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***Reaction phenomena of iron oxide leaching in an
evaporative acid bake reactor***

by

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of the requirements for the Degree

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(CHEMICAL ENGINEERING)**

in the Chemical Engineering Department

at the University of Cape Town

Supervised

by

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**CAPE TOWN
August 2012**

DECLARATION

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Date: 2012/09/07

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ABSTRACT

Namakwa Sands is a heavy mineral mining and beneficiation business within Tronox, and produces two major products, zircon ($\text{ZrO}_2 \cdot \text{SiO}_2$ 99.9%) and rutile (TiO_2 99.9%) at a combined annual rate of 140kt. The heavy mineral concentrates are exported to international markets to make specialist coatings for the paints and ceramics industries. The ceramic industry is very strict on the purity of the minerals used. Namakwa Sands prides itself in being able to produce zircon and rutile at these requirements; however, strict requirements, especially in terms of Fe impurities (Fe_2O_3 content in zircon concentrate must be $< 600\text{ppm}$), limit the productivity and come at a cost to recovery. The concentration and separation of heavy minerals is a complex process, which utilizes conductivity differences between minerals. Zircon coated with iron oxides (Fe_2O_3 , FeOOH) reports as more conductive during electrostatic separation, which can result in a zircon particle to behave like a rutile particle and in this way cause both products (rutile and zircon) to become off specification.

The Hot Acid Leach (HAL) circuit was established in the Namakwa Sands plant to effectively leach, scrub and wash off coatings on mineral particles. Within the leaching process a dry-bake semi-adiabatic rotating kiln contacts coated (in Fe_2O_3) minerals with sulphuric acid at 160°C at a solid/liquid (S/L) ratio of 10.8. The kiln product is cleaned through an attritioning stage. Though this circuit has been successful at producing of primarily ceramic grade zircon ($\text{Fe}_2\text{O}_3 < 600\text{ppm}$) in general, day-to-day variation in the residual Fe_2O_3 grade in zircon and rutile production is not fully understood. Microscope images of final product zircon particles reveal that surface staining varies from day to day, which can be traced back to the efficiency of the HAL reactors.

Plant surveys revealed that leaching inefficiency could vary as much as 30% on a given day, which revealed that the conversion of iron oxides across the reactor is inconsistent. The reaction mechanisms occurring in the HAL reactor are poorly understood and have not been studied systematically, which is subject of the present study.

Thermodynamic analysis of the reactor system revealed that the dissolution of Fe_2O_3 is strongly dependent on the amount of water evaporating. It was postulated that during the contact of the acid solution and the hot mineral, rapid evaporation of water within the adiabatic kiln results in an increase in concentration of ferric in solution. As the dehydration and leaching process continue, the ferric concentration approaches super-saturation, which

results in ferric precipitation as a jarosite/ferric hydroxide complex. It was further postulated that the final conversion is governed by how fast the reaction reaches the super-saturation point.

Laboratory work was conducted to characterise the acid-dry-bake environment. This work showed that iron conversion is strongly promoted by high temperatures, however above 110°C the conversion of iron to ferric did not increase. The activation energy of the dissolution reaction was determined to be 38 kJ/mol (Fe_2O_3). It was found that the equation that best described the rate was one for a diffusion-hindered reaction. It was concluded that the rate is initially reaction controlled, but after a very short period (due to the evaporation of water) the concentration of ferric becomes saturated and eventually super-saturated. It was confirmed that the precipitation of a ferric complex does slow down the reaction due to the formation of a solid product layer.

A MATLAB model of the reactor was developed and was validated using plant samples. The results indicate that the conversion profile along the length of the reactor is highly dependent on the S/L ratio and temperature of the feed. The phenomena experienced by various plant personnel were explained by the model, which suggested that running lower temperatures and higher S/L ratios were preferred over the current plant operating conditions.

It is recommend that, to stabilize conversions across the reactors, the kiln should be housed in an environment that is not susceptible to diurnal and seasonal environmental changes in addition to the external environment it is further recommended that the reactor air-blower is switched off and scrolls installed to drive the solids down the reactor or alternatively pre-heated air is blown into the reactor.

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NOMENCLATURE

N_i	Number of ionic species
F	Faraday's constant
R	Ideal gas constant
T	Absolute temperature
z_i	Ionic charge
C_i	Molar concentration
$D_{ef,i}$	Effective diffusivity
I	Ionic specie
X_i	Fraction converted of specie i
A	Unit
k_1	Rate of reaction
k_2	Rate of active site formation
N	Number of active sites
V	Average number of particles
Φ	Coefficient which is proportional to nucleus volume
t/a	Tons per annum

KEY WORDS

Progradation	Lateral out-building (the formation of strandlines)
HAL	Hot acid leach
Conversion	$x_{Fe_2O_3_final} / x_{Fe_2O_3_initial}$
XRF	X-ray refraction
XRD	X-ray diffraction
S/L	Solid/liquid ratio
Conversion	Conversion of iron oxide based minerals (measured as Fe_2O_3) or ferric
Ferric	Fe^{3+} /also relates to $Fe(III)$
PCP W/E	Primary Concentration Plant at West mine or East mine
SCP	Secondary Concentration Plant
MS	Minerals Separation Plant

“To strive, to seek, to find, and not to yield”

– Alfred Lord Tennyson

CHAPTER 1

INTRODUCTION

1 Introduction

The Namakwa Sands mineral processing plant is based on the West Coast of South Africa 350 km north of Cape Town. The mining operation and mineral processing plants produce altogether four products, two non-magnetic products (total 140 kt/a): zircon (ZrO_2SiO_2), rutile (TiO_2) and 400 kt/a of ilmenite ($\text{FeO}\cdot\text{TiO}_2$) which is smelted to form pig iron (FeO) and slag (TiO_2). These products are exported via Saldanha to international markets in the Middle East, Europe and Asia. Rutile and zircon are used as additives (raw material) in ceramics, tile industries and as heat resistant refractories. The current market price for pure zircon and pure rutile is \$2200/t and \$1500/t respectively (Table 1) and is thought to increase in the near future (TZMI, 2010).

Namakwa Sands prides itself in being able to produce zircon ($\text{ZrSO}_2\text{SiO}_2$) at the very high purity requirements, which sets the price as displayed in Table 1, at less than 600 ppm Fe_2O_3 and 0.10% TiO_2 . This gives Namakwa Sands a competitive market advantage over other mineral sands producers. Namakwa Sands sells two zircon products: the first is an Opacifier grade, while the second is a Prime zircon grade. Processes to clean and separate the zircon particles are at the core of the Namakwa Sands flow-sheet, but these strict quality requirements limit the productivity of the operation.

Table 1: Zircon product specifications (de Villiers, 2011) and (TZMI, 2010)

Product (maximum)	Fe_2O_3 %	TiO_2 %	ZrO_2 %	U. & Th. (ppm)	Market price (\$/t)
Zircon Opacifier Grade	0.06	0.10	65	500	2500
Zircon Prime Grade	0.10	0.15	65	500	2200
Zircon Uncalcinated Grade	0.10	0.15	65	500	2200
Zircon Standard Grade	0.25	0.30	65	500	2000

The separation of heavy minerals is a tedious and complex process utilizing the various magnetic and conductivity differences between minerals. The illustration in Figure 1 provides a brief summary of the process.

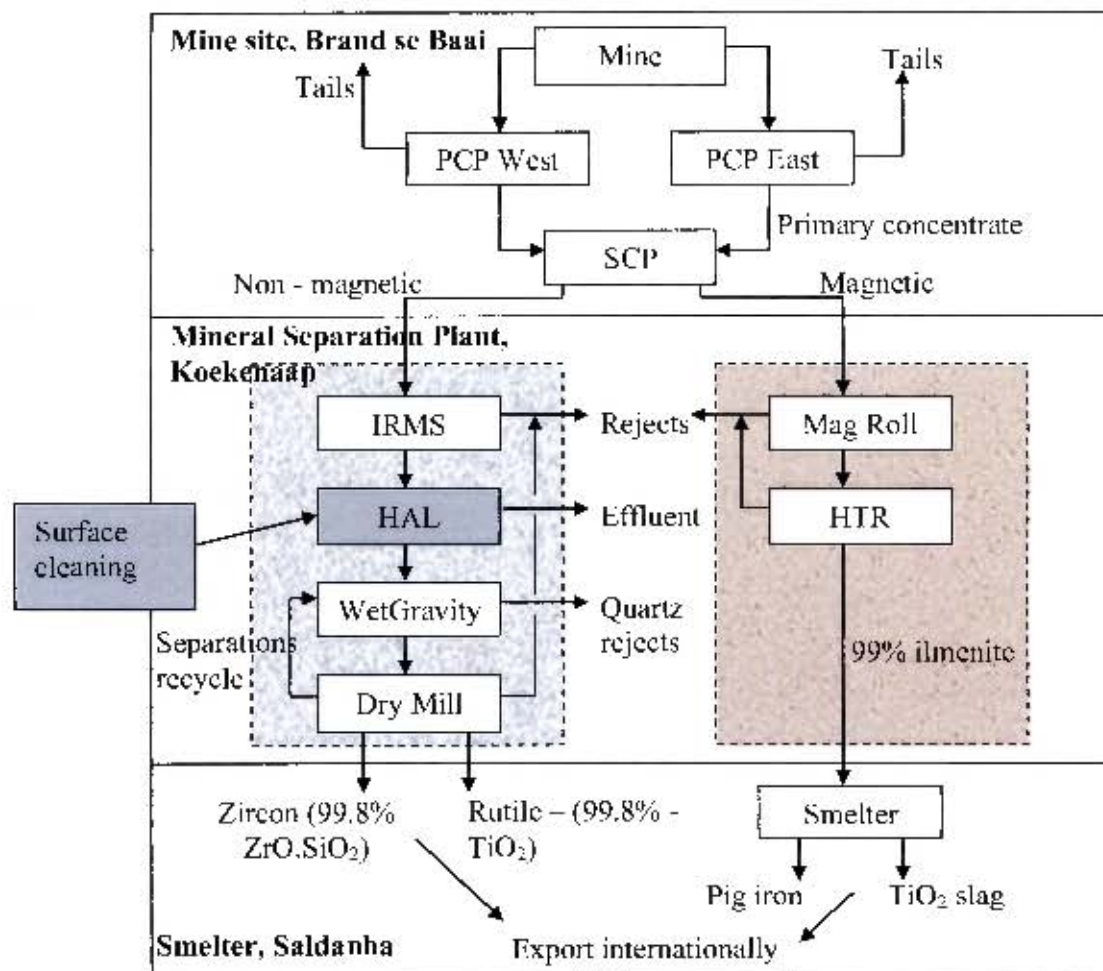


Figure 1: Namakwa Sands process overview from the mining operation to the smelting of Ilmenite

Heavy minerals are mined, concentrated and then magnetically separated into non-magnetic and magnetic material at the mine site (BSB). The non-magnetic material is then trucked to the Mineral Separations Plant (MSP), where it is separated further. The separability of minerals within the MSP is dependent on the differences in conductivity, magnetic susceptibility and specific gravity of the various minerals.

Studies completed by Philander & Rozendaal (2009) show that the Namakwa Sands ore-body contains heavily weathered mineral grains. The coatings are predominantly iron oxide and calcium oxide minerals. The metal-oxide coatings covering the minerals are chemically removed via the hot acid leach system (HAL), whereby strong acid is contacted at 160 °C with non-magnetic mineral in a rotary semi-adiabatic kiln (not a fired kiln). The acid leaching

process converts the metal oxides to metal sulphates, which are subsequently removed by attritioning.

The cleaned minerals are then sent to wet gravity plant for further concentration before reporting to the Dry Mill. The Dry Mill separates particles based on their conductivity, electrostatic properties and, to an extent, particle size. Electrostatic separation is primarily driven by surface properties, which if not true to the mineral (i.e. obscured by coatings) can cause high recirculation loads and also reduce mineral recovery. The desired final products from the Dry Mill report as zircon, rutile and ilmenite.

Dirty zircon particles are rejected by the Dry Mill if they don't meet the quality specification as displayed in Table 1. The performance of the Hot Acid Leach circuit is paramount to the recovery of high quality zircon. The Hot Acid Leach reactors, however, produce varying results, indicating that the conversion across the reactor is highly erratic. It is also very difficult to measure the HAL reactors performance. This is primarily due to the large number of reactions occurring in the high temperature environment evaporative conditions. The focus of this study is on the HAL reactors at Namakwa Sands.

Hot Acid Leach process (HAL)

The Hot Acid Leach takes place in a rotary kiln/drum reactor. Leaching of mineral sands is a solid – liquid multiphase reaction. The need for this reactor configuration followed by surface scrubbing was highlighted very early during the feasibility study of the Namakwa Sands project (Bentley, 1989).

This led to the introduction of the (HAL) circuit for contacting minerals with sulphuric acid at 160 °C to remove this interfering coating. The reactor is not a traditional fired kiln but rather a semi-adiabatic reactor. Namakwa Sands operates two kilns; the two have the same residence times of 20 minutes and Length/Height (L/H) ratios of 9. The second reactor was placed into production as part of phase 2 of the Namakwa Sands project. The total volumetric filling inside the kiln is 11 – 20 % and is dependent on the moisture content of the leach residue. The feed is pre-heated to 160 °C using a fluidized bed heater. This material is then fed to the reactor via a chute as illustrated in Figure 2. Air is introduced onto the chute to drive the mineral further down the reactor. The air is ambient air.

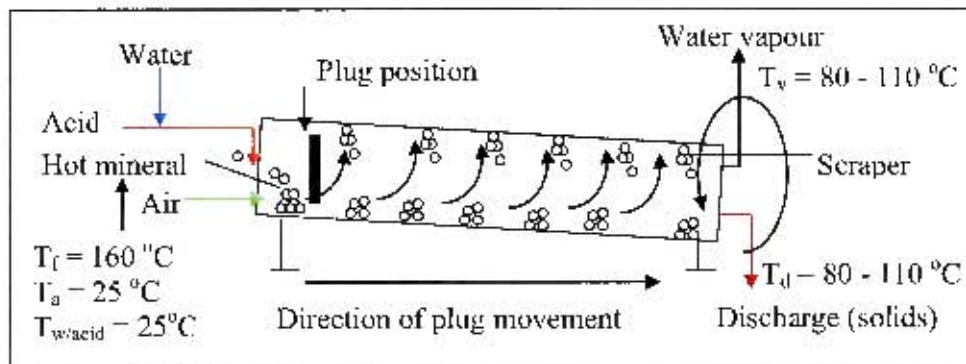
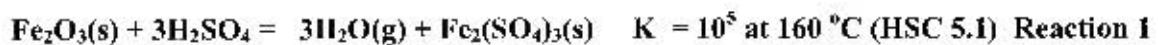


Figure 2: Namakwa Sands Hot Acid Leach reactor, the flow patterns within the reactor can be noticed (T_f – feed, T_a – air, T_{w/a} – acid, T_d – discharge, T_v– vapour)

The discharge from the reactor is quenched in a low pH (<1) solution and then pumped to a number of attritioner banks before being sent to the wet gravity section.

The prominent reaction occurring within the reactor is that of surface hematite, at 0.3% Fe₂O₃ in the feed, with sulphuric acid. This reaction produces water vapour and an iron sulphate precipitate. Due to the evaporation of water and the endothermic nature of the reaction, the material temperature drops from the feed to the discharge end. This creates a temperature profile across the reactor.



Other reactions occurring are those of ilmenite and leucoxene with sulphuric acid (both are iron titanium minerals at concentrations of between 1 – 2 % in the feed) and the dissolution of other iron-based minerals (Table 4). The latter also pose a significant problem in leaching, as these iron-based minerals tend to dissolve at higher rates than hematite and consume acid. This in turn may leave too little acid for the target surface reaction. Alumina based iron minerals are also present. Calcium oxide is also present on the mineral surface, albeit at much lower concentrations than that of hematite. Characterisation of the feed to the reactor is imperative for proper understanding of the reaction dynamics. The conversion of hematite to iron sulphate is very difficult to measure due to a large number of different iron contaminants present in the feed.

Table 2: Iron-containing contaminants in the HAL feed (Philander & Rozendaal, 2009) and (Ledgerwood, 2011)

Fe- Bearing contaminant		
Mineral	Formula	%
Hematite	Fe_2O_3	0.33
Ilmenite/leucosene	$\text{FeO} \cdot \text{TiO}_2$	1.10
Magnetite	Fe_3O_4	0.30
Iron hydroxide	$\text{FeO} \cdot (\text{OH})$	0.32
Almandine	$\text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12}$	0.30
Andradite	$\text{Ca}_3\text{Fe}_2\text{Si}_3\text{O}_{12}$	0.40

Throughout the production life of the HAL reactors, a number of phenomena have been regularly observed in the HAL circuit:

- The formation of hardened reactor discharge material (moon-rock)
- Day-to-day (season-to-season) fluctuations in effective iron oxide conversions
- Zircon particles still coated with iron oxide coatings reaching final product
- Temperature and moisture changes at the discharge of the reactor
- Free acid concentration fluctuations of the HAL effluent water

The above observations have never been properly explained. An anecdotal report by Huisamen (2000) suggests that running at higher S/L ratios, higher acid concentrations (65 %) and lower temperatures (140 °C) allows for better quality zircon and overall higher product yields. However the reason why these measures would work is not understood.

It is firmly believed that the variance in production of ceramic grade zircon is driven by performance of the HAL circuit. The key reaction 1 is a multi-phase reaction with the 'solid', as the mineral coating, reacting with liquid sulphuric acid at high temperatures (>100 °C) and high acidic environment (40 wt.% H_2SO_4). It is postulated that an iron-sulphate based solid product layer forms with the formation of water vapour, as the iron that is initially released into solution is subsequently re-precipitated, inhibiting further dissolution.

The progress of the leaching reaction is thought to be governed by a number of factors:

- The driving force for evaporation of water from the mineral surface (the temperature difference between the mineral surface and the acid/water mixture partial pressures)
- The nature of the iron phases present on the mineral surface

- Initial feed temperature and discharge temperature
- The formation of a solid-product layer
- The residence time in the reactor

The thermodynamic limitation to the reactor system is not clear, however it is accepted that the reaction of metal-oxide and the hot acid is endothermic (based on studies by Huisamen (2000)). The exact reaction mechanism has, however, not been studied previously.

1.2. *Problem statement and objectives of the study*

For years, leaching conditions in the HAL reactors were thought to be optimum and conversions were thought to be at a maximum. This notion has come under question recently, since it was discovered that the leaching of iron was insufficient, causing a loss in prime Zircon production and an overall drop in product yields. The Namakwa Sands HAL reactors are not well understood; the leaching dynamics, mixing dynamics and the reported fluctuations in day-to-day conversions all have detrimental effects on dry mill recovery of zircon. Plant personnel and metallurgists have run a number of ad-hoc interventions with little success.

1.2.1. Problem statement

Incomplete removal of surface impurities from the surface of zircon particles results in poor electrostatic separation of zircon mineral in the Dry Mill and off-specification product. This is attributed to the erratic performance of the HAL reactor, which is related to the lack of leach control.

1.2.2. Objectives of the study

In order to address the problem statement it is necessary to develop the right understanding of the various interactions in the HAL reactor. The objectives of the project are to:

- Study the fundamental reaction mechanisms for leaching reactions, water evaporation and the formation/precipitation of product layer(s)
- Investigate the influence external environmental conditions have on the reaction rate.
- Construct a dynamic model for determining change of certain process parameters along the length of the reactor, such as temperature profiles of gas, solid and liquid and the conversion of hematite.

- **Calibrate the model against process data and then conduct a rigorous optimisation study around key operating parameters, inlet conditions and outlet conditions.**

CHAPTER 2

PROCESS DESCRIPTION

Primary objectives of this chapter are:

- Detail the HAL circuit
- Discuss previous work completed on the HAL circuit
- Provide details on iron excursions seen at Namakwa Sands

2 Process description

This chapter will detail the environment where leaching is conducted: the HAL process will be discussed in more detail, then a brief overview of previous work completed by Namakwa Sands personnel, followed by published literature on leaching. A discussion on the theoretical aspects to iron/calcium and stability in sulphuric acid solutions will follow. The work then progresses to detail the stability of calcium sulphate as solid gypsum.

The external literature review sourced the majority of its information from the quartz industry, which is similar to the mineral sands industry, where high purity quartz used in the electronic industry is highly sought after. Other sources include patents on zircon leaching, these are used to draw similarities with the Namakwa Sands process, while other processes, such as the leaching of laterites, is also considered. The internal literature review focused on the three main issues with iron excursions: inadequate leaching, insufficient attritioning and reattachment.

2.1. *Brief process overview*

The Namakwa Sands operation is a subsidiary of Tronox Limited and forms part of their base metals division. Namakwa Sands is one of the largest mineral sands operations in South Africa, supplying customers in China, Asia and Europe with Zircon and Rutile. These are exported via ship from Saldanha. The operation consist of three sites, the mine site at Brand se Baai located 390 km from Cape Town, the mineral separation plant (MSP) located at Keokenaap, 320 km from Cape Town, and the smelter located in Saldanha 100 km from Cape Town.

2.1.1. Geological and geographical details

Namakwa Sands geological ore body is found along the West Coast of South Africa. Located near to Brand se Baai this ore body contains roughly 10 % total heavy minerals (Table 2). The economic minerals of interest are ilmenite ($\text{TiO}_2 \cdot \text{FeO}$), zircon ($\text{ZrO}_2 \cdot \text{SiO}_2$), rutile (TiO_2) and leucoxene ($\text{FeO} \cdot \text{TiO}_2$ FeO > 55%) Other, less economical minerals (gangue) consist of Feldspar ($\text{CaAl}_2\text{Si}_2\text{O}_8$), Monazite (CePO_4), Garnets ($\text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12}$) and Magnetite (Fe_3O_4). The ore body originates from pre-Cambrian age metamorphic rocks from the Namaqualand Metamorphic Complex and Van Rhynsdorp Group. Continental uplift during the late Cretaceous period and the erosive events that followed caused heavy mineral assemblage liberation. Then 6 million years ago east – west draining fluvial systems eroded the hinterland and transported these sediments into a J-shaped, paleo-bay coastal environment (Figure 3) (Prinsloo, 2006).

Then sea level still-stands, trans- and regression events during the Tertiary and Quaternary periods from 6 to 2 million years ago produced enriched mineral deposits called strandlines at 20, 35 and 50 m above sea level (Philander & Rozendaal, 2009). This landscape now exposed to the Benguela current and also incoming south-westerly waves produced a concentrated wave action within the paleo-bay. This allowed the selective deposition of heavy minerals and the removal of lighter minerals.

