk of having to stockpile the lesser demanded rare earths in order to meet the demand for the more valuable rare earths. The issue of stockpiling is a risk for any plant in the valuable commodity industry. Stockpiling the lesser demanded rare earths prevents swamping the rare earth market and maintains the market value for these lesser demanded, more abundant rare earths. Production rates that swamp the rare earth market can be considered (initially) to be that greater than 5 % of the current market as discussed in Section 4. It is important to find a balance in the supply and demand curves for the rare earth market.

The robustness of the recovery process is another technical risk to consider. The possibility of rare earths reacting with the leaching agent and becoming soluble results in the loss of valuable rare earth products. It is not known how much of the rare earths might dissolve into solution, if any, as very few reliant and comprehensive studies have been published on this phenomenon. Furthermore, risk is associated with the success of the proposed recovery method and the lab-scale testing. Association to the lab-scale risk is whether the recovery process performs well against predicted outcomes. Possibility of the $\text{CH}_3\text{CO}_2\text{H}$ leaching and the H_2S leaching providing differing outcomes. Lab-scale risk also involves carbon and ash sediments remaining in the residue as a result of the reduction process. This requires implementation of processes such as flotation in order

to remove the carbon or ash left behind during combustion. These risks are mitigated with proposed variable analysis and similar recovery processes conducted at lab-scale as detailed in Section 7.

5.3 Alternative Phosphogypsum Resources

Resource risk is encountered if the recovery process is successful but the amounts of rare earth produced per annum at the Richards Bay plant is insufficient in meeting market demand. Risk includes possibility of a degraded ore encountered or plant shutdown at the Richards Bay plant. This links to a decline in production rates. To mitigate this risk, alternative resource sites are introduced. This too is advantageous to a successfully commissioned recovery process, in the sense that more profit can be made by expanding available resources. The following alternative resource sites are available locally which could be studied to mitigate the risk of resource availability:

- Glenover - There is an estimated 30 000 tons of stockpile available of phosphogypsum which has been mined from phosphate rock (Glenover, 2020) (Galileo Resources Plc, 2012). Analysis has been done on the stockpile reported by Galileo Resources Plc (2012) to show an approximate 1.24 % of rare earth content in the stockpiles. However, the ore grade of the phosphate rock is known as mentioned in Section 4.1.1.
- Phalaborwa - Study has been done at the Phalaborwa cite which concluded a recovery of a 2.8 % mixed rare earth oxide from phosphogypsum (Preston *et al*, 1996). This site is currently known to be inactive. However, since study has already been completed on this site, there is reduced risk associated with this site.

6 Financial

According to Foskor (2016), a total of R158 000 000, upon plant commission, was allocated to discharge the waste phosphogypsum into the sea in a manner which was passed as environmental friendly. The recovery process proposed by van Vuuren & Maree (2018) shows that, in doing a mass balance across the process, waste disposal is reduced by approximately 90 %. Seeing a proportional relationship between the cost of disposal and the amount needed to be disposed, translates to a proportional reduction in disposal costs.

Waste disposal cost reduction is not the only cost benefit of the recovery process. The price of sulphur for 2018, as reported by Foskor (2018), was around R2000 per ton. Foskor (2018) also reports a total sulphuric acid production of 1 377 881 tons. A mole balance would imply an input requirement estimated at 450 000 tons of elemental sulphur. Taking into account that for 2018 a total of 452 526 tons of phosphoric acid was produced. According to Section 3, 2 035 917 tons of phosphogypsum was produced for 2018. 17 % of this phosphogypsum production proves that the recovery process is able to produce approximately 75 % of the elemental sulphur used in the sulphuric acid production. This in turn, reduces cost spent on importing elemental sulphur.

The CaCO_3 has high value in the paper and construction industry. However, this CaCO_3 used in these industries has a high-grade, having the ability to sell the CaCO_3 adds further value to the recovery process. Large volumes of production result in the high-purity CaCO_3 (sold at about R225 per kg) having to be dissolved into the limestone industry at an average resale value of R700 per ton. The amount of CaCO_3 sold, needs to be carefully calculated in order to prevent swamping the market.