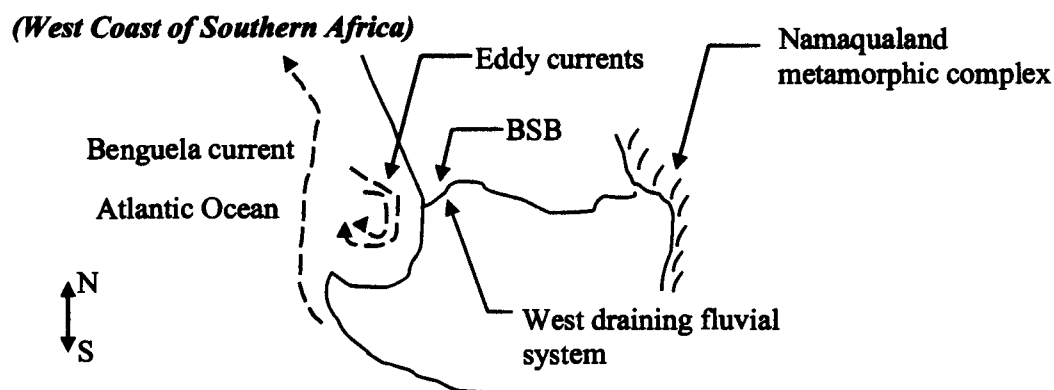


Figure 3: J-bay system - natural heavy minerals concentration system - Brand se Baai mining operation located on the coast

Westward progradation of the dune field was followed by large redistribution of sediments by the south-southwest winds (Gous, 2006). The Namakwa Sands ore body is well researched by

Philander & Rozendaal (2009) and Table 3 provides a concise breakdown of the mineral ore bodies and the assemblage.

Table 3: Mineral distribution for different ore bodies found at Namakwa Sands mine site (Philander & Rozendaal, 2009)

% wt.	Zircon	Ilmenite	Rutile	Leucoxene	Garnets	Pyroxene	Others
Red Aolean Sand (RAS)	17.3	63.1	5.7	3.6	6.7	0.3	3.3
Orange Feldspathic Sand (OFS)	9.7	34.6	4.2	4.7	21.7	16.6	8.5
Strandline	3.8	24.9	1.4	1.9	25.2	40.2	2.6

From Table 3, it is clear that ore-bodies found at the Namakwa Sands deposit contain a wide range of heavy minerals. RAS ore is mined at the Easterly mine site and is found as a sand dunes formation, while strandlines are the more commonly found assemblage in the Westerly mine site. The exploitation of OFS is under economical investigation.

2.1.2. Mining

The two mining areas are located east and west of the secondary concentration plant. Both mines use excavators and front-loaders for ore removal from the open-pit type operation. The mining process involves trucking ore sands to the primary concentration plant. The ore sand is dumped onto a conveyor that transports the sand via screens to the Primary Concentration Plants (PCP).

2.1.3. Primary concentration plant (PCP)

The primary concentration plant receives run-of-mine (ROM) ore and passes these through trommels. Wet screening is employed; water is also introduced as a transport medium. The mineral is sized and oversize materials (+1 mm) is sent for scrubbing while undersize material (-1 mm) is sent to a large spiral bank where gravity and specific density are used to separate heavy minerals from the gangue material. Scrubbed material is further passed through screens and undersize is sent to the spiral banks while oversize is recycled and a fraction of this stream is purged. The gangue material is dewatered via liner screens and then reports to tails (Aelion sand with Feldspathic). Tails are then transported back to the mine and used as rehabilitation material. The concentrate (6-8 % in Zircon) is pumped to the secondary

concentration plant. The tails material is used as backfill and the sand dunes are then ultimately restored to their original state.

2.1.4. Secondary concentration plant (SCP)

The SCP produces two products, a non-magnetic stream (zircon, rutile and leucoxene) and a magnetic stream (ilmenite). Wet High Intensity Magnetic Separation (WHIMS) units are used to separate the magnetic from the non-magnetics, spirals upgrade the non-magnetics further, and surface coatings are scrubbed using mechanical attritioning. The energy consumed in attritioning is quite high 2.5 kWh/ton (throughput). The feed is upgraded from a 6-8 % zircon concentrate to a magnetic stream of 90 % ilmenite and 10 % garnets and a non-magnetic stream with 55 % zircon, 15 % rutile, and 12 % leucoxene and another 18 % of other gangue (Fe/Ca-oxide based).

2.1.5. Mineral separation plant (MSP)

When proceeding through this section please refer to Figure 1, the mineral separations plant at Koekenaap. The mineralogy of the feed to the MSP will be discussed first followed by a brief process overview of the MSP. The MSP uses differences in specific gravity, magnetic properties and surface susceptibility to electrostatic charge to separate minerals from each other; it is important to understand the difference in these properties, which allows for separation to occur. Table 4 gives a concise account on the mineral properties. The desired minerals are zircon, rutile and ilmenite.

Table 4: Mineral summary details the MSP feed type (M – Magnetic, N/M – non-magnetic, C- Conductive, N/C – non-conductive)

Mineral	Molecular formula	Specific gravity	M	N/M	C	N/C
Zircon	$\text{ZrO}_2 \cdot \text{SiO}_2$	4.7		x		x
Rutile	TiO_2	3.6 - 4.3		x	x	
Leucoxene	$\text{FeTiO}_3 (\text{TiO}_2)$	3.6 - 4.3	x		x	
Ilmenite	FeTiO_3	4.7	x		x	
Kyanite	Al_2SiO_5	3.6 - 3.7		x		x
Monazite	$(\text{Ce, La, Y, Th}) - \text{PO}_4$	4.9 - 5.3	x			x

Process overview and description

Figure 1 - the mineral separations plant will be discussed in more detail below.

Induced Roll Magnetic Separation (IRMS)

Non-magnetic feed at 55 % zircon, 15 % rutile and 12 % leucoxene is transported to the MSP via trucks and fed as a semi-batch type operation to feeder tanks. This section is termed the receiving section of the plant. The main purpose of the Induced Roll Magnetic Separator (IRMS) section is to remove the feebly magnetic material found in the feed: magnetic quartz, magnetic garnets and more importantly to remove iron based scavenging minerals. Monazite is also removed using the IRMS. A screen, with an aperture of 250 μm , is used to separate oversize gangue material. Product from the IRMS section leaves to provide feed to the HAL process.

Hot Acid Leach (HAL) circuit

The HAL circuit is responsible for removing surface coatings from the zircon and rutile minerals. The process involves contacting sulphuric acid with the mineral concentrate at 160°C in a kiln type adiabatic reactor. The minerals are then quenched and sent through a counter current decantation (CCD) circuit, where the mineral surfaces are washed and attritioned. Once the minerals have been processed through the CCD circuit they are then sent to the Wet gravity plant.

Hydrosizer and wet gravity

The material from HAL circuit is sent to a cyclone, which feeds a hydrosizer. The discharge from the hydrosizer then gravitates to the Constant Density (CD) tank. The hydrosizer's primary function is to split fine particles from coarse particles. The two output streams (fine and coarse streams) then feed individual spiral circuits where the material is further concentrated to 75 % zircon and a 2:1 rutile to leucoxene ratio. The concentrates from both circuits are combined before being sent to a drier and then finally report to a day bin as dry mill feed at < 1% moisture (free flowing sand).

Dry Mill operations (HTR and Magnetic roll circuits)

The Dry Mill separates particles based on their conductivity (electrostatic properties). The method employed to achieve the required separation is based on surface and inherent particle structures. The final products from the dry mill report as previously reported are zircon and rutile (also two lower grades of zircon and rutile products). These are then freighted to Saldanha before being shipped to the international market.

2.2. Detailed description of the Hot Acid Leach (HAL) circuit

To remove the coatings from the surface the minerals are first contacted using sulphuric acid, (to first soften the coatings) then scrubbed (removal of softened coatings) from the mineral using mechanical attritioning. Finally, a counter-current circuit prevents the reattachment of the precipitates back onto the mineral surface formed in the process by washing of the minerals. This section will detail all three processes and the various challenges facing each. However, the nature of the HAL feed will be discussed before the study moves onto the complex HAL circuit dynamics.

2.2.1. Nature of HAL feed

The feed to the mineral separation plant has been discussed in the previous chapter, however further in-depth analysis of the minerals is imperative for understanding of the HAL system.

Zircon ($ZrO_2 \cdot SO_2$):

Zircon mineral is the most valuable mineral produced at Namakwa Sands. In the ore-body the mineral is found in three different forms: Clear (translucent) type zircon (A), a stained (coloured) type zircon (B) and a Metamict (red-brown stained) type zircon (C) – this is detailed in Figure 4. The HAL reactors primary function is converting B type zircon into A type zircon i.e. cleaning up the zircon. Type C is rejected.

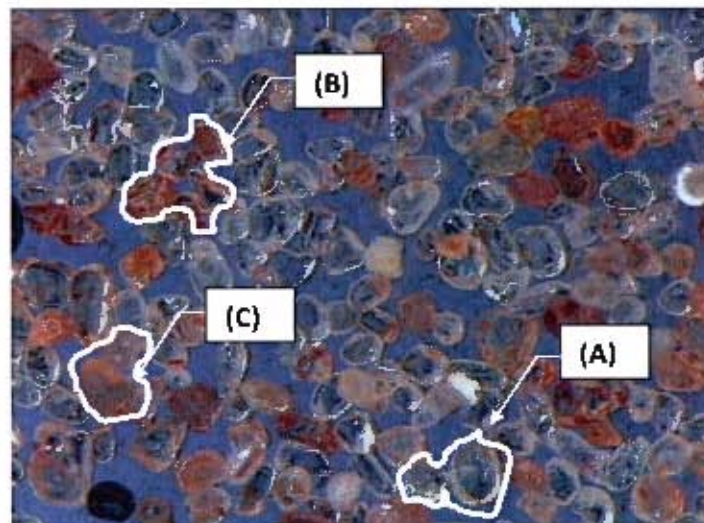


Figure 4: Zircon mineral (micro-image) shows the three types of zircon minerals found

It is evident from the Philander and Rozendaal (2009) study that on average all zircon types contain 65 % ZrO_2 . A whole host of impurities such as rare earths elements, iron oxides and

other impurities can be found in the matrix. The crystal chemistry is very consistent in all types of zircon, with Metamict zircon containing a large portion of heavier elements (REE is 0.04 %). The Metamict zircon is caused by coupled substitution with REE and is primarily due to radiation damage. Ca and Al elements form the smallest part of the crystal structure, while Fe_2O_3 is the largest contribute of impurities (Philander & Rozendaal, 2009). The details are displayed in Table 5 below.

Table 5: Zircon mineralogy and mineral constituents as oxides (Philander & Rozendaal, 2009)

% wt	Clear	Coloured	Metamict
ZrO_2	64.74	64.27	63.84
SiO_2	33.12	33.86	32.25
HfO_2	1.19	1.34	1.5
CaO	0.01	0.06	0.08
Al_2O_3	0.01	0.07	0.09
P_2O_5	0.10	0.14	0.24
Fe_2O_3	0.01	0.07	0.28
REE	0.01	0.01	0.04

TiO₂ based minerals:

According to Rozendaal et al. (2010), there are a number of different TiO_2 based minerals present in the Namakwa Sands ore-body, which find their way to the HAL feed. A full list of the iron containing impurities (gangue) will be presented towards the end of this section.

(a) Rutile:

The rutile contained in the Namakwa sands ore body is close to 98 % pure TiO_2 , indicating little crystal space for impurities (<2 %) present in the mineral crystal.

(b) Magnetite and Hematite:

Magnetite contains < 2 % TiO_2 , undifferentiated titanium based hematite and magnetite contains 6 – 25 % TiO_2 .

(c) Ilmenite and leucoxene:

Pure ilmenite is on average 51 % TiO_2 . Leucoxene can be subdivided into two groups: namely low Ti levels 70 – 82 % TiO_2 and high Ti levels 83 – 94 % TiO_2 .

TiO₂ and ZrSiO₄ mineral surface contaminants:

Zircon surface contaminants are normally iron oxide (as hematite 0.1 %) and calcium oxide (0.08 %) coatings; however other iron bearing minerals have also been noted such as goethite

(FeOOH) (Philander & Rozendaal (2009)). Rutile surface coatings can also be iron and calcium oxide based; iron may also be in the form of the goethite (FeOOH) (Philander & Rozendaal (2009)). Rutile is also said to show conductive properties when heated; this is exploited at the MSP when separation of minerals from a non-magnetic stream is required. Characterisation of the feed to the reactor is imperative for proper understanding of the reaction dynamics. The true conversion of hematite to iron sulphate is very difficult to measure due to the large number of different iron contaminants present in the feed, as depicted by Table 6 (Chapter 2), and the possibility of a large number of simultaneous reactions and iron-complex based products. The presence of this large number of iron containing minerals is hard to measure accurately, and is further complicated by the fact that impurities can be in the form as separate grains, coatings on the grains or inside the grains, which vary considerably.

Gangue Minerals (non-valuable minerals):

The following minerals are classified as gangue and are an ever present problem in separation process; whether it is magnetic induction or magnetic roll, electrostatic plate or screen sorting, these valueless particles pose a significant problem: garnets, pyroxene, kyanite, titanite and collophane, elemental speciation is presented in Table 6.

- (a) Garnets and pyroxene contribute the most to gangue minerals. Garnets are found in shades from red to colourless.
- (b) Kyanite and pyroxene are removed together with the garnets in the wet gravity section of the MSP.
- (c) Titanite and collophane are partially leached in the HAL circuit.

Common garnet types: Almandine ($\text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12}$) and Andradite ($\text{Ca}_3\text{Fe}_2\text{Si}_3\text{O}_{12}$) both contain iron, calcium and aluminum and therefore also represent a concern when tracing the true conversion of hematite across the reactor.

Table 6: Elemental composition of gangue material (Philander & Rozendaal, 2009)

Elemental oxide (%)	Garnet	Pyroxene	Kyanite	Monazite	Collophane	Titanite
SiO ₂	39.01	52.58	37.42	8.72	6.31	27.68
TiO ₂	0.04	0.39	0.04	-	-	39.63
Al ₂ O ₃	22.47	2.14	62.48	-	-	2.69
Cr ₂ O ₃	0.03	0.38	0.02	-	-	0.02
Fe ₂ O ₃	1.36	0.01	0.09	-	5.14	-
FeO	28.28	11.37	-	-	-	2.97
MnO	1.08	0.27	-	-	-	0.05
MgO	6.92	18.19	-	-	-	0.16
CaO	3.21	14.65	-	2.66	56.91	25.16
P ₂ O ₅	-	-	-	32.03	32.42	-
REO				58.53		

2.2.2. HAL circuit

The Hot Acid Leach circuit at Namakwa Sands makes use of an adiabatic kiln reactor to contact the hot mineral with sulphuric acid. This environment is quite hostile to any form of metal-oxide that readily dissolves in sulphuric acid. Figure 5 – illustrates the HAL circuit in more detail.

Heating:

The feed to the HAL reactors is stored in a large 340 t bin and is gravity fed to the two fluidized bed driers, each via a variable speed conveyor: Stream 1. Before entering the kiln-reactor the feed is preheated to 160 °C and gravity fed to the feed chute.

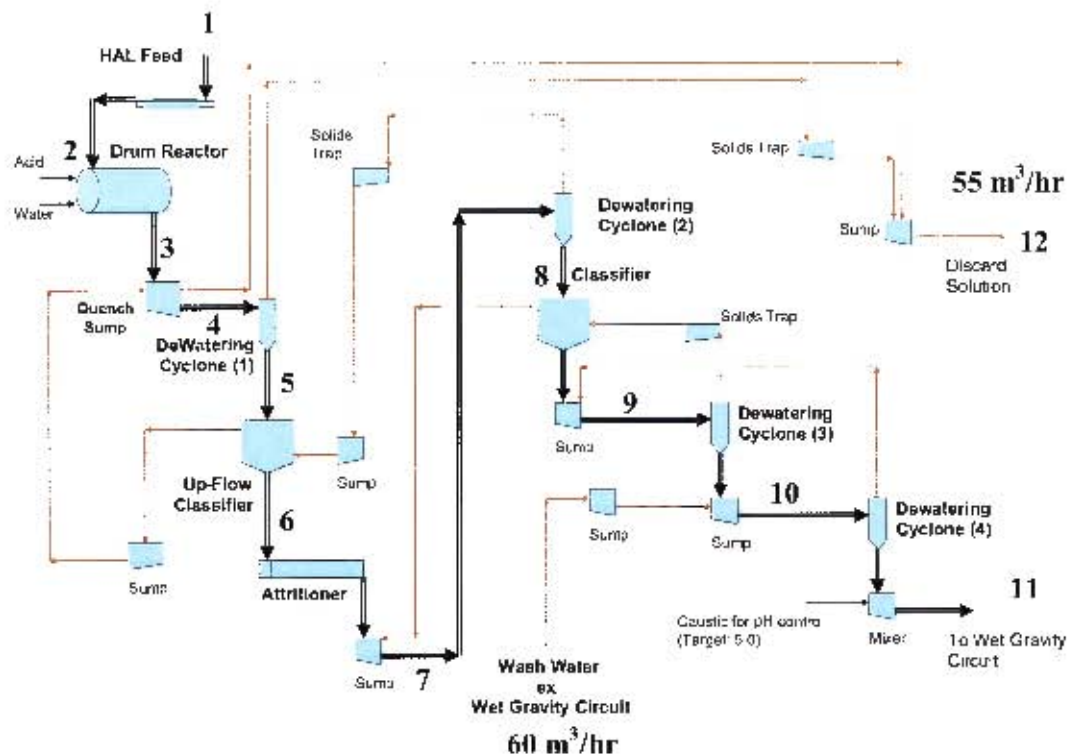


Figure 5: HAL process flow diagram

Leaching:

The mineral is fed at a constant rate of 12 t/hr (for HAL A) and 27 t/hr (for HAL B): Stream 2; both reactors have residence times of 20 minutes. Once the mineral is in the reactor, it is contacted with sulphuric acid at 40 wt% (and at 35 kg-acid/tonne-mineral). The solids are discharged with a moisture content of 2 – 4 %: Stream 3, at temperatures of 80 – 90 °C these temperatures are also affected by the external atmospheric temperature. The surface of the mineral becomes heavily populated with ‘nodules’ of ferric-precipitate in the course of leaching.

Three-stage counter current decantation:

The solids are then quenched at a $\text{pH} < 1$; a low pH environment provides an ideal condition for iron to remain in solution. The temperature of the discharge from the quench sump ranges from 40 – 50 °C: Stream 4. The process post-leaching involves first washing the leached coatings from the mineral via a counter-current decantation circuit, as illustrated with Streams 5 and Stream 6. Counter-current decantation circuits are quite common in leaching circuits, the HAL circuit however uses the counter current circuit to rather wash the minerals

from precipitates (nodules) in solution and prevent reattachment, rather than leaching of the solids as in most mining applications.

Attritioning (mechanical scrubbing):

Mechanical attritioning is applied to remove residual surface 'nodules' from the mineral surface. The attritioning process (which is similar in energy requirements to a ball mill) scrubs the mineral surface clean of the precipitate and removes soft coatings. The process applies significant amount of energy into scrubbing (2.5 kWh/t) at 70% solids density. The attritioner process involves solids being pumped into the first stage of attritioning and churned; using 75 kW motors driving an impeller. The impeller will rotate as depicted in Figure 6, depending on what stage it is in, the flow of solids in each stage is dictated by the rotational spin of the impeller: a clock-wise rotation drives the solids upwards, while an anti-clock-wise rotation drives the solids downwards. This action together with the added baffles in the attritioner gives it a residence time of 20 minutes.

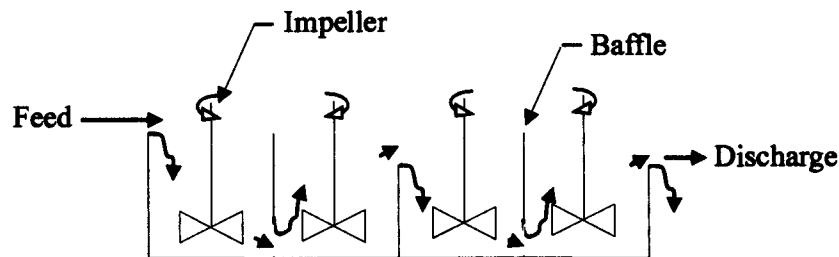


Figure 6: Attritioner layout (shows the pulping action of the blades)

Three-stage counter current decantation:

After scrubbing of the mineral solid/liquid separation in a three stage counter-current circuit is then used for removing the 'nodules' from the solution and prevents reattachment or re-precipitation from occurring.

Acid and iron treatment plant:

The leach circuit produces 250 kg/hr of iron (Fe^{2+} and Fe^{3+}) and rejects 99.9% of this through the counter-current circuit which is sent to the effluent treatment plant at 55 m³/hr (4g/L - Fe^{Total} and free acid is 3.5g/L) in Stream 12, where the acid is neutralized and the iron precipitated as FeOOH and calcium as gypsum. The final product reports to the wet gravity circuit (Stream 11) where the quartz is gravity-separated from the heavy minerals before they are fed to the Dry Mill, which is fed at 28 t/hr and at 75 % zircon.

2.2.3. HAL reactor dynamics

The reactor is not a traditional fired kiln but rather an adiabatic reactor. Namakwa Sands operates two kilns; the two have the same residence times of 20 minutes and Length/Diameter ratios of 9. The second reactor was placed into production as part of phase 2 of the Namakwa Sands expansion project. The total volumetric filling inside the kilns is 11 – 20 % and is dependent on the moisture content of the leach residue. The feed is pre-heated to 160 °C using a fluidized bed heater. This material is then fed to the reactor via a chute as illustrated in Figure 2. Air is introduced onto the chute to drive the mineral further down the reactor (Figure 7). The ‘hot’ heavy mineral is gravity fed to discharge from the feed pipe, while the acid holder pipe contains the hot sulphuric acid which (depending on the dosing and concentration) will have a certain exit temperature. The water/sulphuric acid mixture exits the acid pipe at a high velocity and produces a water vapour, while the mixture is slowly mixed with the solids. Typically, the acid concentration is 30-40 % wt. and the dosing is 30-40 kg (acid)/(ton-feed).



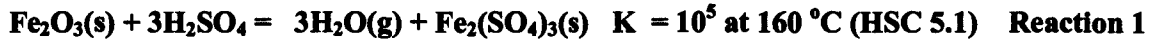
Figure 7: HAL mineral feed pipe and acid feed pipe

As the mineral moves down the reactor it is churned with the acid. This is due to the rotating action of the kiln and the slight declination towards the discharge-end. The discharge from the reactor is quenched and then pumped, as previously discussed, to a number of attritioner banks before being sent for gravity separation.

Kiln reactions:

The prominent reaction occurring within the reactor is that of surface hematite, at 0.3% Fe_2O_3 in the feed, with sulphuric acid (H_2SO_4). Reaction 1 produces water vapour and an iron sulphate precipitate. Due to the evaporation of water and the endothermic nature of the reaction, the material temperature drops from the feed to the discharge end. This creates a

temperature profile across the reactor. Feed temperatures are 160 °C while the discharge temperatures range from 75 to 90 °C, this varying change has a major effect on reaction conversion.



Other reactions occurring involve:



Other reactions, besides the ones listed above, involve gangue minerals and sulphuric acid (the so-called scavenger minerals - kyanite, pyroxene, ilmenite/leucosene and different forms of iron-oxide-hydroxides). The number of simultaneous reactions is quite large; however the key reactions are presented above (reaction 1-4). Based on the values for Gibbs-free energy it appears that some reactions are favoured above that of the hematite conversion (Table 7).

Table 7: Heats of reaction and Gibbs free energy of reaction (at 160 °C) (HSC 5.1, standard state at 25 °C)

Reaction No.	ΔG_{rxn} (kJ/mol)	ΔH_{rxn} (kJ/mol)
1	-48.21	+281.3
2	-111.6	+418.2
3	-71.5	+97.4
4	-102	+47.2

Due to the hot mineral (above the boiling point of water), water vapour is produced (dictated by the Vapour-Liquid equilibrium curves (Appendix A – V/L equilibrium curves) for the sulphuric acid/water mixture) which causes the moisture of the solids to decrease along the reactor.

The conversion of hematite from the zircon minerals to a nodule-type precipitate in the reactor varies from day to day. The exact reason for this is not known, however it is thought to be a function of a number of factors: discharge temperature, discharge moisture, weather conditions and the iron phase present.

2.3. Previous work

Ever since the start of Namakwa Sands, recovery issues pertaining to zircon quality have persisted. Iron excursions are common at Namakwa Sands and because of this a substantial amount of work has been compiled over the past decade.

2.3.1. Iron excursions at Namakwa Sands

A number of plant metallurgists have dedicated their time to studying the root-cause of the iron excursions. Figure 8, below presents the three main forms of iron excursion problems encountered at Namakwa Sands. An iron excursion may be due to either one of these or a combination of them.

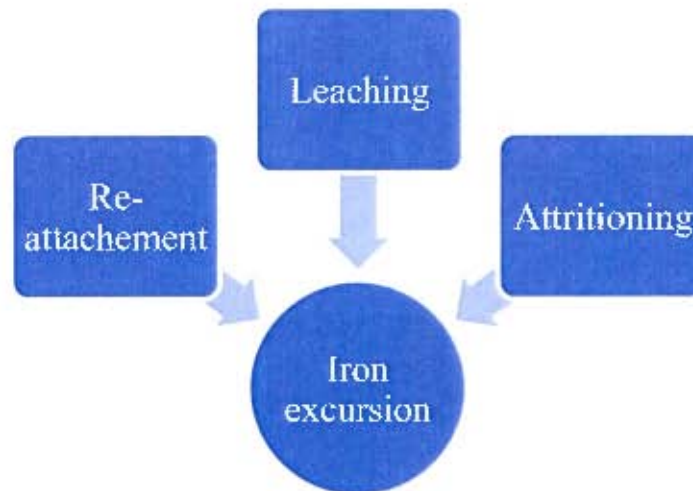


Figure 8: Iron-excursions at the Namakwa Sands mineral separations plant

Optimisation studies on the above three aspects were covered by Prinsloo (2006), Huisamen (2000), Engelbrecht (2011) and others. Their research both focused on specific iron excursions problems relating to attritioning or reattachment, however very little work focused on leaching optimisation. Figure 9 displays 4 periods during which zircon production has been limited due to iron related problems (data excludes plant downtime and other related zircon limiting cases). Each case was investigated for the root cause of decreased zircon production.

The following list represents the study's findings (Table 8) which were extracted from Figure 9:

Table 8: Iron excursion report detailing findings (plant data)

Case	Time period (month(s))	Lost tons (impact)	Details of iron excursion report
A	5	3760	Caused by reattachment issues in IIAL circuit, pH of solution was higher than design (precipitation of $\text{Fe}(\text{OH})_3$).
B	2	1500	Attritioners offline for maintenance and reattachment issues.
C	1	700	Unfavorable leaching (microscope images indicate a tremendous amount of half leached mineral) – re-leaching tests confirmed that HAL reactors were performing poorly.
D	2	1500	Unfavorable leaching (microscope images indicate a tremendous amount of half leached mineral) – re-leaching tests confirmed that HAL reactors were performing poorly, reattachment issues also suspected.

The analysis conducted indicated that throughout the history of Namakwa Sands a systematic approach to studying the problems with the reactors was never applied. The result of this is ‘bucket-engineering-type’ improvement projects that only satisfy the present issue rather than looking at the underlying root causes. Once this analysis was compiled it clearly indicated that the leaching stage of the IIAL circuit is inefficient.

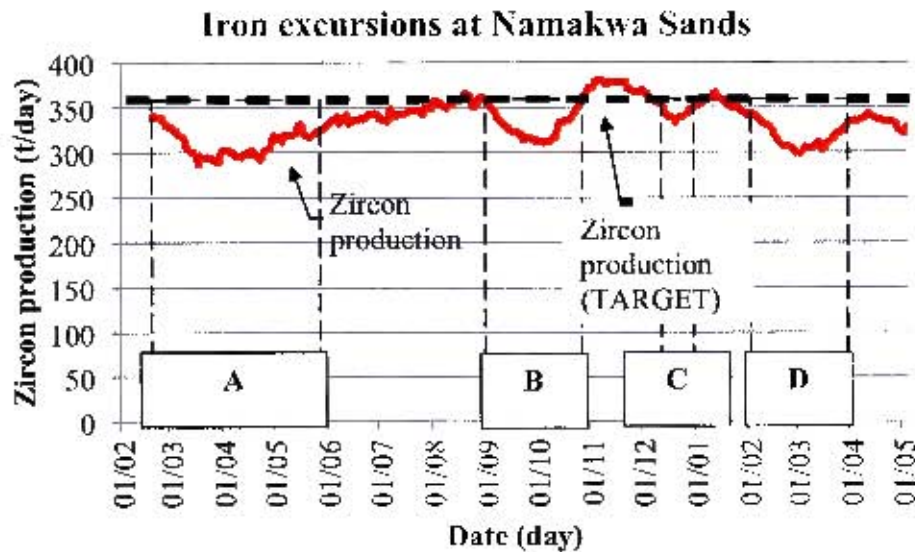


Figure 9: Zircon production trend (plant data)

2.3.2. Internal literature review at Namakwa Sands

Internal work completed by various groups and personnel can be divided into three groups:

- (a) Attritioner work
- (b) Leaching optimization
- (c) Reattachment studies

Attritioner work:

Internal leaching test work conducted on the prefeasibility stage of Namakwa Sands was the largest contribution to understanding of the reaction dynamics. An internal report by Bentley (1990) explains the extent of test work that had been carried out before a technology for the leaching problem was formulated. The report details that a number of companies worked on the leaching process AMMTEC, Reading and Anglo Research. For instance, the AMMTEC test work indicated that leaching achieved a ceramic grade zircon, using HAL technology. Reading indicated that the leaching only chemically modified the iron oxide rather than removing it from the surface; as depicted in Figure 10. The mineral surfaces become spotted with a number of nodules, which is easier to remove using mechanical attritioning than the initial hematite coating. The product was a ceramic grade zircon. Their work only considered iron and not calcium-based phases.

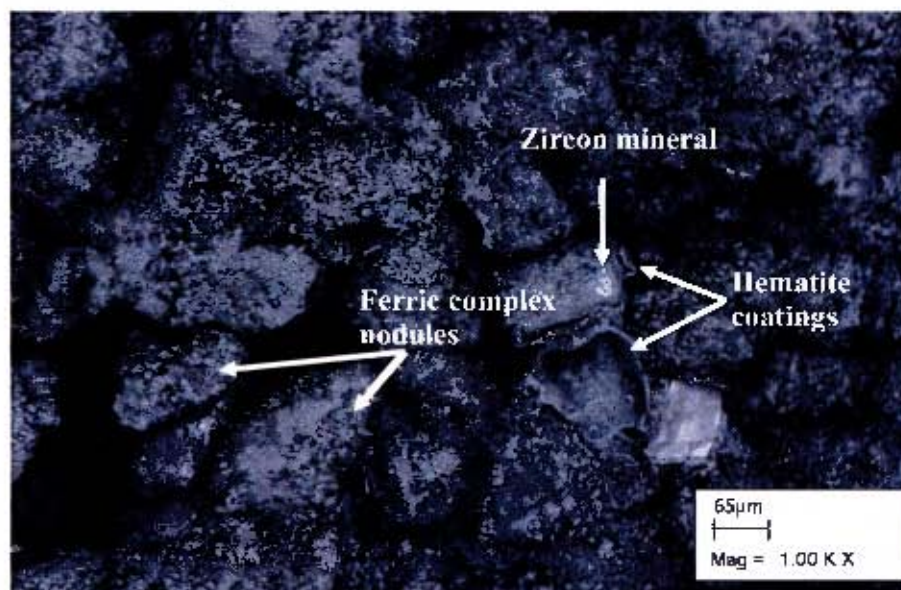


Figure 10: Post leaching image shows nodules formed

Little information exists on what the nodules are, however it is accepted that to produce ceramic grade zircon mechanical attritioning must be employed post leaching.

Reattachment:

Ferric hydroxide reattachment to mineral surfaces was the primary focus of Prinsloo's (2006) study, which revealed that iron excursion problems may be caused by the susceptibility of zircon mineral to re-attachment of iron hydroxide precipitates, and that under the right pH environment the surface adsorption of ferric-hydroxide is highly possible. Prinsloo's (2006) work did not detail HAL reactor test work but rather focused on the downstream processes such as the counter-current decantation.

Leaching:

In a study report by Huisamen (2000) it is mentioned that the conversion of hematite to iron-based sulphate is dependent on a number of factors. This work indicated that higher conversions could be achieved when higher solid/liquid ratios are run. However, when this was implemented it caused frequent blockages by "moon-rock" (hardened agglomerates) and this approach was stopped. The exact reason as to why higher solid/liquid ratios would have promoted the conversion of hematite to iron sulphate was not mentioned.

Work completed by Huisamen (2000) in a separate study showed through work in a pilot scale unit that lower feed temperatures in combination with higher solid/liquid ratios was far preferable (in terms of the quality of zircon produced) to higher temperatures and lower solid/liquid ratios. However, after running the plant reactors for a period of 3 months at lower feed temperatures, the project was aborted due to major plant blockages caused by moon-rock. This is contrary to what was expected from the thermodynamics of the leach reaction, which indicates that higher temperatures are preferred. However Huisamen (2000) didn't mention the reasons for the higher quality zircon produced.

Then, as part of the present project work, a study completed in 2011 (Ledgerwood, 2011) investigated the effect of discharge moisture on iron conversion. This was correlated to dew-points and ambient temperatures, which clearly indicated a strong correlation between discharge conditions and the surrounding temperatures, which was subsequently linked to conversions. Huisamen (2000) also noted this effect. Their work also indicated that the conversion was highly dependent on the type of coating i.e. the type of iron oxide present. The effect of other minerals, such as those containing calcium, was also seen to correlate with leaching efficiency.

Summary of Namakwa Sands HAL circuit optimisation efforts:

In summary, the initial work conducted and methods tested during the course of the prefeasibility years at a number of different laboratories resulted in a lot of inconclusive, contradictory and irreproducible data. In the end, rather swift decisions were made to move from piloting work to full scale production, ignoring the fact that piloting studies were unsuccessful in produce zircon of the required grade. A number of subsequent studies on the operating system looked at achieving higher conversions, however very few interventions were successful in achieving any substantial improvements.

CHAPTER 3

THEORY AND LITERATURE

Primary objectives of this chapter are:

- Provide the theoretical basis for this project
- Give detailed information on iron and calcium thermodynamic stability
- Provided a literature review of current leach trends
- Give direction to experimental work to be completed

The following chapter will detail the theoretical and literature aspects of iron and calcium leaching in sulphuric acid, it will also detail work completed by other researchers.

3 Theory and literature review

The glass and the mineral sand industry are very similar: for both industries the type of iron and calcium phase(s) present on the surface of mineral grains are very similar (both use feed derived from Feldspathic sand). Both industries use leaching as a chemical aid in producing high quality products; metallurgical grade silica is priced based on its purity. However a literature review on the relevant processes in these two industries indicates that the leaching dynamics and their limitations with respect to iron removal are not well known or understood.

3.1. Characterisation of surface coatings and gangue minerals

The use of quartz as a supply to glass manufactures is controlled with maximum iron oxide concentrations never exceeding strict specifications: for household glass the requirement is 0.05% as Fe_2O_3 and for clear or crystal glass 0.025% as Fe_2O_3 . In the study by Styriakova et al. (2010) the mineral investigated was split into magnetic and non-magnetic fractions. The iron content of the non-magnetic fraction was 2.21% Fe_2O_3 and otherwise consisted of 86% quartz, 7% feldspars, 3% plagioclase, 2% mica, 1% kaolinite and 1% chlorite. The coatings present on the quartz mineral were predominantly: hematite, maghemite, goethite, lepidocrocite and ferrihydrite. This sand is very similar to that of Namakwa Sands feed type.

The sand used in the study by Taxiarchou et al. (1997) showed a greater total Fe_2O_3 content relative to the quartz content. Vegilio et al. (1998) used quartz sand which contained 0.026% Fe_2O_3 as a surface coating.

The method used to characterize the Namakwa Sands minerals (see section 4.2) was very similar to that used by Stryiakova et al. (2010) and that used by Taxiarchou et al. (1997); both used magnetic fractionation as their primary sorting tool, followed by various analytical techniques to determine the mineral phases present.

An internal study at Namakwa Sands (Ledgerwood, 2011) identified and characterised the iron-phases present as bulk minerals as per Table 2 and the major surface components of the mineral sand particles.

Surface contaminants:

- hematite,
- goethite and
- other coatings were similar to ferrihydrate,

Gangue minerals were found to be:

- magnetite,
- ilmenite,
- leucoxene and
- two dominant forms of garnets.

The total iron concentration is a function of the surface based iron contaminants and the non-magnetic bulk iron contaminants.

3.2. Influence of different iron phases on leaching rates

From the literature study only two patents (Gilman et al. (1995) and Gilman et al. (1998)) were found discussing zircon leaching, showing the highly secretive nature of the industry. Two patents reveal that some work into leaching of zircon minerals surfaces has been completed. The patents are quite similar with the first covering the pre-calcination step and the second that of a pre-alkaline step. They attempt to address the complexity involved with trying to soften the coating, without spending too much capital. The details indicate two significant differences between Namakwa Sands system and the processes proposed.

3.2.1. Leaching of zircon concentrate post calcining:

A number of processes have been proposed, such as the HAL circuit at Namakwa Sands and a variation of the HAL processes as disclosed by Gilman et al. (1995). The process involves first exposing the mineral concentrate surface (99% zircon) to calcining (process detailed in Figure 11), then reacting the hot mineral with dilute sulphuric acid at 5-25% in a 'quench' held at temperatures above 60 °C. Afterwards the mineral is washed, attritioned, dewatered and then dried. It is claimed, by Gilman et al. (1995), that this process causes the decomposition of coatings on the mineral surface. The calcination pre-step is thought to convert goethite (FeOOH) to hematite (Fe_2O_3), above 475 °C, which allows for higher conversions as, according to Gilman et al. (1995), the hematite is far more 'leachable'. Subsequent to leaching, the mineral is attritioned to remove the weakened coatings.

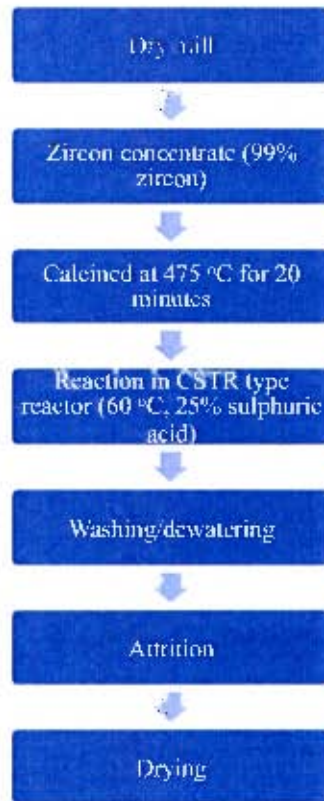


Figure 11: Overview of calcining process as proposed by Gilman et al. (1995)

They were able to produce a zircon mineral containing less than 0.01% Fe_2O_3 , from initial concentrations of up to 0.07% Fe_2O_3 . This is equivalent to a conversion of 85% Fe_2O_3 . The process and feed type is very different from Namakwa Sands, where the feed typically

contains less zircon ($55\% < \text{zircon} < 65\%$) and higher iron concentrations, typically 100 – 300 times greater than what this process has been evaluated for.

It is reasonable to say that the capital and operational costs associated with building and running a calcination unit are significantly higher than that of using a simple preheating method used in the Namakwa Sands flowsheet.

3.2.2. Calcining with coated basic reagent and then leaching of zircon concentrate

Another patent by Gilman et al. (1998) discloses a process whereby zircon concentrate (99% zircon) grains are first coated with a strong basic reagent. Sodium hydroxide is used as the coating agent, then the mineral is calcined at 600 °C for at least 20 minutes after which the minerals is contacted with dilute acid. This process is presented in Figure 12. If the process occurs via a gas-fired kiln, the sodium hydroxide converts to sodium carbonate with CO_2 from the kiln gasses. The mineral reacts with dilute acid to form iron carbonate complexes. The removal of the surface coatings is further enhanced by the formation of $\text{CO}_2(\text{g})$ produced by the acid/carbonate reaction. It is claimed that this process is slightly less operationally ‘intensive’ than posed by Gilman et al. (1995) where higher acidic strengths are used.

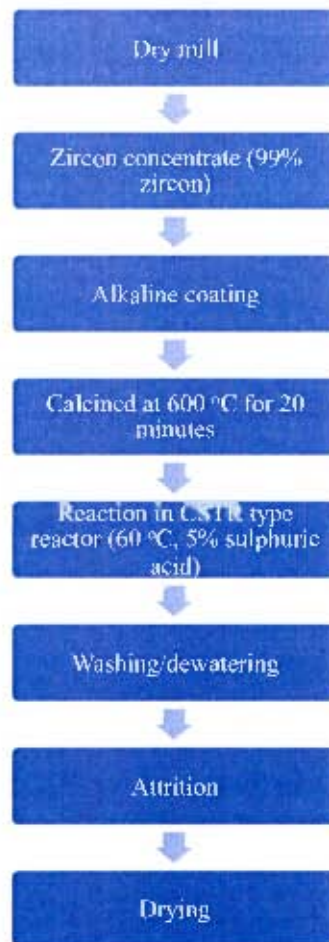


Figure 12: Overview of alkaline pre-calcining process as proposed by Gilman et al. (1998)

Yet another variation of the leaching process (not presented here) involves pre-calcining the zircon mineral at 600 °C and then contacting the mineral with strong acid at 100 °C for at least an hour, using a tumbling reactor (kiln). These processes are similar to the HAL circuit; however Namakwa Sands does not use a pre-calcination stage and thus relies heavily on the kiln reactor. The major difference between Namakwa Sand's process and the ones proposed by Gilman et al. (1998) is that the leach circuit is placed right at the end (Gilman et al. (1998)) of the process rather than at the beginning. Namakwa Sands leaching circuit is before the Dry Mill.

3.2.3. Pre-calcining effect on hematite and magnetite dissolution

Studies done by Chastukhin et al. (2003) looked at a number of factors affecting the dissolution of magnetite and hematite and then used a chain mechanism model to describe it.

Their work looked at the dissolution behaviour in sulphuric acid at different concentrations, at different temperatures and various iron-oxide forms. Their theory is based on the fact that for leaching to occur, a reaction front needs to advance continuously. For hematite synthesised from goethite post annealing the reaction rate was: $k_0 = 0.011 \text{ min}^{-1}$ and the pre-annealing reaction rate was: $k_0 = 2.6 \times 10^{-3} \text{ min}^{-1}$. For magnetite the reaction rate was $1.2 \times 10^{-4} \text{ min}^{-1}$ indicating that the leaching of pure hematite occurs at a faster rate than a mixture of hematite and goethite and pure magnetite. Their observation may explain why both Gilman et al. (1997 & 1998) studies indicated that the dissolution of iron from the zircon mineral surface is faster under post calcination conditions.

3.2.4. Pre-calcining effect on laterite dissolution:

Laterite is highly weathered material, rich in secondary oxides of iron, aluminium or both. These materials contain an abundance of quartz and kaolinite and can also contain trace elements of chrome, nickel and cobalt. What is of relevance to the present study is that the significant amount of iron (III) oxide (Agtzini-Leonardou et al., 2008) in laterite is making it ideal for comparison with the reactions relevant to the current study.

Work compiled by Oderinde and Olanipekun (1992) showed that the rate of dissolution of iron oxide in hydrochloric acid was very slow. The dissolution rates were well expressed by a rate equation based on the rate-determining step of the surface chemical reaction. Further work compiled on the rate of dissolution after pyrometallurgical calcination was employed as an initial step and then leached using hydrochloric acid. The calcining conditions allowed for complete goethite-to-hematite conversion (Sukla & Das, 1987).

Pre-calcining showed comparatively higher rates of leaching of iron oxide. The conversion of goethite to hematite, as previously considered by Gilman et al (1995) and Chastukhin et al. (2003) also enhanced the leaching rates for both zircon leaching and quartz sand.

Two shrinking core models were adapted to the dissolution kinetic curves:

$$1 - (1 + a)^{\frac{1}{3}} = k_1 t \quad \text{Equation 3.2.4(a)}$$

$$1 - \frac{2}{3}a - (1 - a)^{\frac{2}{3}} = k_2 t \quad \text{Equation 3.2.4(b)}$$

Olanipekun (2000) then studied the above equations and fitted them to his data. The a (in Equation 3.2.4 (a) and (b)) is the fraction of iron converted, while t is time and k_1 , k_2 are the

overall rate constants. The reaction Equation 3.2.4(a) is used when the rate is reaction controlled, however, if it is controlled by diffusion through a product layer, Equation 3.2.4(b) is used.

From least squares fitting-plots it was found that Equation 3.2.4(a) gave straight lines for both raw and calcinated laterites. These results led Olanipekun (2000) to deduce that the pre-calcination of laterites did not change the mechanism of iron-oxide leaching, and after visual inspection, the residue solids were found to be far more porous. This further supported the idea that the increased rate of leaching for the roasted samples was due to the increased porosity of the product layer, which increased the specific surface area and the conversion of ore from the main goethite to hematite base via 'dehydroxyoxide' and dehydration.