Table 3 shows potential revenue from the rare earth recovery process for full capacity plant operation (3 240 000 tpa phosphogypsum) and the reported (Foskor, 2018) production for 2018 (2 035 917 tpa phosphogypsum). The prices were taken from Section 2 (mineralprices.com, 2019) with exchange rates taken in December 2019 (due to COVID-19 unprecedented variance) (PoundSterling Live, 2019a; PoundSterling Live, 2019b). Section 2 also illustrated that neodymium is the rare earth with the highest market value, followed by praseodymium and gadolinium. These three rare earths are accounted for in the first row of Table 3 as separated products. The mixed rare earth oxide revenue uses a weighted average and accounts for extraction and separation costs (30 % of the gross revenue) shown in the second row of the table.

Table 3: Predicted potential revenue from rare earth oxides for the proposed recovery process.

	Full capacity ($\frac{R}{\text{ton phosphogypsum}}$)	2018 reported capacity ($\frac{R}{\text{ton phosphogypsum}}$)
Separated	2 300 000 000	730 000 000
Mixture	365 000 000	230 000 000

It is to be noted that this proposal focuses on implementing the recovery process as a secondary or "side operation". This implies that financially, the plant is primarily dependent on the already established, stable and successful phosphoric acid production. In doing this, risk is mitigated against the volatile rare earth market.

7 Research and Development Plan

The key question of the research is: will H_2S used as a leaching agent provide sufficient concentration of the rare earths in a mixed rare earth oxide? The research and development stage of the recovery process is phased. The scope for the initial phase aims to practically demonstrate the ability to concentrate the rare earths to an economically viable percentage. Inclusive in this initial phase is variable analysis and experimentation completed at lab-scale. This includes conducting chemical analysis, using ICP-OES, to determine the composition of the rare earth oxide mixture; how valuable is the concentrated mixture and how efficient is the leaching agent? Electron microscope analysis will provide insight into the topology of the mixture to determine if the rare earths are liberated from coal, ash and phosphogypsum particulate that remain in the rare earth residue after chemical treatment. The experimentation of the initial phase was looked at by Preston *et al* (1996). Preston *et al* (1996) conducted study at the Phalaborwa site, where the aim was to recover rare earth oxides from a calcium sulphate sludge. Leaching efficiencies of up to 85 % were achieved at laboratory scale, yielding a rare earth oxide mixture of about 2.8 %. This result was achieved using 1 M nitric acid as the main leaching agent. Variable effect into the lab-scale phase could also be explored evaluating the performance of different leaching agent concentrations. The initial phase has a budget of around R50 000, with a timeline estimated at 1 year.

Pre-investigation was conducted on how the rare earths will react with the leaching agent and what would be a suitable substitute for the leaching agent. Solomon & Lee (1994) provided insight into the possible reaction of rare earths with dilute acids, such as HCl and HNO_3 . However, Silver (1995) states that Solomon & Lee (1994) "perpetuates the widespread misconception that the rare earth metals dissolve in acids yielding only typical, trivalent rare earth salts", further stating that research into this chemistry would be an "excellent topic". Therefore, evidence for and against the dissolving of rare earths in the leaching agent is inconclusive.

Laboratory scale experiments impose certain restrictions, such being the ease of access to and cost of materials and equipment. Additionally, using H_2S as a leaching agent requires specific safety care to be taken. These are complications which make laboratory work using the proposed leaching agent challenging. Therefore, to complete the investigation at a lab-scale, leaching tests with an acid of similar properties to H_2S will be used. Table 4 provides possible substitutions for H_2S along with the respective pK_a values in descending order. The table is compiled based on leaching agents used in previous literature as well as taking acids with a pK_a value relatively close to H_2S . Multiple pK_a values are given for those acids which are polyprotic..

Table 4: A table which provides the acid strength and calcium-conjugate base compound product solubility for the leaching of CaS in the recovery process (Kotowski, 1957; Kotz *et al*, 2015; Perry & Green, 2008).

Acid	pK_{a_1}	pK_{a_2}	pK_{a_3}	Solubility ($\frac{\text{g Ca-conj} \cdot \text{base}}{\text{L H}_2\text{O}}$)
HCN	9.4	-	-	decomposes
HBrO	8.6	-	-	2300
HClO	7.46	-	-	decomposes
H ₂ S	7	12.92	-	298
H ₂ CO ₃	6.38	10.32	-	0.012
C ₃ H ₆ O ₂	4.89	-	-	105
CH ₃ COOH	4.74	-	-	520
H ₃ AsO ₄	2.24	6.96	11.5	0.13
H ₃ PO ₄	2.12	7.21	12.44	0.025
HNO ₃	-1.4	-	-	2660
H ₂ SO ₄	-3	1.92	-	2.23
HCl	-7	-	-	595

From Table 4 three possibilities arrive being: HBrO, C₃H₆O₂ and CH₃CO₂H due to the similarity in strength in relation to the solubility of the calcium-conjugate base product. HNO₃ provides really high solubility for the calcium-conjugate base product. However, the strength between H₂S and HNO₃ are vastly different.

Despite this, from Table 4, the acetic acid is chosen as a replacement leaching agent, the reasons being:

- Acetic acid is cheap and readily available for experimental purposes. Whereas HBrO and C₃H₆O₂, are more difficult to obtain for lab-scale purposes and are more expensive.
- Acetic acid has a strength relatively similar to that of H₂S.
- The solubility of the Ca(CH₃COO)₂ is high enough which ensure the product will dissolve in water and the rare earth residue will be able to be filtered.

A suggested experimental plan is provided below, using acetic acid as the leaching agent for initial phase experimentation. The following experimental plan was drawn up based on the fact that a safe amount of H₂S to be exposed to for extended periods of time (8 hour exposure), with minimal harmful side effects, is 10 ppm (Seaman, 2017). This is a conservative guide for conducting experimentation that involves the production of H₂S. The MSDS document for this chemical and the hazards associated can be found

in Appendix A. Special caution is to be taken when performing the experimentation, adhering to guidelines and safety documentation.

1. Dehydrate the phosphogypsum for 5-6 hours in a furnace increased incrementally 2°C per minute, until approximately a final drying temperature of 300°C is maintained.
2. Grind and screen the gypsum to prepare for mixing.
3. Screen the gypsum to 600 μm .
4. Once the screened gypsum is collected. Mix the dehydrated gypsum to form a mixture with coal.
5. For the gypsum and coal mixture, a ratio of 1 part phosphogypsum to 2.5 parts fixed carbon is used for the mixing.
6. Mix the phosphogypsum with the coal, forming 5 kg of the mixture.
7. Once the anhydrous gypsum is collected and mixed, the reduction process can begin. Reduce the CaSO_4 to CaS in a furnace using carbon as a reducing agent in the reduction process. Reduce the CaSO_4 at a temperature of 900°C
8. Reduce 5 kg of the gypsum and coal mixture.
9. During the extraction phase of the process, H_2S is produced. Therefore, a cautious approach needs to be taken when performing the extraction. Perform extraction in a certified chemical variable air volume fume hood.
10. Weigh out 50 g of CaS mixture ($\rho \approx 2590 \frac{\text{kg}}{\text{m}^3}$) in a 600 mL glass beaker. Add 60 mL of water to the CaS to create a 25:75 ratio of solid to liquid, sludge.
11. Stir the slurry in the 600 mL beaker using a magnetic stirrer, maintain the stirring for continuous mixing throughout the extraction process.
12. Consider the certification of the fume hood used, do a calculation based on the airflow rate through the fume hood to obtain the addition rate of the acetic acid. This calculation procedure is provided in Appendix B. Note: Q_{air} is used to denote the volumetric air flow rate for the fume hood as detailed in Appendix B.
13. Fill a burette with 3 M acetic acid.
14. Slowly drip the acetic acid into the CaS and H_2O mixture at a steady rate of $0.05Q_{air} \frac{\text{mL}}{\text{s}}$. Addition of acetic acid at the rate given will result in a H_2S of 10 ppm

in the fume hood. This is an acceptable ppm according to H₂S MSDS. If the reaction is not performed in a fume hood the rate of H₂S production will cause irritation to the eyes. Take caution.