3.3. *Solid/liquid ratios effect on leaching*

The effect of solid/liquid (S/L) ratios on surface leaching of quartz sand was studied by Veglio et al. (1998) at a temperature of 90 °C. It was found that increases in the S/L ratio from 2.5 to 5 caused a decrease in the percentage of iron leached. Their rate data showed that for all tests conducted, a 30% conversion of iron oxide was achieved within the first hour. However, after this initial extraction, the rate slowed down, and to progress from 30 to 45% conversion took another 3 hours. This was explained by the relatively lower solubility of iron phases at higher S/L ratios (Veglio et al. (1998).

It was observed, by laboratory work at Namakwa Sands, that higher S/L ratios in the range of 2 to 5, tend to reduce the reaction conversion from 40% to 20% after 2 hours (Ledgerwood, 2011). At the high S/L ratios it was established that the formation of a brownish precipitate was very rapid (within the first 20 minutes). However, even running at a S/L ratio of less than 1 the reaction conversion levelled off at 40% after 2 hours and reached 45% conversion after another 45 minutes. Similar S/L ratios effect on conversion was observed by Veglio et al. (1998).

Most of the experiments reported in the literature where quartz minerals were leached, were conducted at low solid/liquid ratios: Taxiarchou et al. (1997) and Farmer et al. (2000) conducted their research at ratios of 0.1, while Ubaldini et al. (1996) completed their work at ratios of 1. This does not allow for direct comparison to the very high S/L (~10) system used at Namakwa Sands. However, the effect of S/L ratio on conversion provides a useful

indicator. It can be expected that at higher S/L ratios the establishment of this equilibrium occurs much more rapidly, resulting in a lower overall percentage dissolution of iron oxide.

3.4. Ultrasonically assisted leaching

The use of ultrasound in assisting the dissolution of iron oxide coatings has been reviewed by a number of researchers (Ubaladini et al., 1996) (Farmer et al. 2000). Previous studies indicate the potential for the use of ultrasound in the mining industry, particularly for surface related leaching processes (Farmer et al., 2000). The concept is based on cavitation, i.e. micro-scale mechanical attritioning. The studies found that the dissolution of iron oxide occurred via two distinct mechanisms. The first is a faster rate of leaching and is short lived 2-3 minutes in these experiments, other reports suggest up to 20 minutes for different temperatures. The second mechanism occurs when the rate of reaction slows down quite dramatically. The authors explain this based on the fact that the iron on the surface of the quartz sand exists in two phases:

- (a) that of iron hydroxyoxide (goethite) and
- (b) an iron oxide (hematite), leaching of the hydroxyl - oxide

Farmer et al. (2000) explain that (a) occurs first and rapidly, while leaching of the iron oxide (b) occurs slower. Increasing the ultrasound power to 150 W (sample was 100 g in size), the dissolution rate increased from 30 % to 60 % conversion iron oxide.

3.5. Temperature and kinetics

The dependence of equilibrium conversion on temperature for the system described by reaction 1 to 4 is presented in Figure 13. This relationship is developed using Gibbs free energies (detailed above and extracted from (HSC 5.1)) and shows the distinct curve for a endothermic reaction. This curve is derived from the Gibbs- Helmholtz equation:

$$d \left(\frac{\Delta G_{rx}^0}{T} \right) = - \frac{\Delta H_{rx}^0}{RT^2} \quad \text{Equation 3.5(a)}$$

Accounting for changes in heats of reaction for temperature the Gibbs-Helmholtz equation can be expanded to the following form:

$$\frac{d \ln K_a}{dT} = \frac{\Delta H_{rx}^0}{RT^2} \quad \text{Equation 3.5(b)}$$

This relationship clearly illustrates that for endothermic reactions an increase in temperature results in an increase in K_a and the converse for exothermic reactions. Further inclusions of enthalpies can account for changes in the heat of reaction with temperatures and the heat capacities. The adiabatic line, given by an energy balance for the adiabatic HAL reactor (it included evaporation) provides the reaction path-way (X represents the conversion of hematite to ferric sulphate via reaction 1, for more on the energy balance see chapter 6):

$$X = \frac{\frac{UA}{FAO}(T - T_a) + \sum \theta_i C_{Pi}(T - T_o) + H_{evap} \cdot n_{vap}}{[-\Delta H_{Rx}^o(T_R)]} \quad \text{Equation 3.5(c)}$$

The adiabat line provides the reaction pathway - as the reaction progresses, both the heat of the reaction and evaporation cool the system until equilibrium line is reached. This curve is constructed for a system where water vapour is in equilibrium with water in solution and does not consider changes in the volume of the reaction solution. The reaction environment involves the reaction of sulphuric acid at a 40 wt% concentration. The reaction tends to favour the reaction products at high temperatures of 160 °C, which results in the evaporation of water, at the solution boiling point (as predicted by the vapour/liquid diagrams). The evaporation of water results in increasing molar concentration of sulphuric acid. Figure 13 can be used to calculate the reaction conversion for respective feed (160 °C) and discharge (80 °C) temperatures using the reaction adiabatic line. If the discharge temperature changes, even only slightly (say 10 °C), the impact on reactor conversion is dramatic (10% in conversion). The reaction conversion has a strong dependency on temperature (both discharge and feed temperatures).

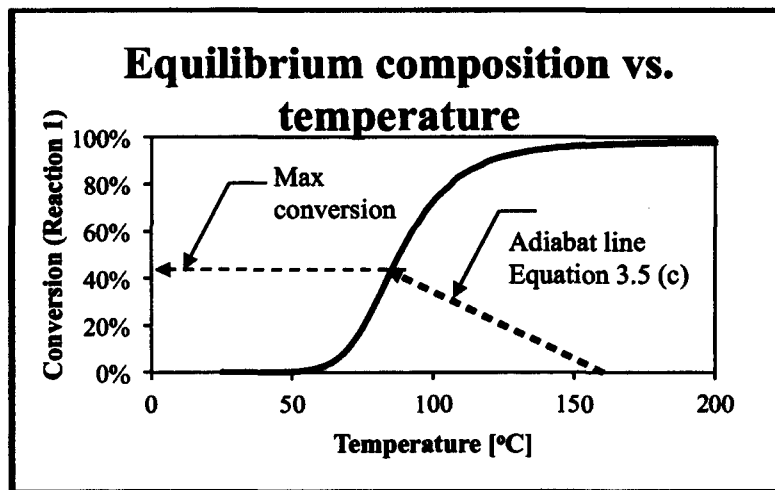


Figure 13: Reaction equilibrium curve for the reaction of hematite and sulphuric acid

Modeling the HAL reaction as shown in Figure 13 is quite difficult because the reaction solution is constantly evaporating along the length of the reactor and the iron species in solution become highly saturated, and because evaporation is dependent on temperature gradients and dew points. This can in part explain why the conversion of surface iron in the HAL reactors is very erratic. Previous work (Huisamen, 2000) indicated that most of the work conducted by previous researches focused on running the reactions at lower temperatures. Their reported conversions don't quite agree with the reaction equilibrium curve presented in Figure 13. Table 9 contains a brief summary of the literature surveyed, for the temperatures referenced, all conversions agree closely with the equilibrium (indicated above) curve.

Table 9: Literature survey on temperature effect on conversion

Temperature	Conversion	Solid/liquid ratio	Acid concentration	Duration	Reference
90 °C	40% max	0.1	pH < 4	after 2 hr	(Taxiarchou et al., 1997)
80 °C	30% max	0.1	pH < 1	after 2 hr	(Farmer et al, 2000)
80 °C	60% max	0.1	pH < 1	after 2 hr	(Farmer et al, 2000)
100 °C	40% max	2.5 - 5	pH unknown	after 1 hr	(Veglio et al., 1998)
80 °C	43% max	-	pH < 1	after 2 hr	(Chastukhin et al., 2003)
80 °C	32%	1	pH=2.5	after 8 hr	(Ubaladini et al., 1996)

For the HAL reactor, it is speculated that the conversion is a function of a number of iron phases present (as seen and discussed by Taxiarchou et al. (1997)), however it never exceeds the 40 – 50 % conversion. Increases in temperature up to 180°C or even changes in higher acid concentration have not lead to higher iron conversions. This is thought to be due to a solid precipitate (product layer) layer formed during leaching, which further inhibits the reaction from reaching the thermodynamic equilibrium. For the HAL reactor, modeling

higher solution concentrations at high temperatures becomes quite complicated and simple thermodynamics cannot provide accurate models for these types of systems.

3.6. Solid product layer formation

The thermodynamics of the reactor are complicated by the large number of iron-phases present at the reaction start, as intermediates and as possible products.

All studies indicated that the initial rate was very rapid and then after 20 minutes approached an apparent equilibrium. Guimares et al., (1987) and Vegilio et al., (1998) agree that the formation of a product layer was the major cause for the decreased rates, however Styriakova et al. (2010) explained this by suggesting that the iron on the surface of the quartz sand exists in two phases, the first is that of iron hydroxyl-oxide (goethite) and the second an iron oxide (hematite). Post-leaching SEM images indicated that iron based solid phases were present as precipitates attached to the surface as solid coatings.

There does seem to be some discrepancy as what is published by the researches and what is noted at Namakwa Sands. According to Taxiarchou et al., (1997), Veglio et al., (1998), Ubaldini et al., (1996) and Styriakova et al. (2010) all agree that higher temperatures are preferential for faster rates. This is contrary to the dynamics in the HAL reactors, as higher feed temperatures do not translate into higher conversions (Ledgerwood, 2011). Based on the thermodynamics it is expected that higher conversions are achieved at higher temperatures too. Studies done by Chastukhin et al. (2003) looked at a number of factors affecting the dissolution of magnetite and hematite, and they proposed a chain mechanism to explain their results. Their work confirmed that the equilibrium was reached very rapidly during the first half hour of reaction, and they too suspected the formation of an insoluble product layer inhibited access to active surface sites.

The formation of a stable solid precipitate layer around the reacting particle is dependent on the stability of the reaction products. According to Dutrizac and Monhemius (1987) the stability of hematite, jarosite, magnetite, ferric-hydroxide and ferric iron in solution is not well understood. However, it is accepted that hematite forms at higher temperatures, higher iron concentrations and higher pH values compared to jarosites; which prevail at very low pH values (Welham et al., 2000).

3.7. Ferric and ferrous chemistry and their stability

The stability of iron minerals found in nature serves as a guide to the stability of their precipitated compounds and their respective solubilities, which also provides a peak into the complex world of iron hydroxides (Dutrillac & Monhemius, 1987).

Iron is abundant in its natural form as a hematite ($\alpha\text{-Fe}_2\text{O}_3$) or as goethite ($\alpha\text{-FeOOH}$ and to a lesser extent $\beta\text{-FeOOH}$). Jarosite compounds have also been noted: $\text{MFe}_3(\text{SO}_4)_2(\text{OH})_6$ where M is the H, Na, Rb, Ag, Ti, K, NH_4 , $\frac{1}{2}$ Pb or $\frac{1}{2}$ Hg. Two forms of Fe_2O_3 (hematite and maghemite), four forms of FeOOH (goethite, akaganeite, lepidocrocite and ferroxhyte) and six forms of jarosite compounds (potassiumjarosite, hydroniumjarosite, ammoniumjarosite, argentojarosite, natrojarosite, plumbojarosite) are known to occur naturally.

3.7.1. Hematite and maghemite, Fe_2O_3

Iron oxide occurs most commonly as ilmenite ($\text{TiO}_2 \cdot \text{FeO}$), magnetite ($\text{FeO} \cdot \text{Fe}_2\text{O}_3$) and hematite (Fe_2O_3) (the order is not associated to the abundance). The two polymorphs of hematite are hematite ($\alpha\text{-Fe}_2\text{O}_3$) and maghemite ($\gamma\text{-Fe}_2\text{O}_3$). The main differences between these polymorphs can be summarised in Table 10.

Table 10: Hematite and maghemite by Dutrillac & Monhemius (1987)

Maghemite ($\gamma\text{-Fe}_2\text{O}_3$)	Hematite ($\alpha\text{-Fe}_2\text{O}_3$)
Magnetic	Mostly non-magnetic, some however are paramagnetic
Synthesis occurs via water through the oxidation of magnetite or the dehydration of lepidocrocite ($\gamma\text{-FeOOH}$), under hydrous conditions	These are generally found in hematite-ilmenite solution assemblages, hematite usually contains high amounts of Ti
Maghemite is common in highly weathered soils of tropical and subtropical climates	During weathering, hematite is formed by oxidation of ferrous minerals (goethite and magnetite), or oxidation of FeCl_2 solutions with other sulphide and silicate minerals, precipitation of these solutions would yield hematite at relatively high temperatures

According to work conducted by Cigan et al. (1980), the Hematite Industrial Process has been in operation since 1972 at the Iijima Eletrolytic Zinc Plant to recover copper from leach residue. This process takes weathered residues and exposes it to return electrolyte i.e. strong sulphuric acid and a reducing agent - SO_2 at 95 – 100 °C. This results in the reduction of ferric iron to ferrous. After copper removal, the solution is then neutralized in two stages at pH 4.5. The iron, being in the form of ferrous sulphate, remains in solution and is finally precipitated as hematite ($\alpha\text{-Fe}_2\text{O}_3$) again by heating the solution to above 180 °C for 3 hours at 18 atmospheres O_2 pressure. Hematite is then filtered at pH of between 7 and 8.

3.7.2. Magnetite, (Fe_3O_4)

According to Cigan et al. (1980) and Prinsloo (2006) magnetite is stable under weekly reducing and neutral alkaline conditions. Magnetite is slightly more stable than $\text{Fe}(\text{OH})_2$ in the presence of a reducing agent such as hydrogen. Studies by Cigan et al. (1980) identified three methods of removing iron from metallurgical streams as magnetite. These can be summarised as follows,

1. Partial oxidation (O_2) of iron to the ferric state with subsequent neutralisation with ammonia
2. Simultaneous oxidation and neutralisation of ferrous sulphate solution with ammonia
3. Separate precipitation of $\text{Fe}(\text{OH})_2$ and $\text{Fe}(\text{OH})_3$ followed by their mixing as reaction in alkaline medium

3.7.3. Iron oxide - hydroxides, FeOOH

Dutrizac and Monhemius (1987) divided iron-oxide-hydroxides into four polymorphs according to mineralogical differences these are listed in the Table below:

Table 11: Mineralogical data for the iron-oxide hydroxide minerals Dutrizac and Monhemius (1987)

	Goethite (α -FeOOH)	Akaganeite (β -FeOOH)	Lepidocrocite (γ -FeOOH)	Feroxyhyte (δ -FeOOH)
Symmetry	Orthorhombic	Tetragonal	Orthorhombic	Hexagonal
Synthesis	Syntheses is from ferrihydrite, most frequent iron oxide mineral found in soils	Naturally formed is very rare, synthetic compound formed by hydrolysis of FeCl ₃	Formed from the alteration of pyrite and arsenopyrite; occurs as platy crystals associated with goethite; in gossans; clays and sediments; occurs in hydromorphic soils and oxidation of precipitated ferrous hydroxide	Very rare, originally found in the Fe-Mn concentrations in the Pacific Ocean and in the Baltic and White Seas. Subsequently found in Fe-oxide precipitates from ground water in glaciofluvial sands and gravels in association with goethite and lepidocrocites
Other elements associated with	Al, Ni, Co, Cr, Ca, Mn	Cl	Mn, Co, Al	Fe-Mn
Other		Above 220 °C will alter to hematite	The reaction of oxygen and FeCl ₂ at pH = 7 will high concentration of KOH will form goethite	Conversion to hematite or maghemite or high temperatures depend on air supply during the heating and the presence of a reducing agent

3.7.4. Goethite, FeOOH

Goethite is formed naturally as a weathering product of iron bearing sulphides, oxides, carbonates and silicates. The mineral is the most stable iron oxy-hydroxide and second to hematite (with respect to stability) in iron oxides, particularly under hydrous soil conditions. Most goethites contain trace elements when in these environments. These environments are particularly similar to Namakwa Sands ore body and therefore worth studying.

Extensive literature studies have been conducted on the formation of different iron hydroxides, but no publications are clear as to what the mechanism or the physical properties that favour the formation of these. Dutrizac and Monhemius (1987) mentioned that the

relative abundance of goethite was evidence to its stability. Goethite is the most common, while ferrihydrite is less common; akaganeite; although rare, it is mostly found in soils. Under conditions of natural surficial weathering, the relative stabilities of hematite and goethite are very similar, variations occur based on the local climate. Under humid conditions (tropical weathering) goethite may be more stable than hematite. Under hot, dry desert conditions, hematite is more stable. High temperatures (70 – 90 °C) favour the formation of hematite rather than goethite. Goethite stabilizes at a maximum at 40 °C, 1 atm. However at higher temperatures and dryer environments the formation of hematite is more common.

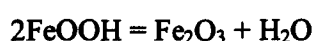
To some extent, Dutrizac and Monhemius (1987) mentioned that elemental substitutions can affect the hematite-goethite stability. Work covered by them also indicated that when goethite contains traces of aluminum, the stability of goethite is more favourable. This is also supported by experiments where a solution containing $\text{AlO}(\text{OH})$ and ferric iron was subject to increased levels of $\text{AlO}(\text{OH})$ at higher pH. From their literature review they concluded the following,

1. The stability of goethite and hematite is affected by the solution environment, pH and variations in elemental substitutions, however under conditions of normal surface weathering their relative stabilities are very similar
2. High temperature in excess of 70 °C favour the formation of hematite
3. High pH values favour goethite stability
4. Goethite stability is enhanced by aluminum ion substitution
5. Low pH and high Eh favour the stability of hydronium-jarosit, while higher pH and low Eh favour the stability of goethite

There is some discrepancy as to under what conditions goethite will form compared to those favouring hematite: Preparation of goethite was conducted by Kosmulski et al., (2003) at 80°C. The precipitate was then centrifuged out as goethite 25. Another portion was exposed to an overnight oven at 140 °C; this was referred to as goethite 140. A portion of goethite was sent for X-ray diffraction and the results showed the resulting composition was a goethite-hematite composite, while the earlier precipitate was pure goethite.

Work then compiled by Dutrizac and Monhemius (1987) showed that pure hematite was formed at 80°C, they failed, however, to mention the rate of this formation, an important

factor in iron-oxide-hydroxide formations. Work then compiled by Cigan et al. (1980) showed that in order to precipitate goethite, concentrations of ferric iron of less than 1g/L and moderately high pH values, and temperatures of between 70 and 95°C were more than adequate. This occurred via the 'oxolation' of iron polymers in solution. This resulted in high concentrations of protons which required proper neutralisation. If the pH is too high, the polymerisation reactions drive formation of an iron gel. The formation of these gel- like iron oxides is highly undesirable as these are very difficult to filter or settle. All hydrolysis reactions are favoured by increased temperatures. The higher the temperatures the more likely the formation of hematite over goethite Prinsloo (2006) according to Reaction 3.7.6.



Reaction 3.7.6

The iron polymer, which comes before goethite, is classified as an anion-hydroxyl polymer and the anion plays a significant role in determining the actual compound precipitated. It appears that anions such as ClO_4^- , NO_3^- and Br^- with weak complexation tendencies for iron produce α - or γ -FeOOH; anions such as F^- or Cl^- which are stronger seem to form the β - FeOOH (Cigan et al. 1980). The main qualities of the goethite precipitate formed according to Cigan et al. (1980) are:

1. Excellent filterability of goethite
2. Goethite is relatively stable
3. No additional alkalis are required for precipitation
4. Relatively high pH are required for precipitation
5. Goethite precipitation occurs from dilute ferric solutions
6. Goethite residuals include some cations and anions such as sulphates
7. Goethite is stable above a pH of 2
8. Removing ferric iron by means of goethite precipitation will not remove ferrous since ferrous will only precipitate at higher pH.

3.7.5. Jarosites, $\text{MFe}_3(\text{SO}_4)_2(\text{OH})_6$

There are quite a number of studies that looked at the formation of jarosites because of their industrial significance. Dutrizac and Monhemius (1986) conducted an extensive body of work on jarosites. The jarosites are members of a large family, the alunities $\text{AB}(\text{SO}_4)_2(\text{OH})_6$ in which A is H_3O^+ , Na, Rb, Ag, Ti, K, NH_4 , $\frac{1}{2}$ Pb, $\frac{1}{2}$ Hg and B = Al, Cu or Fe^{3+} . The

formation of these jarosites occurs under complex conditions and their relative stabilities are a matter of much discussion. Prinsloo (2006) suggests that only six jarosite types of minerals are known, but nine have been formed synthetically. These are hydronium jarosite, $(\text{H}_3\text{O})\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6$, ammoniojarosite $(\text{NH}_4)\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6$, argentojarosite $\text{AgFe}_3(\text{SO}_4)_2(\text{OH})_6$, (potassium)jarosite $\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$, natrojarosite $\text{NaFe}_3(\text{SO}_4)_2(\text{OH})_6$ and plumbojarosite, $\text{PbFe}_3(\text{SO}_4)_2(\text{OH})_6$. Jarosite is the most common form, according to Dutrizac and Monhemius (1986). The order of increasing hydronium substitution in the alkali jarosites is $\text{Na} > \text{NH}_4 > \text{K}$ (Prinsloo, 2006). Jarosites can be synthesized from ferric sulphate and an appropriate salt solution at low pH. Jarosites are common amongst siliceous limonitic veins in limestones, highly acid environments, gossans and sulphide rich environments. Jarosites are also formed on oxidation of pyrite and are commonly intergrown with limonite. During weathering, the jarosites break down into goethite and hematite (Dutrizac and Monhemius, (1987); Ismael and Carvalho (2003)). The results showed that jarosite was predominantly stable at very low $\text{pH} < 2$ and for a wide range of temperatures from 38°C to 140°C , while goethite was more prominent at $\text{pH} > 3$ and being stable at a temperature of 70°C . The stability of hematite increases with higher temperatures, while hematite is stable at temperatures above 70°C and higher lower $\text{pH} < 3$. From Figure 14, it is clear that for a pure system the relative stabilities of jarosites, goethite and hematite are well defined. However, in nature jarosite is commonly associated with hematite, and in some cases all three are found.

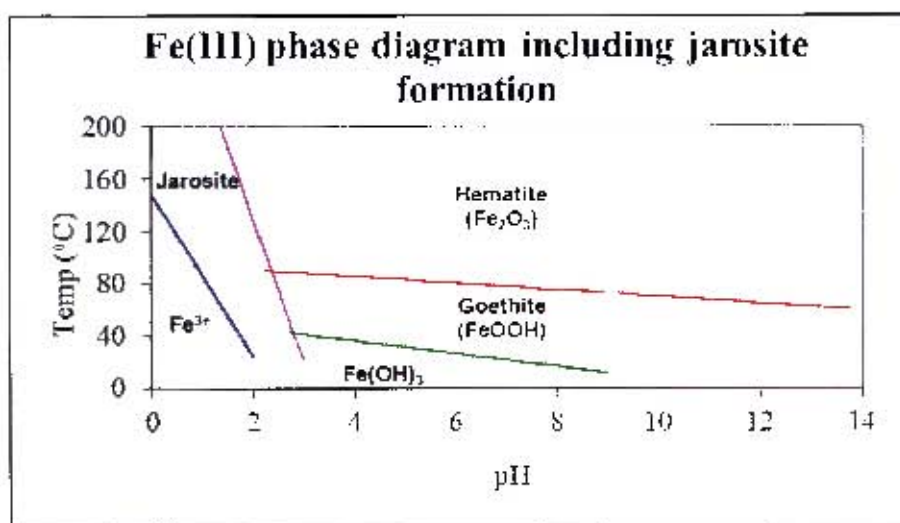


Figure 14: Ferric iron stability diagram as a function of pH and temperature. Formation from a solution of 0.5 M $\text{Fe}_2(\text{SO}_4)_3$ from 20 to 200°C (Dutrizac and Monhemius, 1986)

The view that jarosite is typically a high temperature phase may well be due to the slow kinetics of formation at low temperatures. Most metallurgical operations require rapid treatment of waste streams by precipitation, necessitating fast kinetics and therefore elevated temperatures. Jarosite has been shown to form by precipitation of acid mine drainage solutions only at $\text{pH} < 2.8$. A similar trend for jarosite formation at low pH and goethite at higher pH has been observed during biological oxidation of ferrous iron and sulphate solutions (Welham et al., 2000).

Thermodynamic data for jarosite is unreliable; this is mainly due to the poor definition of the anion, the composition and the crystallinity. The most reliable data is for potassium jarosite, which has a measured free energy of formation of -3309.8 ± 1.7 kJ/mol, according to Welham et al. (2000). An estimate by these authors of the free energy of formation of hydronium jarosite was done by assuming that there is a complete and ideal solid solution series between potassium and hydronium jarosite, and the value is given as -3027.6 kJ/mol. This was then used to construct stability diagrams for ferric iron in equilibrium with hydronium jarosite as a function of pH and sulphate activity. The effect of sulphate on the stability of ferric iron is predominantly due to the speciation of sulphuric acid (i.e. HSO_4^- and SO_4^{2-}); at $\text{pH} < 1.99$ HSO_4^- is predominant while above $\text{pH} > 1.99$ SO_4^{2-} is predominant. The effect of HSO_4^- on the solubility of goethite is greater than the effect of SO_4^{2-} . The inverse is thus true for jarosite as indicated by Figure 15.

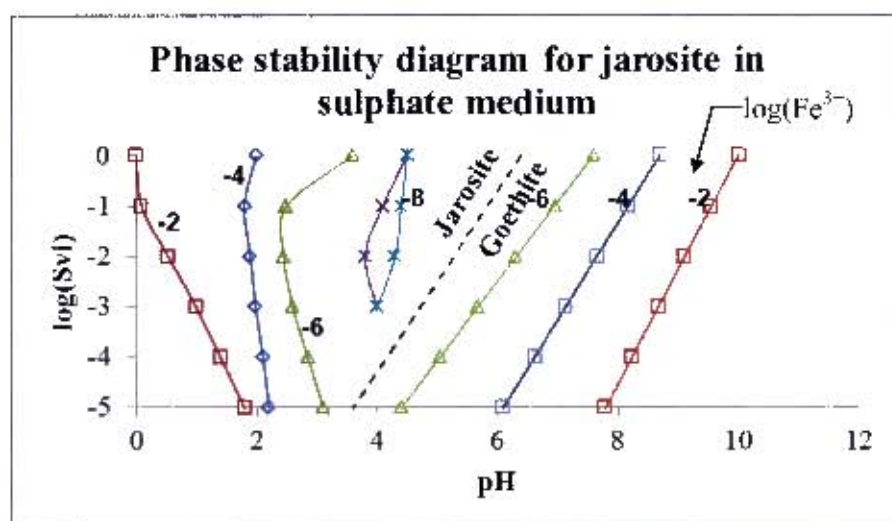


Figure 15: Solution iron(III) activity as a function of ligand concentration and pH for goethite and hydronium jarosite, the dashed line represents the equilibrium between jarosite and goethite (Welham et al., 2000)

It is quite clear from Figure 15 that jarosite is far more stable at lower pH, higher sulphate concentrations and higher or lower iron concentrations. Cigan et al. (1980) found that at lower temperatures the solubility of jarosite was increased, according to a study conducted on neutralizing excess acid. The amount of iron precipitated depends on the initial ferric iron concentrations and free acid. According to Cigan et al. (1980) the main properties of jarosite process are that precipitation occurs at low pH < 1.5 and moderate temperatures 95 °C at atmospheric pressure.

3.8. Calcium sulphate(s)

Calcium sulphate is an abundant form of sulphate, it can be found in the anhydrate of gypsum form. Evaporated mineral (due to natural percolation) deposits contain various amounts of double or triple salt minerals such as syngenite, $K_2SO_4 \cdot CaSO_4 \cdot H_2O$ glauberite, $Na_2SO_4 \cdot CaSO_4$, or polyhalite, $K_2SO_4 \cdot MgSO_4 \cdot 2CaSO_4 \cdot 2H_2O$. Calcium sulphate is also used in building and construction materials as a binder. Extensive research has looked at its dehydration-rehydration under various conditions. A number of important processes, such as the wet limestone-gypsum flue-gas desulphurization (FGD) process, production of phosphoric acid, hydrometallurgical production of zinc and copper, recovery of natural gas and oil are accompanied by the crystallisation of calcium sulphate. Much attention has been placed on inhibiting or slowing the rate of growth in the context of scaling. A number of factors affect the crystallization of gypsum complexes and these include temperature, pH, pressure, and dissolved electrolytes or to some extent organics (Freyer & Voigt, 2003).

3.8.1. Calcium sulphate $CaSO_4$

In contact with water, three phases of calcium sulphate can crystallize: gypsum ($CaSO_4 \cdot 2H_2O$), anhydrite ($CaSO_4$) and hemihydrates ($CaSO_4 \cdot xH_2O$, x ranges from 0.5-0.8) i.e. Plaster of Paris. The common structure of all three $CaSO_4$ phases is the $[-Ca-SO_4-Ca-SO_4-]$ chains; the sulphate tetrahedral is coordinated through oxygen atoms with two neighboring Ca ions (Freyer & Voigt, 2003).

All calcium sulphate hydrates are relatively insoluble and they form wherever calcium sulphates occur. The most common cause of scale formation is the transformation of the metastable $CaSO_4$ hydrate to the stable one, usually gypsum.

Theoretically, gypsum is the stable solid phase in water up to 45 – 50 °C, above this temperature it will transform into anhydrite (Azimi & Papangelakis, 2011). However, the exact transformation temperature is highly dependent on the concentration of sulphates and calcium. The exact temperature at which that happens is a controversial topic, but most authors agree that it is between 45 and 50 °C. The ability of gypsum to transform from one state to another is based on Ostwald's set rule. The gypsum is first formed due to its higher solubility and then gradually it is transformed to the anhydrite which is less stable, at temperatures of 100 °C and high sulphate environments. The result is scaling and is known to result in major operational issues (van Santen, 1984).

3.8.2. Calcium sulphate hemihydrates and related phases

The stability of calcium in solution is dependent on a number of different impurities – iron and aluminium show the greatest effect. This was confirmed by work completed by Kruger et al. (2005); sulphuric acid is reacted with phosphate rock to produce phosphoric acid and calcium precipitate. This process seems quite straightforward, but technical difficulties arise when the phosphate rock contains minor impurities like, Fe^{3+} , Al^{3+} , K^+ and Na^+ . These impurities are found to influence the solubility of calcium sulphate in solutions, which changes the filterability of the precipitate. During the process acid is filtered and cooled, and small amounts of calcium sulphate become supersaturated, which then leads to precipitation of more calcium sulphate. One compound that is formed is $(\text{Fe,Al})_3\text{KH}_{14}(\text{PO}_4)_8 \cdot 4\text{H}_2\text{O}$, the growth rate of the crystal is found to be influenced by the concentration of impurities present.

The substitution effect of ferric on hemihydrate formation was found to be very similar to ferrous, with ferrous being oxidized to ferric (Kruger et al., 2002). Work compiled by Freyer and Voigt (2003) indicated that the formation of hemihydrates can be done by preparing gypsum and then drying this at elevated temperatures, this particular hemihydrate was indicated as β -hemihydrate. In aqueous solutions, however, hemihydrates are called α -hemihydrates and can be crystallized by using a 60 % HNO_3 solution. This will happen at 50°C; for concentrated NaCl-solution this occurs at higher temperatures of 80 °C, while at higher concentrations of MgCl_2 the crystallization occurs at temperatures less than 55 °C. Most research has considered the difference between the alpha and beta hemihydrates as illustrated by Table 12 depending on what method is used. Much controversy still exists as to whether there are differences between the two hemihydrates.

Table 12: Structural differences between alpha-hemihydrate and beta-hemihydrate (Veglio et al., 1998)

Investigated properties and methods	Main conclusion
X – Ray	No basic difference for alpha and beta hemihydrates
Surface – Electron microscope	Very high specific surface for beta hemihydrate compared to alpha
IR	Weaker bonds for beta hemihydrates
Hydration heat	Lower heat of hydration for alpha hemihydrate than for beta hemihydrate
Structure	Alpha hemihydrate mono-clinic and beta hemihydrate trigonal

3.9. Solution thermodynamics

The HAL reactor system solution thermodynamics are largely dependent on the sulphate and proton concentrations in solution. The chemistry involved in hydrometallurgical process mostly involves ion species, where electron transfer occurs. There are three fundamental reaction types in hydrometallurgy, association/dissociation, proton transfer reactions and electron transfer reactions. They are all very important within hydrometallurgical process and to some extent these reactions form the foundation on which hydrometallurgical postulations are made.

a) Association and dissociation reactions

These types of reactions involve the reaction of ionic-type molecules and water, during which they dissociate to form their respective ions. During association they combine and form a more stable ion or a solid, which subsequently will precipitate from the solution. The dissociation of salt, NaCl to form Na^+ and Cl^- , $\text{Ag}(\text{NO}_3)$ will form Ag^+ and NO_3^- .

b) Proton transfer reactions

The concentration of protons to a large degree controls the solubility of a whole range of metals/metallic ions. These commonly exist as hydroxide salt and also sometimes form complexes with water by hydrolysis. pH is the standard measure for proton concentration in solution. The dissolution of many minerals is increased by higher concentrations of protons in solutions. The simplest example is that of ferric (Fe^{3+}), reacting to form $\text{Fe}(\text{OH})^{+2}$ at a pH ~ 2 $\text{Fe}(\text{OH})_2^+$ at a pH ~ 3 and $\text{Fe}(\text{OH})_3$ at a pH ~ 5 .

c) Electron transfer reactions

A large number of reaction involve ions exchanging electrons. The potential of a solution to transfer electrons however is still the electron potential measured as volts. Many ionic species can change the number of charges they carry by accepting or losing electrons. This is normally termed oxidation or reduction reactions. Examples of these include the oxidative leaching of chalcopyrite and reductive leaching of ferric based iron oxides. These types of reactions are of great importance to mining as they are the most studied of all types.

3.9.1. Theoretical thermodynamic solubility

A large portion of hydrometallurgical reactions tend to be reversible, referred to as a dynamic equilibrium. The ability to use thermodynamics to predict this dynamic equilibrium is very useful. In general the mathematical equation can be described by the Law of mass action:



The equilibrium constant is computed as K:

$$K = \frac{a_C^\gamma \cdot a_D^\delta}{a_A^\alpha \cdot a_B^\beta} \quad \text{Equation 3.7.1(b)}$$

The a_i is referred to as the specie ionic activity. For ionic solution, the thermodynamics become very complicated due to the many interactions between the ionic species and water and with each other in solution; these include the electrostatic interactions, hydrogen bonding energies, co-ordinations, ion-pairing, etc. Determining the activity of an ionic species accurately at higher ion concentrations becomes very difficult. Thus the individual activity of

ions in solution is highly dependent on the activity of other species in solution. For dilute solutions the activity is related to the concentration via the activity coefficient as demonstrated by Equation 3.7.1(c):

$$a_i = \gamma_i \cdot m_i \quad \text{Equation 3.7.1(c)}$$

The molality is approximately equal to concentration for very dilute solutions where $m_i < 1$ mol/kg. The activity coefficient can then be determined by either using the Dubye-Hückel law or others as presented in the next paragraph:

$$-\log_{10} \gamma_{i\pm} = \frac{az_i^2\sqrt{I}}{1+aB\sqrt{I}} \quad \text{Equation 3.7.1(d)}$$

The A and B coefficients are calculated based on the solute characteristics. The alpha and beta are given from experimental tables and is also dependent on solution temperature (Table 13).

Table 13: Values for the Parameters in Dubye-Hückel limiting law equations for aqueous solutions (Sandler, 1997)

T (°C)	A (mol/L) ^{-1/2}	B [(mol/L) ^{-1/2} Å] ⁻¹
0	1.132	0.3248
10	1.149	0.3264
20	1.167	0.3282
30	1.188	0.3301
40	1.212	0.3323
50	1.237	0.3346
60	1.265	0.3371

The average radius is given by a in Angstrom, in practice however the product of βa is normally set at unity or treated as an adjustable (Equation 3.78.1(d)) parameter (Sandler, 1997). Finally the ionic strength is determined using the following equation:

$$I = \frac{1}{2} \sum_i^n z_i M_i \quad \text{Equation 3.7.1(e)}$$

As noticed by the above equation the ionic strength is also dependent on solutions speciation, which in turn requires the activity of the solutions. This requires an iterative algorithm to

solve. These models hold quite well for low concentrations of species. But the higher and more non-ideal the concentration of the solution gets, the models tend to be less accurate. To account for that a model developed for non-ideal high concentration of electrolytes has been suggested as follows:

$$\frac{G^{ex}}{n_w RT} = f(I) + \sum_i^n \sum_j^m \lambda_{ij}(I) M_i M_j + \sum_k^r \sum_i^n \sum_j^m \delta_{kij}(I) M_i M_j M_k \quad \text{Equation 1.3.6}$$

The Gibbs excess energy is calculated from G^{ex}/n per kilogram solvent. M_i is the molarity of each ion in solution and $f(I)$ is the Debye-Huckel equation. The above equation, although very cumbersome to compute due to the high number of constants, has been used to calculate from low activities to higher activities such as molten salts (Sandler, 1997). The relevant constants need to be determined from extensive experimentation, however, which is why the approach is not applied very often in practice.

3.9.2. Solution conductivity as a measure of speciation

Another measure of solution speciation is by measuring the conductivity of a solution. This method is very useful especially when dealing with protons in solutions. As indicated by Casas et al. (2005), their work showed that using the diffusivities of various ions in solutions together with the measure of conductivity, one is able to deduce what species will form. The theory behind this is based on the following:

$$\kappa = \frac{F^2}{RT} \sum_i^{NI} z_i^2 C_i D_{eff,i} \quad \text{Equation 3.7.2(a)}$$

Where kappa is the conductivity of solution measured using a conductivity cell (mS/cm), (R – ideal gas constant, T – temperature (K), F – Faraday constant, z_i this formula takes into consideration the number of ionic species in solution, NI, the concentration of the individual species (C_i) and the effective diffusivity ($D_{eff,i}$) of that specie. For a case where hydrogen ions are present in solution and due to their mobility, above that of other ions in solution, the above equation can be rewritten to obtain a relationship between hydrogen ion diffusivity and conductivity.

$$\kappa = \frac{F^2}{RT} D_{ef,H^+} [C_H^+ + \sum_i^{NI-1} \frac{z_i^2 C_i D_{ef,i}}{D_{ef,H^+}}] \quad \text{Equation 3.7.2(b)}$$

The effective diffusivities can then be computed using standard diffusivities at 25 °C and for dilution solutions using the following equations:

$$\frac{D_{ef,i}}{D_{ef,H^+}} \sim \frac{D_i^0}{D_{H^+}^0} \quad \text{Equation 3.7.2(c)}$$

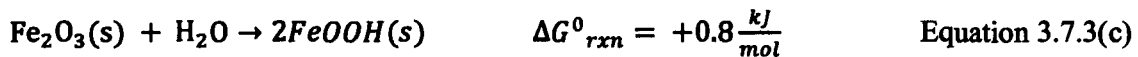
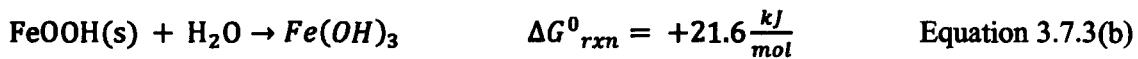
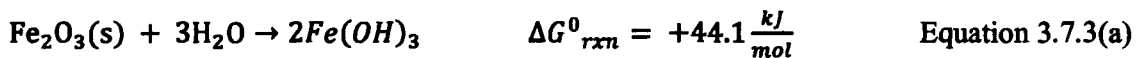
For complex solutions where multiple ionic species are present the effective diffusivity can then be approximated using the following:

$$D_{complex}^0 = \frac{|Z_{complex}|}{\left[\sum_{j=1}^{NI} \left(\frac{z_j^2}{D_j^0} \right)^3 \right]^{1/3}} \quad \text{Equation 3.7.2(d)}$$

The above equation developed by Anderko and Lencka (1997) is used widely for computing the effective diffusivities of complex solutions. This can then be used to establish the behavior of hydrogen ions in solutions by measuring the conductivity of the solution and associating this to the solution speciation.

3.9.3. Calculation of solubilities for the iron – water system

For a ferric system there is quite a large number of possible solid phases. These include the several oxide phases (Fe₂O₃ and maghemite) and hydrated phases such as jarosite, goethite, lepidocrocite, ferrihydrite, ferrihydrite and akaganeite.



Quite clearly the stability of both goethite and hematite is greater than that of iron hydroxide. This is not unexpected as iron hydroxide (Fe(OH)₃) does not appear naturally, whereas goethite and hematite are abundant in nature. Work conducted by Welham et al. (2000) showed that in most cases when, in a solution containing ferric and sulphates, the pH is increased, the result is goethite precipitation. Thus for solid phase calculations the chosen

solid was goethite. However, using hematite as the solid phase does not make a large difference in the position of the calculated equilibrium lines. Table 14 presents the thermodynamics data obtained from literature (Dutrizac & Monhemius, 1987) used in this study.

Table 14: Thermodynamic data used to calculate solubility by (Dutrizac & Monhemius, 1987)

Species	$\Delta G_f^\circ / \text{kJ mol}^{-1}$	Species	$\Delta G_f^\circ / \text{kJ mol}^{-1}$
H ₂ SO ₄	-744.63	Fe ₂ (OH) ₂ ²⁺	-467.27
HSO ₄ ⁻	-756.01	Fe ²⁺	-91.5
SO ₄ ²⁻	-744.63	FeOH ⁺	-277.4
Fe(OH) ₄ ²⁻	-769.9	Fe(OH) ₂ (aq)	-441.0
FeO(c)	-251.6	Fe(OH) ₂ (c)	-486.7
Fe _{0.942} O – wustite	-245.2	Fe(OH) ₃	-605.2
Fe ₃ O ₄	-1015.4	HFeO ₂	-376.4
Fe ³⁺	-16.7	FeO ₂ ²⁻	-301.1
FeOH ²⁺	-229.4	Fe(OH) ²⁺	-438.1
Fe(OH) ₃ (aq)	-660.0	Fe(OH) ₃ (c)	-705.5
Fe(OH) ₄ ⁺	-842.2	Fe ₂ O ₃ – hematite	-743.6
FeOOH – goethite	-490.0	Fe ₂ SO ₄ ⁴⁺	-772.8
Fe(SO ₄) ₂ ²⁻	-1524.6	Fe ₂ (SO ₄) ₃ (aq)	-2243.0
HFe ₃ (SO ₄) ₂ (OH) ₆	-3027.5	H ₂ O	-237.2

Constructing the equilibrium curves for an aqueous solution containing ferric iron:



The equilibrium constant can be calculated using the Gibbs-Helmholtz following equation:

$$\Delta G = -2.303RT \log(K_n) \quad \text{Equation 3.7.3(i)}$$

Then at equilibrium the following relationships will hold:

$$K_1 = \frac{\{FeOOH\}\{H^+\}^3}{\{Fe^{3+}\}} \quad \text{Equation 3.7.3(j)}$$

$$K_2 = \frac{\{FeOOH\}\{H^+\}^2}{\{FeOH^+\}} \quad \text{Equation 3.7.3(k)}$$

$$K_3 = \frac{\{FeOOH\}\{H^+\}}{\{Fe(OH)_2^+\}} \quad \text{Equation 3.7.3(l)}$$

$$K_4 = \frac{\{FeOOH\}}{\{Fe(OH)_3\}} \quad \text{Equation 3.7.3(m)}$$

$$K_5 = \frac{\{FeOOH\}}{\{Fe(OH)_4^-\}\{H^+\}} \quad \text{Equation 3.7.3(n)}$$

Based on the fundamental thermodynamics, the solids activity is assumed to be unity. Rearranging the above equations and replacing the proton concentration with pH, the equilibrium curves for the ferric-H₂O system can be constructed.

The total soluble iron is therefore represented using the following relationship:

$$\{Fe^{III}\} = \{Fe^{3+}\} + \{FeOH^{2+}\} + \{Fe(OH)_2^+\} + \{Fe(OH)_3\} + \{Fe(OH)_4^-\} \quad \text{Equation 3.7.3(o)}$$

Systems containing complexed ligands, such as sulphates ($FeSO_4^+$), need to be considered, however, for simplicity it is left out of this equation, and is presented in the following section.

The solubility of ferric is dependent on the number of complexing ferric ions and specific pH. Figure 16 indicates that lower pH allows for higher ferric solubilities. Figure 16 also indicates that three major species control the solubility of goethite: for low pH it is the concentration of Fe^{3+} , for slightly higher pH (where removal of ferric via neutralization occurs) it is the $Fe(OH)_3$ concentration, and for predominantly high pH it is the concentration of $Fe(OH)_4^-$. The activity of ferric between the pH of 5 and 9 is constant, which indicates that ferric is a good oxidation state for ferric removal as the resulting solids are insoluble over a wide pH range and hence safe for disposal as depicted by Figure 16.