15. Once a net total of 470 mL of 3 M acetic acid solution (80 mL of pure acetic acid or glacial acetic acid) has been added, continue stirring the mixture for additional 10 minutes to allow for completion of the leaching process.
16. Bubble through air for 5 minutes to ensure complete removal of the H₂S once the leaching process is complete.
17. Prepare an Erlenmeyer flask, funnel and filter paper for filtration of the solution. The calcium acetate solution will be the filtrate and the rare earths will be the contents of the filter cake. The filtration process can be done using gravity filtration or vacuum filtration.
18. Conduct electron microscope analysis on the filter cake to examine topology of the rare earth oxide mixture.
19. Re-conduct the experiment under the same conditions to determine the reliability and validity of the experimentation results.
20. Consider improvements on the leaching process and possible alternatives to concentrate the rare earth oxide mixture.

8 Conclusions and Recommendation

Experts predict that the rare earth market will continue to expand. The demand for a stable rare earth production is propelled by the market for advanced electronics, green technologies and clean energy production. The environmental concern of reducing waste and pollution is becoming ever more prevalent. The utilisation of phosphogypsum waste is advantageous for the sustainable supply of rare earths. Subsequently, the penetration of the rare earth market with sustainable techniques possesses great value and opportunity.

The recovery process proposed by van Vuuren & Maree (2018) will impact the rare earth market while generating a secondary source of income for the plant in Richards Bay. The recovery process provides an alternative for the disposal of the phosphogypsum. The economic viability of the recovery process is enhanced with the implementation of the recovery process as a secondary or "side" operation.

The proposed process is considered theoretically realisable. The realisable factor of the recovery process is supported by similar study conducted by Preston *et al* (1996), who proved a 2.8 % mixed rare earth oxide is achievable. It has been shown that the recovery process proposed in this study and by van Vuuren & Maree (2018) holds benefits for the environment and for the Richards Bay plant.

It is recommended that further studies be conducted on the topics discussed in this proposal. Emphasis should be placed on performing experimentation to support the efficacy of this technique. Simultaneously, the feasibility of the experimentation may be documented to provide initial insight into cost of implementation and recovery. This could be compared to the estimated revenue from the production of the rare earth oxide mixture. Variable experimentation and investigation regarding the effect of the type and concentration of the leaching agent would provide further insight into the recovery process.

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Appendix A Safety, Health and Environmental Impact

The following MSDS was taken from AFROX (2011).