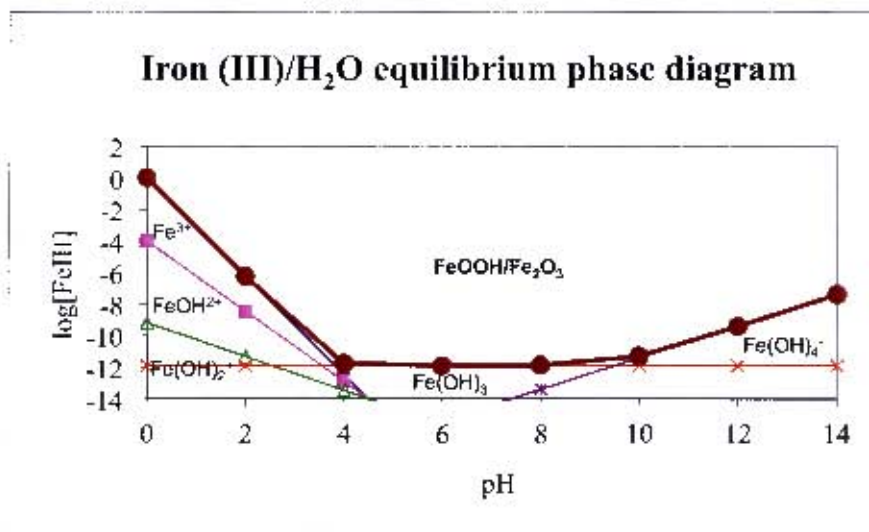


Figure 16: Phase stability diagram for ferric-water binary system (Prinsloo, 2006)

It must be stressed that the relative solubility's for ferric is very dependent on the concentration of complexing ligands in solution.

3.9.4. Calculation of solubilities for iron – sulphuric acid systems

In aqueous sulphuric acid solutions, iron distributes as dissolved ferric and ferrous or as complex compounds such as $[\text{FeSO}_4^0, \text{FeSO}_4^+, \text{Fe}(\text{SO}_4)_2^-]$. The concentration of these species is strongly dependent on the solution composition and temperature.

Ferric ions are soluble up to up to 25g/L in sulphuric acidic environments of above 120g/L H₂SO₄, according to Casa et al. (2005). They also noted that at pH < 1: 28 g/L of Fe¹³ is soluble. The ferric concentration in the HAL reactor is 42g/L and acid concentrations of 250 g/L, there is no data in literature to suggest these environments are understood or have been studied properly.

There is a tremendous amount of data from the zinc industry to support the idea that ferric sulphate is soluble/stable (pressure leaching/pachuca leaching). Dutrizac and Monhemius (1987) add that when the ferric precipitates at temperatures of above 120 °C, it would follow a hydration mechanism, i.e. the reverse of Reaction 1. Also, they claim that if ferric precipitates under highly acidic conditions, it would do so as FeOHISO₄, again via hydrolysis and produce sulphuric acid.

The data presented throughout literature is very vague on ferric sulphate precipitation, either as the anhydrate or hydrate. CRC Handbook of Chemistry and Physics Edition 8 indicates that the solubility product of ferric sulphate is $K_{sp}=10^{-100}$, while CRC Handbook of Chemistry and Physics Edition 6 indicates that the solubility of the hydrate-form i.e. $Fe_2(SO_4)_3 \cdot 8H_2O$ or $Fe_2(SO_4)_3 \cdot 5H_2O$ as $K_{sp} = 400$.

From the literature it is clear there seems to be confusion with regards to what the true solubility of ferric sulphate is, or what phase ferric most commonly precipitates as. Based on the literature review on ferric compounds (for a system similar to Namakwa Sands HAL reactor i.e. temperatures above 120 °C and for acid conditions below pH < 0 while the Fe^{3+} concentrations above 25g/L) hematite and jarosite are the most likely stable phases. By understanding the solubility of hematite in acidic environments, this section will try and establish what the stability of ferric sulphate is in solution. The five major reactions occurring at equilibrium in a sulphate – water – ferric system are the following:



Depending on the temperature and concentration of species the following solids could precipitate; hematite, magnetite, goethite, hydrous ferric oxides, brucite, hydronium jarosite, schwertmannite, iron-hydroxide-sulphides. Casas et al. (2005) conducted work in very low pH environment by using 2.2 M H_2SO_4 together with 1.3 M Fe (total). Thier work looked at providing experimental and theoretical models for the speciation of aqueous ferric and ferrous (sulphate) solutions at different concentrations of acid and iron. The theoretical models were also then compared to the experimental data and the theoretical models matched quite closely that of the experimental data points. Solutions were held at 25 °C and another

set was completed at 50 °C. Different iron reagents were used $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{FeH}(\text{SO}_4)_2$ the total iron concentration was monitored by AAS.

The extended Debye-Hückel equation (Casas et al. (2005)) was used for calculating the activity of ionic species. Casas et al. (2005) was convinced, based on work compiled by (Tremaine et al., 2004), that the complex HSO_4^- and Fe^{3+} in the form of ion-bisulphates can assumed to be non-existent. This work also confirmed that the ion-bisulphate is a non-complex-forming ion. The total iron in solution was the following:

$$\text{Fe(II)} = [\text{Fe}^{2+}] + [\text{FeSO}_4^0] \quad \text{Equation 3.7.3(f)}$$

Similar equations can be used to calculate the total sulphate concentration and proton concentration. The above equations together with the sulphate equation and total proton equation can be used to solve for solubility data at equilibrium. Casas et al. (2005) used Raman spectroscopy studies to identify what displacement of spectral bands occurred with respect to pure species. This work indicated that there was to a large extent interaction between ionic species. They concluded that species present were HSO_4^- and the complex $\text{FeH}(\text{SO}_4)_2^0$.

The model was verified by experimental data. The reason for using conductivity measurements according to Casas et al. (2005) is that it takes diffusivity of species in solution into account, which is directly related to the speciation of ions in solutions. Using this model as a thermodynamic calibration tool to fit experimental data, one is able to deduce the stability of the ferric species in solutions. According to their work, the conductivity of the bulk solution decreased as the iron concentration was increased at both temperatures. The protons ions provide the path for electrons to flow (due to their higher mobility and smaller size of ion compared to other ions); indicates that in a highly acidic solution with increasing iron concentrations the formation of bisulphate ions is very likely. This is primarily driven by reaction Equation 3.7.3 (d). The degree of ionic association increases with iron concentration Figure 17 indicates that the relative portion of Fe-SO_4 and HSO_4^- complexes increase with higher iron or sulphuric acid concentrations. Indicating that there is a decrease in the mobility of ions in solution.

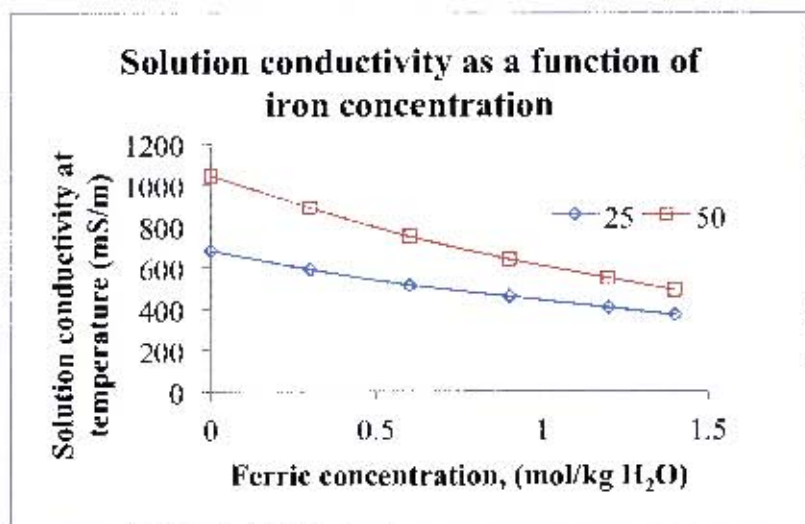


Figure 17: Fe-H₂SO₄-H₂O system a measure of solution conductivity at two different temperatures (25 °C and 50 °C: 1.5 M Fe³⁺, 2.2 M H₂SO₄) Casas et al. (2005).

Casas et al. (2005) mentions that this observations presented in the previous paragraph, agrees with the theoretical captured data and that the experimental versus model relative standard deviation was quite small at 3.2 %. The study found this model to be valid for solutions containing < 2 M H₂SO₄; higher concentrations of acid or ferric made it very difficult to quantify the amount of dissolved species. With increased temperature it is noticed that a decrease of protons and ferric ion concentration the stability of HSO₄⁻ and Fe(SO₄)₂⁻ this is illustrated in Figure 18.

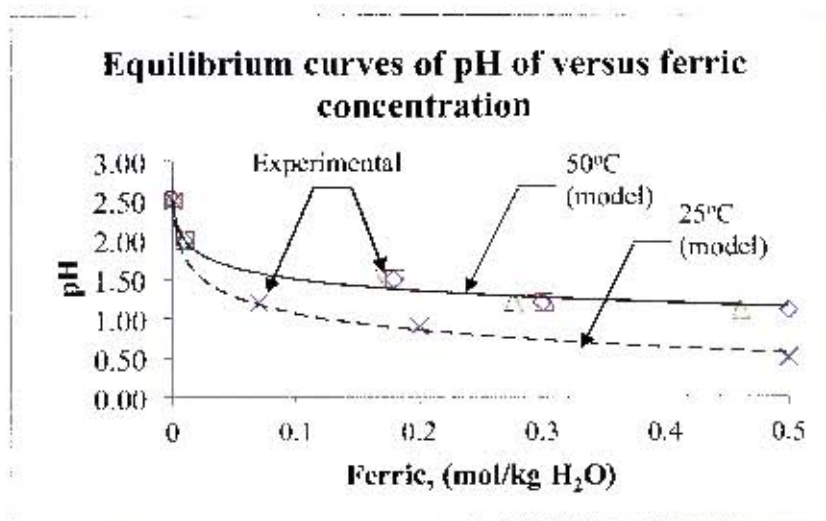


Figure 18: Equilibrium pH of solutions formed by dissolution of rhomboclase [FeH(SO₄)₂] in water as a function of ferric concentration: 1.5MFe³⁺, Casas et al. (2005).

The above literature review indicates that iron in sulphate solutions will complex to form $\text{Fe}(\text{HSO}_4)_2^0$ at the high proton concentrations. Also, with the formation of bisulphate ions HSO_4^- it is also clear that free acidity would decrease with the amount of dissolved iron indicating the existence of association between dissolved iron compounds and hydrogen ions (H^+) to form the $\text{FeH}(\text{SO}_4)_2^0$. Conductivity measurements indicate that with increasing temperature, increase conductivity would be seen and showed a decrease in dissolved iron concentration. This is due to the complexation of $\text{FeH}(\text{SO}_4)_2^0$, at higher temperatures it is noticed that the stability of $\text{Fe}(\text{SO}_4)_2^-$ increases as illustrated by Figure 18.

3.10. Formulation of hypothesis

According to the literature survey, leaching of hematite-based coatings from zircon is not unique to the mineral sands industry but is also applied in the quartz industry. These processes (in the quartz industry) are similar to the HAL circuit; however two significant differences exists between the two processes: the first is that Namakwa Sands does not use a pre-calcination stage and thus the influence of different iron-phases plays a major role in leaching efficiency. The second major difference between these two processes is that the leach circuit is placed right at the end of the Dry Mill process rather than at the beginning. These two factors make it very difficult to compare the two industries directly. It is however interesting that both industries require the softening the coating around the mineral, which is hematite based, such that further attritioning cleans the surface.

At Namakwa Sands, extensive work has indicated that the largest contributor to Dry Mill instability is due to insufficient leaching, as reported by iron excursion reports. Over the life of Namkawa Sands very little work into leaching efficiency has been completed. A few optimisation studies were initiated on the HAL reactor, however these proved inconclusive and were abandoned, due to there being either far too many variables to consider or the difficulty in proving a correlation between what is being measured (temperature, iron in feed, acid concentration or kiln rotational speed) versus the iron conversion.

An internal study at Namakwa Sands by Ledgerwood, (2011) identified and characterised the iron-phases present as bulk minerals and the major surface components of the mineral sand particles. The total iron concentration (of the HAL feed) is a function of the surface based iron contaminants and the gangue minerals (containing iron contaminants). Thus measuring

the true conversion of the surface reaction is very difficult due to the number of separate iron species.

As previously discussed, the theoretical conversion as predicted by thermodynamic data for the endothermic reaction(s) occurring in the kiln is not achieved and is highly erratic. Running the kiln at higher temperatures doesn't translate into higher conversions, but rather the opposite – it results no increase conversions. The reason for this is thought to be due to the formation of a solid product layer at the solid/liquid interphase (on the surface of the mineral as nodules) thus inhibiting the propagation of a reaction front.

3.10.1. Solid product layer formation

The kinetic limitation to the reaction(s) is primarily driven by the formation of a solid product layer around the particle surface (of the minerals) due to precipitation. This creates a diffusion barrier for reaction products, which was postulated by a number of researchers' Veglio et al. (1998), Ubaldini et al. (1996) and Guimares et al. (1987) mention that the decrease in reaction rate is due to the formation of a solid product layer, while Chastukhin et al. (2003) explained this using a chain mechanism theory. Chastukhin et al. (2003) work placed emphasis on the reaction front. It is accepted that the formation of a product layer hinders the rate of reaction, however little evidence is given to indicate what iron phase is precipitated or what the reaction mechanism is.

Researchers mention jarosite (Welham et al., 2000), others researchers mentions goethite (Dutrillac & Monhemius, 1987) while others are positive that the product layer is hematite (Chastukhin et al., 2003).

It is postulated that the primary reason for the reaction not reaching the predicted thermodynamic equilibrium is the increasing solid/liquid ratio within the kiln reactor. When the kiln is run at higher temperatures, the driving force for evaporation increases and this causes the solution to evaporate more rapidly, which changes the concentration of the iron ions within the solution and thus changes the relative saturation point. The result is iron super-saturation and subsequent re-precipitation as hematite/jarosite and gypsum-complex species as 'nodules' (Figure 19).

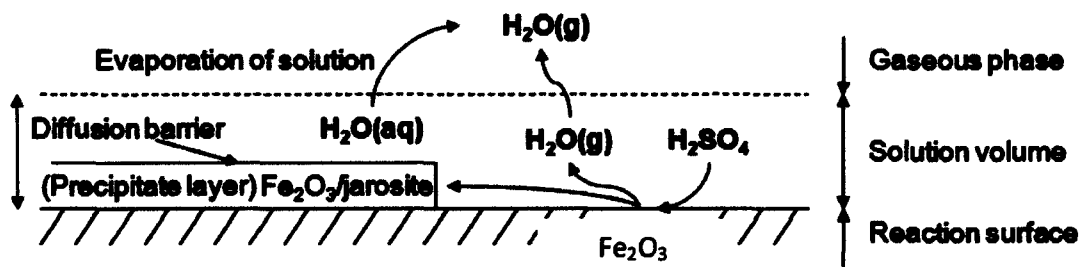


Figure 19: Hypothesis development and illustration

The literature review shows that there seems to be confusion as to what the stability of ferric sulphate is. However, according to most researches at high temperatures, high acidity and drier conditions favour the formation of jarosite/ferric sulphate/proton based complex. It is further postulated that the nodules formed on the mineral surface are complex ferric-oxides-hydroxides.

- (a) Hematite dissolves into solution as ferric, then as the solution evaporates and the concentration of ferric increases and the solution becomes super-saturated, the precipitation of ferric (hydroxides/complex) occurs, which hinders the reaction rate.

CHAPTER 4

EXPERIMENTAL

Primary objectives of the chapter:

- Discuss the experimental methods developed previously by plant metallurgist
- Discuss the use of electrostatic and magnetic separation units.
- Discuss the new experimental methods and what outcomes should be expected.
- Discuss the observations (physical) from experimental work completed.

The following chapter will detail the experimental method followed in this project; it will also detail methods developed by previous metallurgical experts. This chapter will provide the experimental techniques followed, the various samples taken and the method for processing plant samples and laboratory samples.

4 Introduction

This section will detail the various methods and experimental procedures used in developing the understanding of the Namakwa Sands HAL reactor. The experiments were all conducted on site using in the laboratory using smaller scale 1L Pyrex unit inside a oven within a fume cupboard.

The experimental design methodology employed in this study focused on changing one variable at a time while keeping the other variables constant; this allowed for the determination of the effects of each particular variable on the leaching behavior. The primary purpose and objective of the project was to understand the chemical process and the reactions occurring inside the HAL reactors, while optimisation was a secondary objective. Modeling of the process was a third objective. Although there are most definitely interactions between the test variables and measured variables (or both) during leaching, further investigation of these was not part of the project scope.

The objectives of the experiments were to determine the leach kinetics as a function of temperature, acid dosing (kg/ton mineral), acid concentration (% wt.) (solid/liquid ratios) and contact time. The data obtained from the experiments provided basis for developing the fundamental understanding of the various reactions occurring on the surface of the mineral.

The mentioned experiments were conducted by either the author or by other metallurgical support staff during the feasibility study of the Namakwa Sands process.

A substantial number of experiments were conducted to establish optimal operating conditions for leaching and reduced acid consumption. Figure 20 shows the link between the experimental (laboratory) work and the plant surveys conducted. The experiments in the laboratory were set up to represent an ideal case, which is then compared to the plant data and benchmarked according to the rate/conversion for that condition. The kinetic equations developed for the ideal situation were calibrated according to plant data. After each leaching experiment, the iron present on the surface of the zircon mineral is determined by using a fractionation method described later in the chapter and presented during the literature review as described by Stryiakova et al. (2010) and by Tzxiarchou et al. (1997).

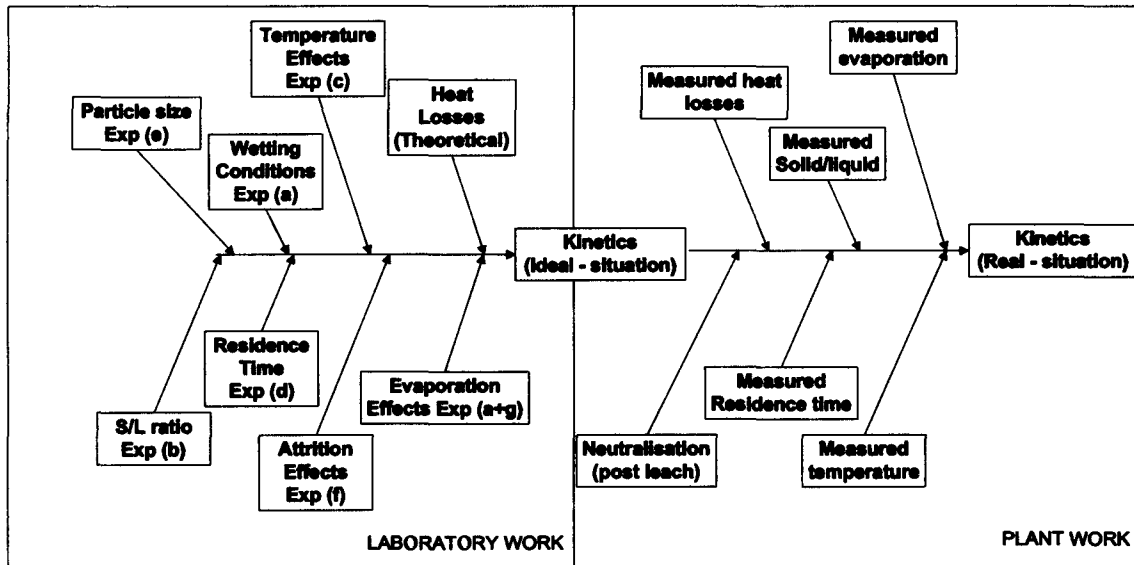


Figure 20: Experimental methodology followed throughout the project

4.1. Heavy mineral characterisation

The first part of the experimental section was the characterisation and feed definition, which looked directly at characterisation of the various metal oxides present, either on the surface of the heavy minerals and/or as the iron contained in other gangue minerals. The characterisation work used magnetic and electrostatic separation for further mineral classification.

The reactor feed material was first treated by means of the isodynamic Franz magnetic separator with coil current of 1.5 A, inclination angle of 30° and axial displacement of 5° with a magnetic flux of 12kG. The magnetic or non-magnetic fraction can be further separated into conductors and non-conductors using the High tension roll separator, run at 80 °C, a humidification of 45% (relative humidity), feed rate of 1.2 t/hr, corona-wire at 28 kV and roll speed at 180 rpm.

The minerals are effectively physically separated into their respective refractory properties, on the basis of magnetic susceptibility and electrical conductivities; as indicated by Figure 21, below; a brief discussion on the properties of these minerals (which was presented in the literature review and thus will not be represented in this chapter).

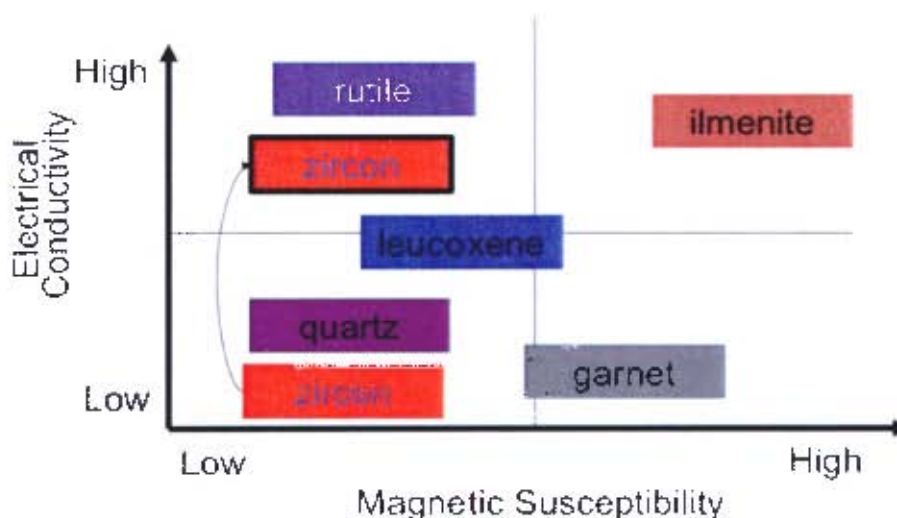


Figure 21: Mineral refractory properties (Philander & Rozendaal, 2009)

The magnetic and conductive fractionation processes is used widely by a number of researches (King, (2003); Philander & Rozendaal (2009), Ledgerwood, (2011). The pure minerals are then sent for a combination of QEMSCAN, X-Ray Diffraction (XRD), X-Ray Fluorescence (XRF) and grain counting is used. It is clear that different ores contribute differently to the reaction dynamics due to the complex mineralogy of the iron/calcium-oxide coatings.

4.1.1. Electrostatic separation principle

Electrostatic separation is based on selective charging of particles. Rutile becomes highly conductive at elevated temperatures while zircon (at elevated temperatures) seems to exhibit

little change in charge (Svoboda, 1993). Charging occurs mostly via corona discharge; however charging could also occur via contact (particle on charged-plate) or friction (particle on particle). Electrostatic separation is based on selective charging of particles (Figure 22). A concentrate of zircon and rutile is introduced at the top of the rotating roll and is carried into a corona field (ionised air field) located between the corona wire and the roll. Within the corona zone particles are charged and can pin to the roll due to electrostatic forces. Higher currents through the corona-wire allow for greater pinning. The turning of the roll allows the material to move through this field. Non-conducting particles lose their charge more slowly and remain pinned to the roll longer. So does fine material that has become entrained in this particle bed, they then detach later or are forced off the roll by the wire brush. As in most physical processes, misplacement causes non-conductors to mix with conductors (Ledgerwood et al., 2011).