 AFROX A Member of The Linde Group		MATERIAL SAFETY DATA SHEET (MSDS) HYDROGEN SULPHIDE (H₂S) Please ensure that this MSDS is received by the appropriate person	
DATE: April 2011 Ref. No.: MS033		Version 2	
1 PRODUCT AND COMPANY IDENTIFICATION		Skin Contact	
Product Name	HYDROGEN SULPHIDE	May irritate the skin upon contact	
Chemical Formula	H ₂ S	Ingestion	
Trade Name	Hydrogen Sulphide	Ingestion is unlikely. Hydrogen sulfide will irritate the mucous membranes causing a burning feeling with excess salivation likely. Irritation of the gastrointestinal tract may also occur.	
Company Identification	African Oxygen Limited 23 Webber Street Johannesburg, 2001 Tel. No: (011) 490-0400 Fax No: (011) 490-0506	4 FIRST AID MEASURES	
EMERGENCY NUMBER	0860111185 or (0860 02 02 02) (24 hours)	Inhalation:	
2 COMPOSITION/INFORMATION ON INGREDIENTS		Very toxic by inhalation. May cause damaging effects to central nervous system, metabolism and gastrointestinal tract. Prolonged exposure to small concentrations may result in pulmonary oedema. Remove victim to uncontaminated area wearing self contained breathing apparatus. Keep victim warm and rested. Call a doctor. Apply artificial respiration if breathing stopped. Delayed adverse effects possible.	
Chemical Name:	Hydrogen Sulphide	Skin/Eye:	
Chemical Abstract Service Number (CAS No.):	07783-06-04	Remove contaminated clothing. In case of frostbite spray with water for at least 15minutes. Apply a sterile dressing. Immediately flush eyes thoroughly with water for at least minutes. Obtain medical assistance.	
UN No.:	1053	Ingestion:	
ERG No.:	117	It is not considered a potential route of exposure	
3. HAZARDS IDENTIFICATION		5 FIRE FIGHTING MEASURES	
Main Hazards	in concentrations of 20 to 50ppm , hydrogen sulphide irritates the eyes. Slightly higher concentrations irritate The upper respiratory tract and, may result in pulmonary edema. Inhalation of 500ppm for 30 minutes produces headache, dizziness, excitement, staggering, and gastroenteric disorder, followed in some cases by bronchitis and bronchial pneumonia. Concentrations above 600ppm can be fatal within 30 minutes through respiratory paralysis. Although the foul odor of hydrogen sulphide is readily detectable in low concentrations, it becomes unreliable as a warning of dangerous concentrations of gas since continuous inhalation leads rapidly to olfactory fatigue.	Extinguishing media Suitable extinguishing media: all known extinguishants can be used.	
Vapour Inhalation	Hydrogen sulfide reacts with enzymes in the bloodstream and inhibits cellular respiration resulting in pulmonary paralysis, sudden collapse and death. Continuous exposure to low (15-50 ppm) concentrations will generally cause irritation to mucous membranes, and may also cause headache, dizziness or nausea. Higher concentrations (200-300 ppm) may result in respiratory arrest leading to coma or unconsciousness. Exposures for more than 30minutes at concentrations greater than 700 ppm have been fatal. Continuous inhalation of low concentrations may cause olfactory fatigue or paralysis of the sense of smell. Thus, detection of hydrogen sulfide by its odor is not effective.	Specific Hazards	
Eye Contact	Low concentrations will generally cause irritation to the conjunctiva. Repeated exposure to low concentrations is reported to cause conjunctivitis, photo phobia, corneal	Exposure to fire may cause containers to rupture/explode. Hazardous combustion products: If involved in a fire, the following toxic and/or corrosive fumes may be produced by thermal decomposition: Sulfur dioxide. Suitable extinguishing media: all known extinguishants can be used.	
		Emergency Actions	
		stop flow of product if possible. Move away from the container and cool with water from a protected position. Do not extinguish a leaking gas flame unless absolutely necessary. Spontaneous/explosive re-ignition may occur.	
		Protective Clothing	
		Use a self contained breathing apparatus and chemically protective clothing.	
		6 ACCIDENTAL RELEASE MEASURES	
		Personal Precautions	
		Evacuate area. Eliminate ignition sources. Ensure adequate air ventilation. Wear self- contained breathing apparatus when entering area unless atmosphere is proved to be safe.	
		Environmental Precautions	
		Do not allow the product from entering sewers and storm water drains.	
		Methods for cleaning up	
		Ventilate area. Keep area evacuated and free from ignition sources until any spilled liquid has evaporated, that is ground free from frost	

MATERIAL SAFETY DATA SHEET (MSDS) HYDROGEN SULPHIDE (H₂S)

Please ensure that this MSDS is received by the appropriate person

7 HANDLING AND STORAGE

Ensure equipment is adequately earthed.
Purge air from system before introducing gas.
Do not allow backfeed into the container.
Cylinders should be stored upright and prevented from falling.
Suck back of water into the container must be prevented.
Use only properly specified equipment, which is suitable for this product, its supply pressure and temperature.
Contact your gas supplier if in doubt.
Keep away from ignition sources (including static discharges).
Secure them away from flammable or combustible materials; in a dry, well ventilated constructed of non -combustible material with firm level floor.
Keep container below 50 deg. Celsius in a well ventilated place.
Use the "first in – first out" inventory system to prevent full cylinders from being stored for excessive period of time. Compliance of all relevant legislation is essential. Keep away from children

8 EXPOSURE CONTROLS/PERSONAL PROTECTION

Occupational exposure hazards sulphide – TLV: 10ppm; STEL: 15ppm	Hydrogen
Engineering control measures	Filling or withdrawal from a Hydrogen Sulfide cylinder must be performed in a well ventilated area and if possible should be in a forced ventilation system or using a hood over the valve.

9 PHYSICAL AND CHEMICAL PROPERTIES

PHYSICAL DATA	
Chemical Symbol	H ₂ S
Molecular Weight	34.08 g/mol
Melting point @ 224 kPa	-86°C
Appearance/Colour:	Colourless gas
Odour:	Rotten eggs
Relative density, Gas @ 101.325kPa @ 25°C	1.188
Specific Volume @ 21.1°C, 101.325 kPa	70.11dm ³ /kg
Dielectric constant; Gas @ 0°C, @ 101.325kPa	1.004

10 STABILITY AND REACTIVITY

Conditions to avoid	avoid heat, flames, sparks and other source of ignition. Minimise contact with material Avoid inhalation of material or combustion by products. Keep out of water suppliers and sewers.
Incompatible Materials	Do not store reserve stocks of hydrogen sulphide cylinder with cylinders containing oxygen or other highly oxidising or combustible materials.

11 TOXICOLOGICAL INFORMATION

Acute Toxicity	unknown
Skin & eye contact	unknown
Chronic Toxicity	unknown
Carcinogenicity	unknown
Mutagenicity	unknown
Reproductive Hazards	unknown

12 ECOLOGICAL INFORMATION

General: Toxic to water organisms.

13 DISPOSAL CONSIDERATIONS

Disposal methods Avoid discharge to atmosphere.
Do not discharge into any place where its accumulation could be dangerous.
Toxic and corrosive gases formed during combustion should be scrubbed before discharge to atmosphere.
Do not discharge into areas where there is a risk of forming an explosive mixture with air. Waste gas should be flared through a suitable burner with flash back arrestor.
Contact supplier if further guidance is required

14 TRANSPORT INFORMATION

UN No.	1053
Class	2.3
ADR/RID Item Nr.	2,2 deg. TIF
ADR/RID Hazard Nr.	263
Labelling ADR	Label 6.1 Toxic Substance Label 3 Flammable

substance

Other transport information Avoid transport on vehicles where load space is not separated from the driver's compartment. Ensure vehicle driver is aware of potential hazards of the load and knows what to do in the event of an accident or an emergency.
Before transporting product containers ensure that they are firmly secured and valve outlet cap, nut or plug (where provided) is correctly fitted. Valve protection device (where provided) is correctly fitted. Ensure that there is adequate ventilation. Comply with applicable transport regulation.

15 REGULATORY INFORMATION

Risk phrases	R26 Very toxic by inhalation
Safety phrases	S (1/2) Keep locked up and out of reach of children S9 Keep container in a well ventilated place S16 Keep away from ignition sources – No smoking S28 After contact with skin, immediately wash with plenty of ... (to be specified by manufacturer) S36/37 Wear suitable protective clothing and gloves S45 In case of accident or if you feel unwell, seek medical advice immediately S61 Avoid release into environment; refer to special instructions/material safety data sheet

Reference: SANS 10265

16 OTHER INFORMATION

Ensure all national/local regulations are observed. Ensure operators understand the asphyxiation hazard.