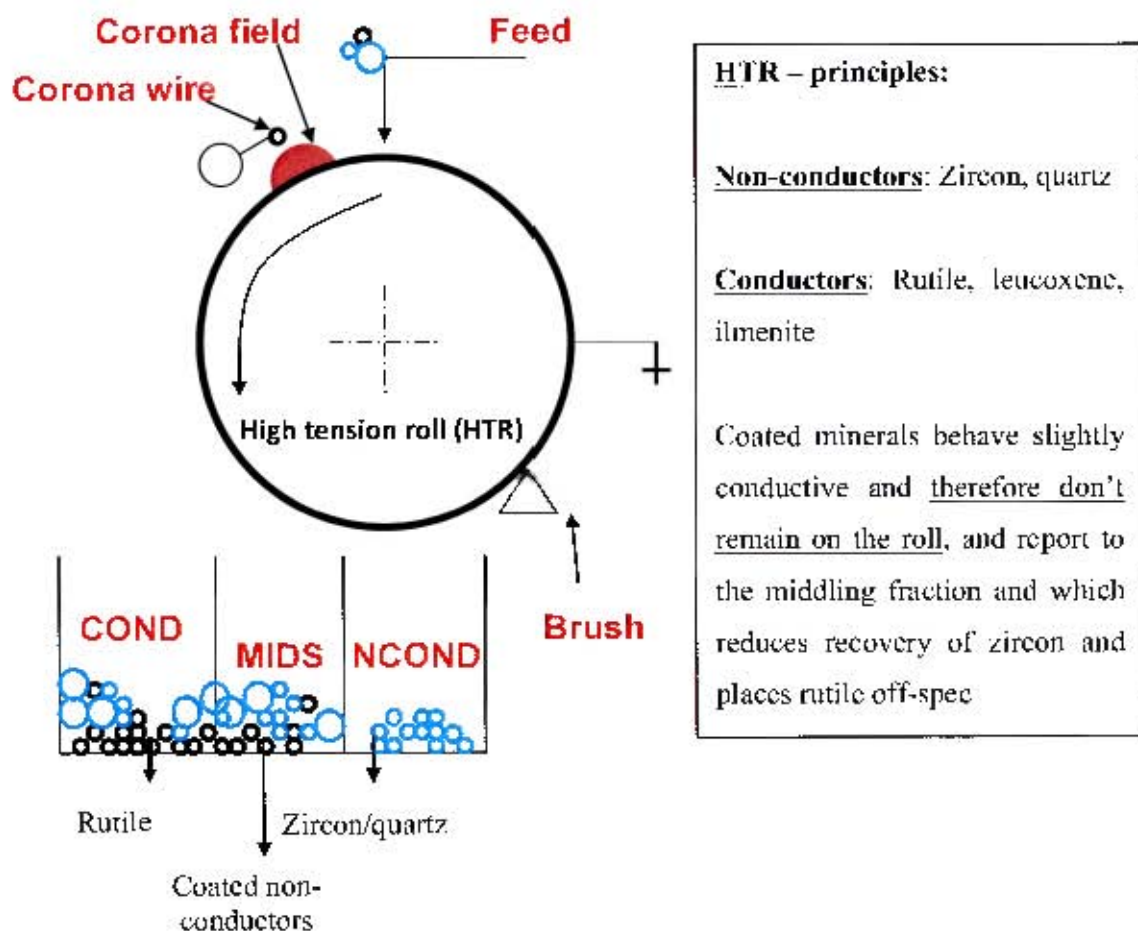


Figure 22: High Tension Roll separating unit (HTR)

4.1.2. Magnetic separation principle

A number of factors affect the magnetic susceptibility of particles and to a large extent these are governed by specific characteristics (refractory properties). If the magnetic force is large enough relative to the non-magnetic fraction then separation will occur. The magnetic susceptibility of particles can be greatly affected by impurities; for instance for zircon coated in hematite the value is 259×10^{-9} Emu/kg, for non-coated zircon: 110×10^{-6} Emu/kg (thus making coated zircon more magnetic) for non-coated rutile 5.9×10^{-6} Emu/kg.

Feed is introduced onto a conveying belt, which arranges the particles such that they form a mono-layer (0.15mm thick). The minerals are conveyed along the belt till they reach the magnetic roll (Figure 23). The magnet (circular) is arranged in a radial direction such to allow the magnetic force to be perpendicular to the axis. The interspacing, which is completed with steel pole pieces, allows concentrated magnetic fields, which allow effective separation of weakly magnetic material. The minerals magnetic susceptibility allows for the particles to be either pinned or thrown from the roll. The turning of the roll allows the material to move through the magnetic field quickly. Entrainment of fine material may occur, however the belt speed and feed layer thickness/feed-rate is adjusted to minimise this. This should be kept close to that of the critical value for separation of the smallest particle (King, 2003).

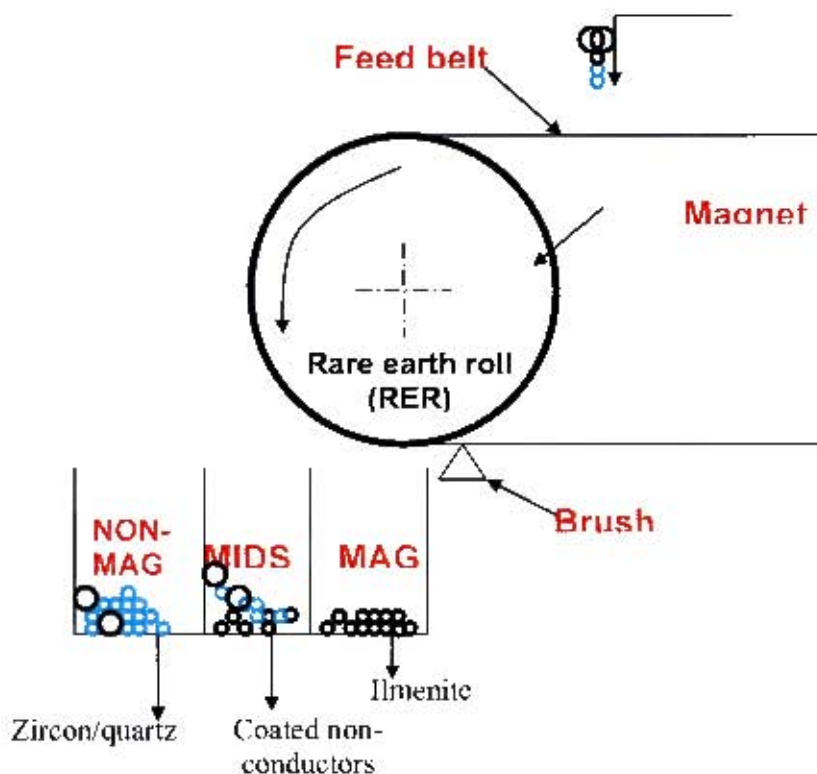


Figure 23: Rare earth roll (RER)

RER – principles:

Non-magnetic: Zircon, quartz

Magnetic: leucoxene, ilmenite

Coated minerals behave slightly conductive and therefore remain on the roll, and report to the middling fraction and which reduces recovery of zircon and places rutile off-spec

4.2. Mineral assemblage determination (feed characterisation)

A few methods were studied to complete the understanding of the leachable iron present on the mineral particles. These included XRD, XRF and QEMSCAN technology – none of the methods proved reliable when used alone. However when used in combination with a physical laboratory method a greater understanding was developed.

XRD results:

XRD results of the HAL reactor feed (Table 15) show that between 58 % - 60 % is Zircon, while between 23.5 % and 24.5 % is Rutile and a small percentage is the pseudo-Rutile at 5 % - 6 % and quartz at 10 % - 11.5 %, the samples indicate that the reactor feed is fairly consistent with respect to mineral feed types, using XRF, on the same samples, tell the same story (Table 16).

Table 15: XRD results on reactor feed - 60% Zircon, 24 % Rutile, 5 % pseudo-Rutile and 10 % quartz.

Mineral	Formula	Sample			
		3e	3f	3g	3h
Zircon	ZrSiO ₄	60	59	58.5	58
Rutile	TiO ₂	24	23.5	25	24.5
Pseudo-Rutile	(SiO ₂) _x Fe _x Al _x TiO ₂	6	5	5	6
Quartz	SiO ₂	10	11.5	11.5	11.5

XRF results displayed in Table 16.

Table 16: XRF results taken during March 2011

Day	Sample No.	Time	Al ₂ O ₃	CaO	Fe ₂ O ₃	MgO	MnO	P ₂ O ₅	SiO ₂	TiO ₂	ZrO ₂
Day 1	1	09H00	1.78	1.65	1.50	0.40	0.09	0.24	29.67	21.16	42.62
	2	10H00	1.79	1.57	1.52	0.40	0.09	0.23	30.02	20.83	42.69
	3	09H00	1.89	1.83	1.14	0.46	0.08	0.25	30.41	22.20	40.93
Day 2	4	10H00	1.73	1.65	1.11	0.42	0.08	0.24	29.18	22.28	42.46
	5	09H00	1.70	1.73	1.10	0.46	0.07	0.25	29.55	22.32	41.98
Day 3	6	10H00	1.75	1.75	2.11	0.44	0.08	0.25	29.78	22.07	40.91
Average			1.77	1.70	1.41	0.43	0.08	0.24	29.77	21.81	41.93
Standard deviation			0.07	0.09	0.39	0.03	0.01	0.01	0.42	0.64	0.82

Combining XRF, QEMSCAN and XRD results:

QEMSCAN technology does not indicate the amount of iron associated with the mineral surface; this still remains a very difficult process, especially as to what phase iron is present as. This problem is solved by combining QEMSCAN, XRD and XRF data and then using a simple laboratory method for fractionation post laboratory leaching (see section 4.3.2.), which is detailed later in the chapter. QEMSCAN data proved the most useful (Figure 24 presented the mineralogy of the HAL reactor feed). However it does not detail the iron contained as mineral coatings, it was found that the best method for determining iron coatings on the surface was by using the physical fractionation test. This method is discussed later in this chapter.

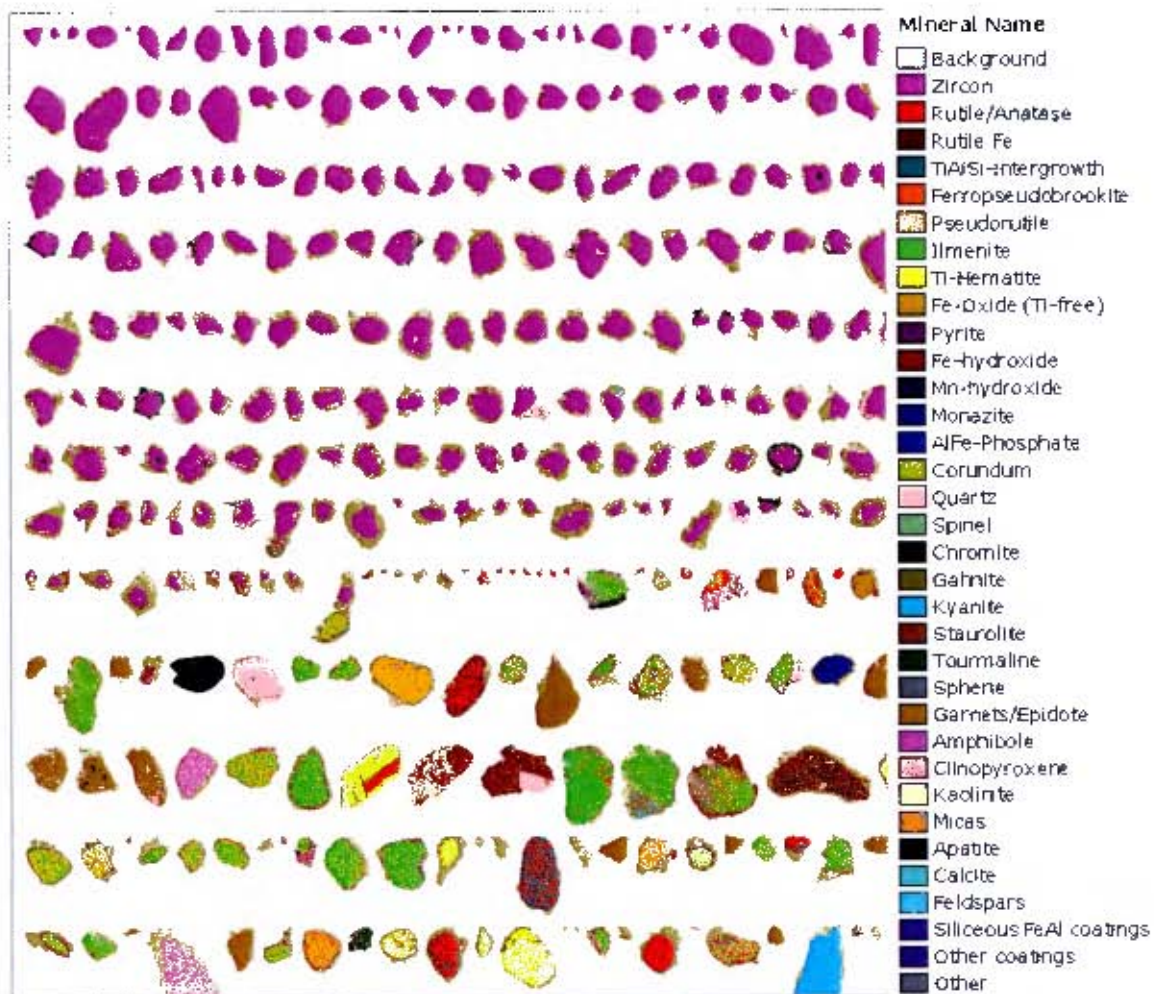


Figure 24: QEMSCAN results of HAL feed

4.2.1. Impurities by particle size:

Another technique used to quantify the percent impurities of the mineral assemblage is by first screening the samples and then using XRF data to quantify the percentage of heavy minerals in each size class. It is clear, from Figure 25, that larger particles contain heavier coatings/more impurities than the smaller size fractions. It is postulated that this is a function of the garnets, kyanite and quartz present at the higher size fractions – their contribution to Fe is quite high.

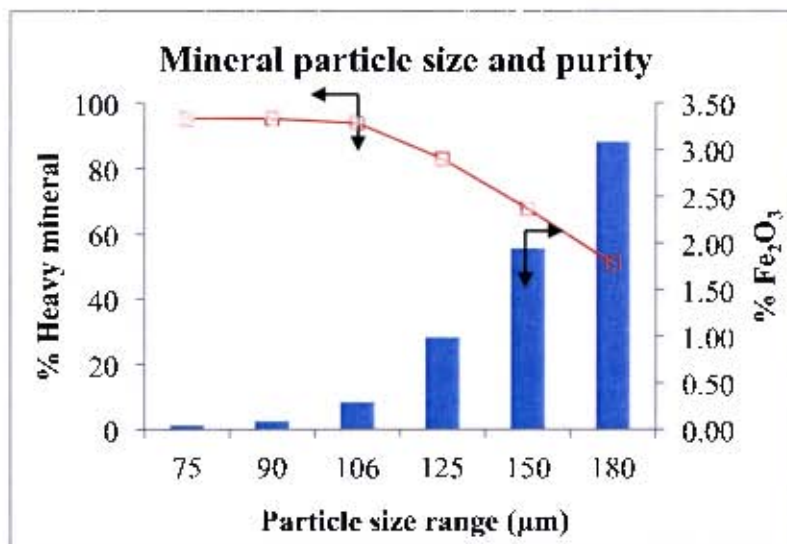


Figure 25: Particle size range versus distribution of gangue material

4.2.2. Influence of surface contaminants on separability:

The effect that surface contaminants have on electrostatic separation is indicated by Figure 26: TiO₂ – based minerals (conductors) are compared to Zircon (non-conductor) separation. For conductor separation, the ideal curve is indicated towards the right hand side, for a pure conductor this curve is relevant. Zircon behaves differently to rutile, with 100 % of the mineral leaving for the non-conductors. A simple demonstration of what the effect of leaching is on recovery is demonstrated in Figure 26 for a sample of HAL reactor feed before and after leaching and attritioning. It can be noticed that mis-reporting of zircon to conductors is reduced by 50 %.

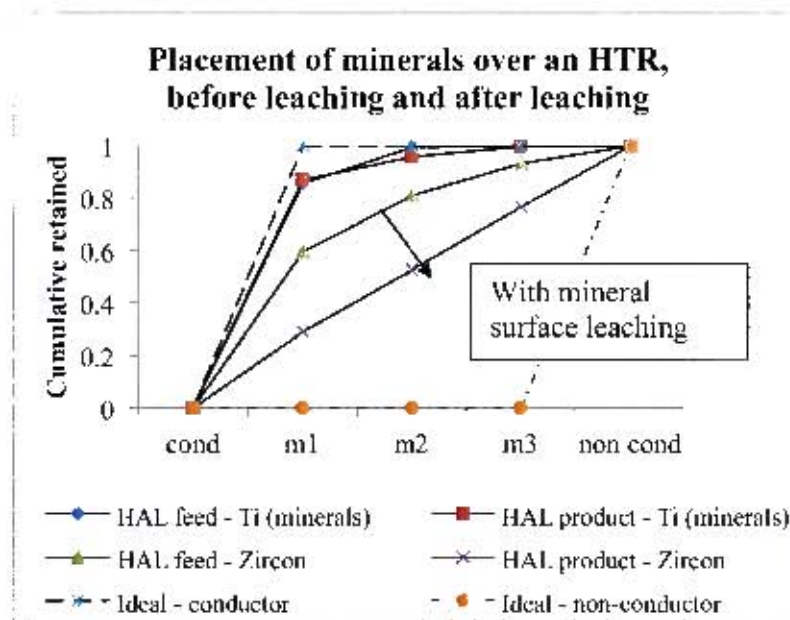


Figure 26: Placement of minerals across an HTR (conductor - separation step) before and after leaching (cond – conductor, m 1-3 middling's fractions and non-conductor)

4.3. Experimental set-up and procedures

The main tests that will be conducted are presented in the following sections.

Batch (1kg) samples were taken from the HAL reactor feed, these were first split using a rotary riffle type splitter into 100 g samples. These were each pre-heated to the desired temperature before being used in the leaching process. Each 100g sample, (details in Table 16 and Table 15) containing on average 42 % ZrO_2 , was leached using sulphuric acid at atmospheric pressure and at temperatures ranging from 60 °C to 170 °C. Acid bake tests were conducted in a baking tray type reactor and placed into an oven which was set at the relevant temperature.

The concentration of the sulphuric acid was varied from 20% wt to 40% wt. The solid-to-liquid ratio was also varied from 1 to 17 for leach tests. The leach residence time was also tested and this ranged from 5 minutes to 2 hours.

For all tests approximately 100 g of sample was slurried in sulphuric acid solution to the target solid-to-liquid ratio, with the targeted acid concentration. Ore leaching was conducted in both sealed and open 1L Pyrex beakers at atmospheric pressure. The unit is then placed in a preheated oven at a desired temperature. The oven is heated by means of electric heaters to

ensure that the target temperature was achieved. A thermometer was used to measure the temperature whenever a sample was taken. When agitation was required a glass rod was used and agitation was completed for a fixed period of time over in the same direction each time. Sealed units were not agitated while units open to the atmosphere were. The leach set-up was done in a fume cupboard.

Slurry samples of 10 ml were collected at the following times, namely 10, 20, 35, 60, 90 minutes, as well as final or main solutions and residue samples (making a total of 6 liquors and 6 solids). The filtered sample residues were re-pulped with 100 mL of acidified water (pH=0.6), followed by a flood rinsing with 100 ml acidified water (pH 2.5) and finally a second flood rinsing using 100 ml de-ionised water.

4.3.1. Laboratory techniques applied

At the end of each leach test, the volume of the entire contents of the reactor was measured and the mass of the slurry recorded, after which the slurry (mixed with 100ml of acid water pH=0.6) was attritioned via a WEMCO cell for 20 minutes. Afterwards it was filtered and a filtrate sample was taken for chemical analysis. The total volume of the filtrate was recorded. The total wet mass of the residue was also recorded. The filter cake was washed twice by re-pulping with acidified water (pH=0.6 and pH 2.5) to prevent ferric from precipitating. This was then followed by flood rinsing of the cake using deionised water. The washed residue was dried, pulverised and analysed for Mg, Al, Si, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, U, Zr Th and Pb by XRF with a detection limit of 500ppm. Fe and Ti was analysed by ICP MS whose detection limit is 10 ppm.

All filtrates and wash waters samples were analysed for Fe, Ca and S, by ICP-OES with a detection limit of 2 ppm for all elements, except for S, which is 5 ppm. The solution samples were also be submitted for Zr and Ti analysis by ICP. U and Th in solution was analysed by ICP, the detection limit is 2 ppm. The free-acid concentration was determined by titration and then be recorded.

4.3.2. Method to determine the iron remaining on the surface

To determine the remaining iron on the mineral surface of zircon, the dried residue samples were separated using the High Tension Roll unit (Corona-stat) and the iso-dynamic Fritz separator to fractionate into their respective 'pure' minerals. This resulted in almost pure zircon, which could then be sent for XRF and grain-count. The iron present on the surface

was then determined by using the laboratory process as is illustrated in Figure 27. A mass-balance for iron is completed after each step, by taking cognisance of the iron present internally as part of the crystal and as part of the remaining iron on the surface.