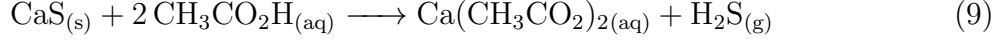
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Appendix B Fume Hood Parameter Calculation

It is known that from Section 7, that it is desired to have 10 ppm of H₂S produced. The H₂S is produced by Reaction 9 given below:



The density of H₂S can be calculated using Equation 10, under the assumption that H₂S behaves like an ideal gas at Standard Temperature (T) and Pressure (P) (STP).

$$\rho_{\text{H}_2\text{S}} = \frac{MM_{\text{H}_2\text{S}} \times P}{R \times T} \quad (10)$$

$$\rho_{\text{H}_2\text{S}} = 1.5 \frac{\text{kg}}{\text{m}^3} \quad (11)$$

Here, $MM_{\text{H}_2\text{S}} = 34.08 \frac{\text{g}}{\text{mol}}$ with R the universal gas constant. It is now possible to obtain an expression in $\frac{\text{mg H}_2\text{S}}{\text{m}^3 \text{ air}}$ using Equation 12.

$$ppm \times \rho_{\text{H}_2\text{S}} = 10^{-5} \frac{\text{m}^3 \text{ H}_2\text{S}}{\text{m}^3 \text{ air}} \times 1.5 \frac{\text{kg H}_2\text{S}}{\text{m}^3 \text{ H}_2\text{S}} \times 10^6 \frac{\text{mg H}_2\text{S}}{\text{kg H}_2\text{S}} = 15 \frac{\text{mg H}_2\text{S}}{\text{m}^3 \text{ air}} \quad (12)$$

To obtain how much CH₃CO₂H is needed for the production of the above specified concentrations, information about the air must be determined. Since the reaction is considered a hazardous and toxic producing reaction, it needs to be carried out in a chemical variable air volume fume hood. Fume hoods have a specific face velocity which is denoted by u_{hood} ($\frac{m}{s}$). The volumetric flow rate of air is given by Q_{air} ($\frac{m^3}{s}$) in Equation 13. $A_{sash \ opening}$ (m^2) refers to the area of the fume hood entrance given in Equation 14.

$$Q_{air} = u_{hood} \times A_{sash \ opening} \quad (13)$$

with

$$A_{sash \ opening} = height_{sash} \times Length_{fume \ hood} \quad (14)$$

According to ESCO Technologies, Inc (2012) and Ward (2018), fume hoods should have a face velocity in the range of $0.3 \frac{m}{s}$ to $0.5 \frac{m}{s}$. Krueger (2015) and Southern Methodist University (2019) state that a sash height must never exceed $\approx 34cm$ (18"). Most floor standing fume hoods have an entrance width of $\approx 1.2m$.

Once the volumetric air flow rate is determined the mass of allowable H₂S can be determined using Equation 15, knowing the concentration of H₂S in air using Equation 12:

$$m_{\text{H}_2\text{S}} = 15 \times 10^{-3} \times Q_{air} \frac{\text{g H}_2\text{S}}{\text{s}} \quad (15)$$

Next the mole of allowable H_2S can be calculated using Equation 17

$$n_{\text{H}_2\text{S}} = \frac{m_{\text{H}_2\text{S}}}{MM_{\text{H}_2\text{S}}} \quad (16)$$

$$n_{\text{H}_2\text{S}} = 4.4 \times 10^{-4} \times Q_{\text{air}} \frac{\text{mol}}{\text{s}} \quad (17)$$

Since the stoichiometry of Reaction 9 is known, the mole of $\text{CH}_3\text{CO}_2\text{H}$ can be calculated as

$$n_{\text{CH}_3\text{CO}_2\text{H}} = 8.8 \times 10^{-4} \times Q_{\text{air}} \frac{\text{mol}}{\text{s}} \quad (18)$$

With $\rho_{\text{CH}_3\text{CO}_2\text{H}} = 1050 \frac{\text{kg}}{\text{m}^3}$ and $MM_{\text{CH}_3\text{CO}_2\text{H}} = 60.052 \frac{\text{g}}{\text{mol}}$ the conversion to a volumetric rate can now be done using Equation 19 to give a final $\text{CH}_3\text{CO}_2\text{H}$ volumetric addition rate shown in Equation 20 in terms of the fume hood air volume (Q_{air}).

$$\dot{V}_{\text{CH}_3\text{CO}_2\text{H}} = \frac{n_{\text{CH}_3\text{CO}_2\text{H}} \times \frac{MM_{\text{CH}_3\text{CO}_2\text{H}}}{1000}}{\rho_{\text{CH}_3\text{CO}_2\text{H}}} \times 10^6 \frac{\text{mL}}{\text{m}^3} \times Q_{\text{air}} \quad (19)$$

$$\dot{V}_{\text{CH}_3\text{CO}_2\text{H}} = 0.05 \times Q_{\text{air}} \frac{\text{mL}}{\text{s}} \quad (20)$$

This addition rate is used provided the acetic acid is 100 % concentrated. Assuming only 3 M $\text{CH}_3\text{CO}_2\text{H}$ solution is available, Equation 21 shows the calculation for the addition rate of 3 M solution.

$$\dot{V}_{\text{sol}} = \frac{n_{\text{CH}_3\text{CO}_2\text{H}}}{3} \frac{\text{mL}}{\text{s}} \quad (21)$$

$$\dot{V}_{\text{sol}} = 0.3 \times Q_{\text{air}} \frac{\text{mL}}{\text{s}} \quad (22)$$

Next, we need to determine the total amount of $\text{CH}_3\text{CO}_2\text{H}$ required for the complete leaching of 50 g of reduced CaS which has $MM_{\text{CaS}} = 72.143 \frac{\text{g}}{\text{mol}}$. Starting off, the amount of moles of CaS can be calculated using Equation 23 followed by a new calculation for the amount of $\text{CH}_3\text{CO}_2\text{H}$ moles (Equation 25), using stoichiometry from Reaction 9. Equation 26 applies basic chemistry to obtain a total mass of $\text{CH}_3\text{CO}_2\text{H}$, which implies then using $\rho_{\text{CH}_3\text{CO}_2\text{H}}$ in Equation 28 provides a total volume of $\text{CH}_3\text{CO}_2\text{H}$ needed to leach 50 g of reduced CaS.

$$n_{\text{CaS}} = \frac{m_{\text{CaS}}}{MM_{\text{CaS}}} \quad (23)$$

$$n_{\text{CaS}} = 0.7 \text{ mol} \quad (24)$$

$$n_{\text{CH}_3\text{CO}_2\text{H}} = 1.4 \text{ mol} \quad (25)$$

$$m_{\text{CH}_3\text{CO}_2\text{H}} = n_{\text{CH}_3\text{CO}_2\text{H}} \times MM_{\text{CH}_3\text{CO}_2\text{H}} \quad (26)$$

$$m_{\text{CH}_3\text{CO}_2\text{H}} = 84 \text{ g} \quad (27)$$

$$V_{\text{CH}_3\text{CO}_2\text{H}} = \frac{\frac{m_{\text{CH}_3\text{CO}_2\text{H}}}{1000}}{\rho_{\text{CH}_3\text{CO}_2\text{H}}} \times 1000 \frac{\text{L}}{\text{m}^3} \times 1000 \frac{\text{mL}}{\text{L}} \quad (28)$$

$$V_{\text{CH}_3\text{CO}_2\text{H}} = 80 \text{ mL} \quad (29)$$

This implies that a total volume of 80 mL for **pure** or **glacial** $\text{CH}_3\text{CO}_2\text{H}$ is required at an addition rate of $0.05 \times Q_{\text{air}} \frac{\text{mL}}{\text{s}}$.

Assuming only 3 M $\text{CH}_3\text{CO}_2\text{H}$ solution is available a total volume of solution added can be calculated as shown in Equation 30.

$$V_{\text{sol}} = \frac{n_{\text{CH}_3\text{CO}_3\text{H}}}{3} \text{ mL} \quad (30)$$

$$V_{\text{sol}} = 470 \text{ mL} \quad (31)$$

This now implies that the 3 M $\text{CH}_3\text{CO}_2\text{H}$ solution must be added at $0.3 \times Q_{\text{air}} \frac{\text{mL}}{\text{s}}$ to amount to a total addition volume of 470 mL.