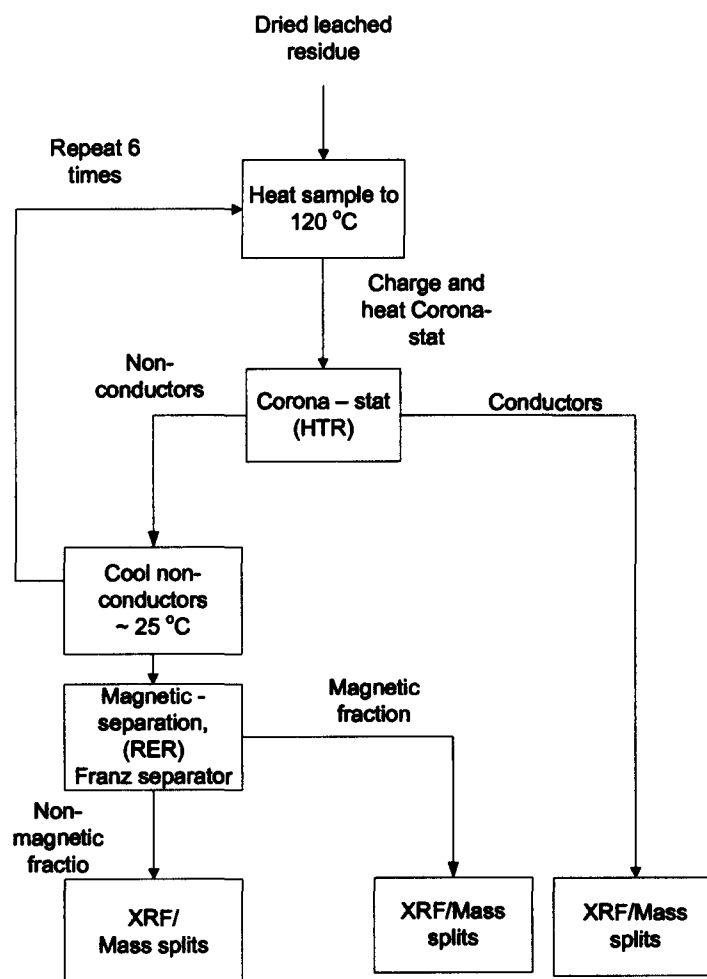


Figure 27: Fractionation of minerals (for determining iron remaining on surface)

4.3.3. Evaporation effects on leaching

The first test was to investigate the effects of evaporation on the leach kinetics. For all tests the mineral is first pre-heated to 120 °C. The evaporation tests were done using the Pyrex unit, by either keeping the reaction vessel lid open or closing it. The reaction vessel (1L-Pyrex) was used for all tests - a glass rod achieved manual agitation. The Pyrex vessel was preheated to 120 °C, using an oven. The experiments were conducted in the oven and held at a constant temperature. The pre-heated solids were added to the reactor vessel before the solution was decanted into the vessel. Pre-made volumes of acid and water were set out

before each experiment. These were then added to the Pyrex unit first water then acid. The lid was closed directly after adding of the solution to the solids. The solid/liquid ratio was kept constant at 13 kg/l.

4.3.4. Acid concentration and dosing ratio effects

The effects of acid concentrations and dosing were determined by adding various concentrations of acid to the mineral. This was done in three S/L ratios; 10.4, 6.62 and 4.7 (concentration of acid was changed each time). The reactor Pyrex vessel was preheated to 170 °C using the oven and insulated using thermo-insulation. The mineral was preheated to 170 °C using a hot-plate. Once the mineral achieved the desired temperature it was removed from the hot plate and added to the Pyrex vessel. All the tests were conducted in the oven. Stirring was achieved by manual glass rod agitation. The acid strength and dosing rate were changed in this experiment while the temperature was set. The reaction residence time was maintained at 90 minutes.

4.3.5. Temperature effects on leaching

The effects of temperature were tested for 90 °C, 110 °C, 140 °C and 170 °C; which were maintained throughout the whole duration of the experiment (4 repeats test were conducted at a single temperature). A single test was completed at 60°C. The experimental setup was done using the same 1L Pyrex unit, as in previous experimental. The unit and mineral were both preheated to the required temperature. Stirring was achieved by manual agitation using a glass rod. The residence time was maintained at 90 minutes while the acid concentration was 30% m/m and the dosing was 23 kg/ton.

4.3.6. Residence time test work

The residence time effect for the mineral sand was conducted using set acid dosing rates and acid strengths. The reaction time however varied, while the condition and temperatures stayed constant at 170 °C, 140 °C, 110 °C and 90 °C (Table 17). The reactor Pyrex vessel was preheated to the desired temperature using the oven and insulated using thermo-insulation. The mineral was preheated to desired temperature using a hot-plate. Once the mineral achieved the desired temperature it was removed from the hot plate and added to Pyrex vessel. All the tests were conducted in the oven. Stirring was achieved by manual glass rod agitation. All discharges from each test were conditioned using the WEMCO cell for 20 minutes as previously discussed.

Table 17: Residence time effects test

Test no	Strength % (m/m)	Add rate kg/t	Preheat time (min)	Reaction time (min)	Temperatures (°C)		
					Wetting	Start	End
1	30	23.0	20	10, 30, 60 ,90	amb	170	170
2	30	23.0	20		amb	140	140
3	30	23.0	20		amb	110	110
4	30	23.0	20		amb	90	90
5	30	23.0	20		amb	60	60

4.3.7. Variation in solid/liquid ratios

High and low solid/liquid test were also conducted to investigate the influence of solid/liquid ratios on the reaction endpoints. The tests were conducted under various acid strengths and acid addition rates (Table 18). The reaction times were constant, together with the start and end temperatures. All these tests were completed in a 1L Pyrex reactor vessel; agitation was achieved by manual stirring. The vessel was also placed in the oven for a fixed temperature 170 °C.

Table 18: Solid/liquid test plan

Test no	Strength % (m/m)	Add rate kg/t	Reaction time (h)	S/L ratio	Temperatures
					Start/End
HI 1	20	23.0	1.5	13.38	120
HI 2	30	36.3	1.5	8.20	
HI 3	40	51.1	1.5	6.64	
HI 4	20	14.6	1.5	11.11	
HI 5	30	23.0	1.5	11.79	
HI 6	40	32.4	1.5	8.80	

4.4. Plant trials

Plant trials were conducted to measure the current performance of the HAL circuit. This was done in two phases, the first was conducted over a period of 24 hours and the second was

conducted over a period of a month. The temperature, pH and density were measured all on site before samples were taken to the laboratory for further analysis using ICP and XRF.

4.4.1. Plant sampling and utilities

Plant surveys were completed in the course of 2011. These included taking samples of the HAL discharge and measuring discharge temperature and moisture, while also submitting samples for ICP and XRF analysis. Composite samples of the reactor feed were taken over the same period. Bed level measurements of the reactor discharge were measurement and the reactor rotation speed was taken. Residence time distribution studies on the reactor were completed using tracer studies and the BLUE CUBE SYSTEM (Huisamen, 2000). A mass balance of the system and energy balance was conducted and confirmed by taking samples for both temperature analysis and ICP for the HAL reactor.

Two plant surveys were conducted; one was conducted over a period of 24 hours while the other was conducted over a period of 25 days. The first sample campaign was completed to establish the variation in HAL circuit pH, iron removal, iron and calcium concentration. The second was conducted to see the variation over a period of 25 days with regards to pH, free acidity, calcium and iron as residuals and in solution. Samples were taken throughout the whole HAL circuit, taken three times a day. These were analysed for residual iron and dissolved iron in solution. An example of the laboratory processes followed for plant samples has already been discussed (Figure 28). The mass balancing principle followed from the data collected for each sample.

4.4.2. Laboratory leaching test work on plant surveys samples

Samples from the plant were first re-slurried, and then attritioned using the WEMCO cell at 80 % solids for 20 minutes at 50 °C. The residue is sent for physical separation work (section 3.3.3) the non-conductor and non-mags fraction (containing majority zircon) is then sent for XRF. The total iron present as a function of the mineral coating is determined.

The samples are then re-leached, conducted in 1L Pyrex vessels. The reactor vessel was maintained at a constant temperature and controlled at that temperature: 160° C and similar conditions to that of a second stage HAL reactor (solid/liquid ratios: 10.8, acid concentration 40% and dosing 40 kg/t). The reactor vessel (1L Pyrex) was agitated intermittently. The re-

leached residue was then attritioned using a WEMCO cell at 80% solids and at 50 °C, then diluted using acidic water as illustrated in Figure 28.

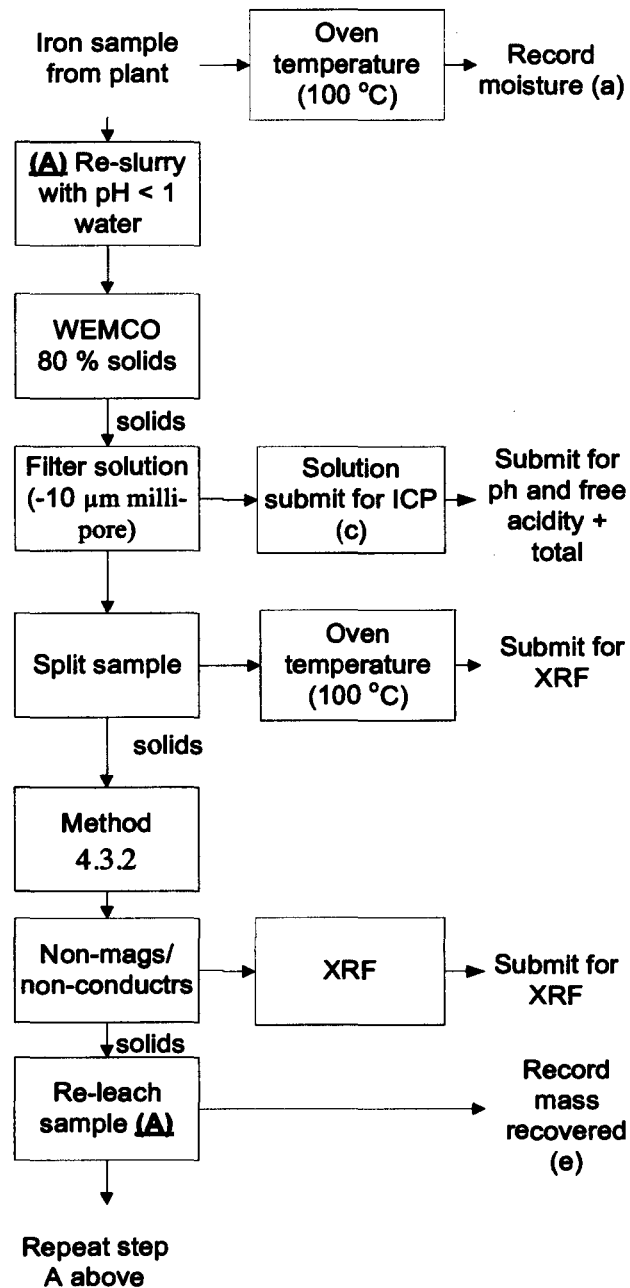


Figure 28: Schematic of method followed for processing plant samples

4.5. Analytical methods

Various analytical methods were used for determining the percent iron and calcium present in solution and remaining on the mineral surface. The two most commonly used methods were

the XRF method together with the ICP-OES. Together these two methods provided this investigation with a mass-balance for computing the leached iron and calcium. The pH of solution was measured using a pH probe, free-acidity was measured using titration of NaOH to an endpoint of pH=4, while total acidity was measured to a pH endpoint of 8.3.

4.5.1. X-ray diffraction methods (XRD)

XRD was used to characterise the proportion of various minerals present as heavy minerals or gangue in the reactor feed. However, experimental samples throughout the leach test work were submitted for XRF rather than XRD, due to the time constraints, availability and the cost of XRD compared to XRF.

Each sample submitted for XRD was subjected to the following procedure, a representative portion of each sample was milled to 100% -20 μ m and prepared for XRD using a standard back-loading preparation technique. It was analysed with a PANalytical X'Pert Pro powder diffractometer using Co radiation with an X'Celerator detector and variable divergence and fixed receiving slits with Fe filtered Co-K α radiation. The phases were identified using X'Pert Highscore plus software. The phase amounts (in weight percent) were determined using the Autoquan software for Rietveld refinement. (Richards, 2011)

4.5.2. X-ray fluorescence (XRF)

Samples submitted for XRF were subjected to the following procedure: a representative sample (80g) from each leach residue was taken and milled to 100% -20 μ m. Then 1g was mixed with 10g of Merck™ flux. The combined flux and milled leach residual was placed in a fluxer where the material was fused at 1600 °C. After fusing for 10 minutes and cooling for 5 minutes the pebble is sent to the X-ray fluorescence machine for analysis. The XRF mineral sand program was used and is certified to measure Mg, Al, Si, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, U, Zr Th and Pb by XRF with a detection limit of 0.05%.

4.5.3. Inductively coupled plasma (ICP) spectroscopy

Leach liquor/filtrates were sent for ICP analysis to determine the metals in solution, Fe, Ca, Al, Cu, Ni, Zn and S, by ICP-OES with a detection limit of 2 mg/L for all elements, except for S, which is 5 mg/L (Manning & Grow, 1997).

4.5.4. QEMSCAN

Samples that required QEMSCAN were sent to Exxaro –R&D site in Pretoria. QEMSCAN creates mineral compositional maps of the sample surface by scanning the surface with a high-energy accelerating electron beam. The software used was developed at the Julius Kruttschnitt Mineral Research Centre at the University of Queensland specifically for mineral sand ore-bodies such as Namakwa Sands; the Mineral Liberation Analyzer (MLA) and Particle Mineralogical Analysis (PMA) expert software (Richards, 2011).

4.5.5. Blue Cube systems

The blue cube unit uses diffuse refractive spectroscopy to identify the minerals present in a stream; light is transmitted from a source in the optical processor via optical fibres housed in a protective hydraulic hose. The light is then reflected off the mineral surfaces as they pass the source, reflected light is transmitted back to a spectrometer which produces raw spectra of the passing minerals. This information is then translated to a mineral percentage using a correlation based on absorbed/reflected spectra and mineral phase (Jansen, 2001). The Blue Cube units were placed on the feed and discharge to the reactors, so that residence time tests could be conducted. A tracer 10% rutile (inert) was added to the feed of the reactor.

CHAPTER 5

RESULTS AND DISCUSSIONS

The primary objectives of the chapter:

- Present experimental results (historic and current)
- Discuss the results obtained
- Link the laboratory data (on baking) to plant observations

The following chapter will detail the results achieved during the laboratory test work, and will also produce historical results, and the various plant surveys completed.

5 Introduction

From a historic point of view, leaching has always been of prime interest to Namakwa Sands. The dynamic ore-body (variation of minerals and concentration) and heavily coated heavy mineral particles challenge the separation processes. An internal report by Bentley (1990), explains the extent of the test work carried out before a technological leaching solution was found for removing the coatings. The report details that a number of companies worked on the leaching process; these included AMMTEC, Reading and Anglo American. However of these three only the Anglo American results were trusted. This chapter will detail the results obtained from plant and laboratory work, an analysis will be done and a discussion on the analysis will follow. Plant surveys in combination with the mass and energy balances are presented first and then the laboratory work is listed, each followed with a discussion. A summary of the section brings together the laboratory and plant work.

Plant surveys

These were carried out during winter and summer months, night and day times. The results from these surveys were used to match the mass and energy balances computed over the kiln reactor. Plant surveys measured temperature at the feed and discharge ends. Data such as moisture conditions, dew points and atmospheric temperatures were recorded. The plant survey samples were sent to the on-site laboratory, where both the solution and the residue (solids) were analysed (see section 4.3.1.). Residence time analysis was also conducted on the kiln reactors.

Laboratory tests

These experiments were conducted in on-site laboratory (see section 4.3). The experiments look at testing specific conditions, which will be detailed in each subsection.

5.1. Plant surveys

The feed composition and the analysis of the mineralogy over the course of the survey can be found in Table 18. The results show that for the iron in the feed the values remained fairly consistent. However leach performance was very erratic throughout the month, as shown in Figure 20. The outcome was a program of interventions where a number of trials were run; leaching parameters such as solids feed temperature, acid concentration (S/L ratios) and residence times were changed. The interventions showed no consistent improvement. The fact that nothing assisted in improving the consistency brought about the current study, (as highlighted in the introduction) which aims to understand the leaching dynamics of the HAL reactor.

5.1.1. Benchmarking reactor performance

The HAL reactors were benchmarked with regards to their performance; this was done to understand the variability in leaching by each reactor. To benchmark the reactors' performance, samples from the reactor discharge were taken and subjected to another laboratory leach step, to test the 're-leachability' of the sample. The same test was used on samples from both reactors. The re-leach step (see section 4.4.2) involved leaching the contents of the reactors at 80°C for 30 minutes at 40 wt.% H₂SO₄ on a hot plate. The leaching vessel was closed for this test. Afterwards the sample was then processed and fractionated into magnetics and non-magnetics. The sample fractions were then sent for XRF analysis. The results are presented in Figure 29. The 're-leachability' is an indication of poor reactor performance, and it is undesirable to have a high re-leachability percentage.

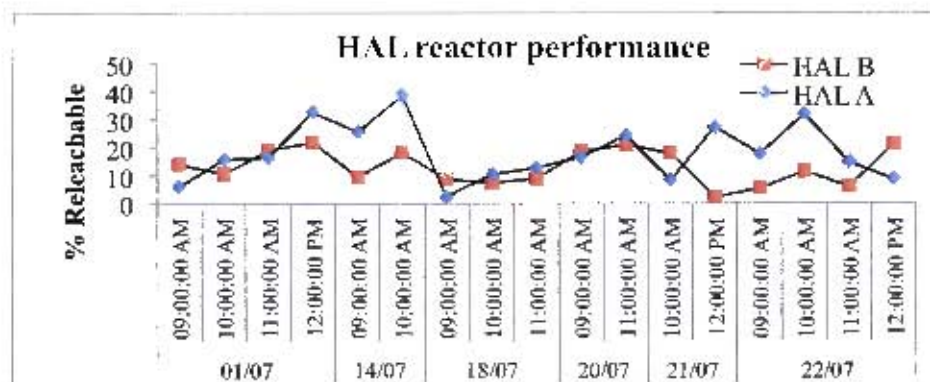


Figure 29: Reactor performance during 2011 ($T_{\text{feed}} = 160^{\circ}\text{C}$, $S/L = 10.8$, 40 wt% H_2SO_4)

Operators had noted that there always seemed to be a large difference in the leaching performance of the one reactor compared to the other. From Figure 29 it is evident that there is no obvious trend relating to the time samples were taken at (which was across a month), however it appears as though reactor B (HAL B) is the more consistent reactor. The reason why this is thought to be is due to better ‘insulation’ of reactor B (i.e. lower heat loss to the environment), and that reactor B is the newer reactor installed during second phase of Namakwa Sands.

After a careful revision of the various parameters that could affect the reactor performance, it was thought that the variance is a function of external conditions, primarily the large temperature differences between day time (highs) and night time (lows), which can be as much as 20°C . Figure 30 shows the day and night-time temperatures during the monitoring period (1 – 22 of the July). The average day temperature was between 20 and 28°C while the nighttime temperatures was much lower at between 4 and 6°C . The differences in these temperatures affect the discharge temperature quite significantly. Whether the effect on leaching is a function of higher evaporation rates during hotter days or energy lost to the environment is the subject of this investigation. It is evident that the daytime temperatures affect the reactor conversion.

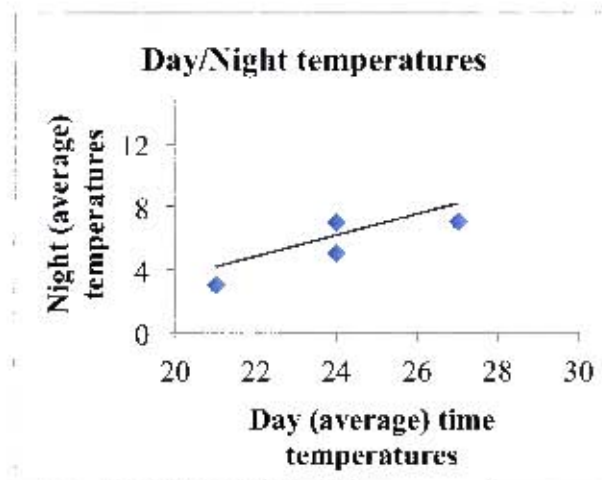


Figure 30: Daytime and night time temperatures (in Koekenaap, 7 km from the plant), data taken during sample period

The heat balance across the reactor does seem to be a strong function of the mean day temperatures. This is illustrated in Figure 31, which has conversion correlated to the reactor discharge temperature (on the left vertical axis and conversion for both reactors on the right vertical axis) while mean day temperature is on the horizontal axis. Samples from the reactor were taken and method applied discussed in Figure 28 was used to analyze these.

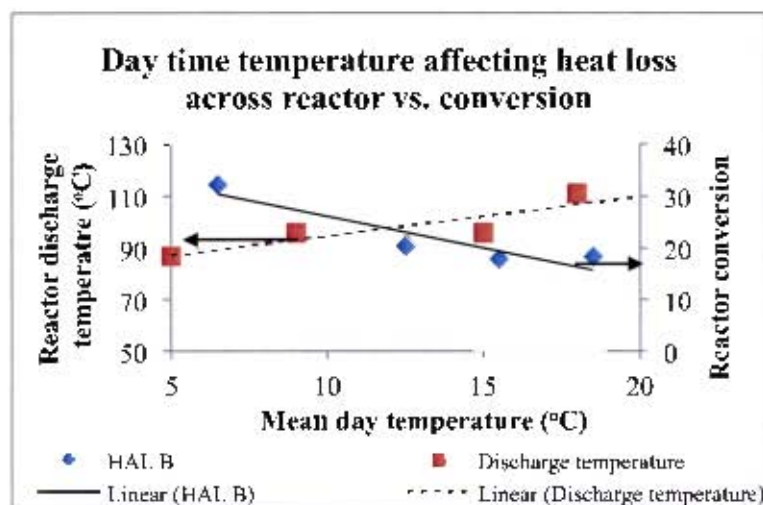


Figure 31: Reactor discharge temperatures as a function of mean day temperatures and conversion

The discharge temperatures can vary from 86 °C at mean day temperatures of 5 °C to 110 °C for mean day temperatures of 18 °C. A clear correlation seems to exist between discharge temperature and mean day temperature. An increasing trend in discharge temperature with

both reactors tends to be caused by higher mean day temperatures as presented in Figure 31. The phenomenon was also noticed when higher feed temperatures were set (170 °C, 180 °C and 200 °C) – the higher feed temperatures resulted in higher discharge temperatures but hardly any change in the iron conversion. The temperature of the acid feed was constant.

It has been reported by Li et al., (2002) that climate conditions can greatly affect the heat transfer inside a kiln and that large temperature differences ($> 10\text{ }^{\circ}\text{C}$) can cause increased thermal inefficiencies. The Namakwa Sands environment is such that during the months of winter the outside mean temperature average ($5 - 6\text{ }^{\circ}\text{C}$) while during the day time in summer this value can be as high as $45\text{ }^{\circ}\text{C}$. The sensitivity analysis, from the mass and energy balance (see Appendix E for full mass balance by Huisamen (2000)), indicates that the reactors are not as sensitive to low air temperatures i.e. ($<5^{\circ}\text{C}$) as previously thought, and these calculations indicate that evaporation accounts for 63% of the energy lost (Figure 32). The simple mass balance conducted clearly shows contradicting results, as the data presented in Figure 31 showed that external air-temperature does influence the reactors discharge temperature and iron conversion. Li et al. (2002) clearly states that climate conditions affect the reactor internal heat conditions. Hence the need to develop an in-depth MATLAB model.

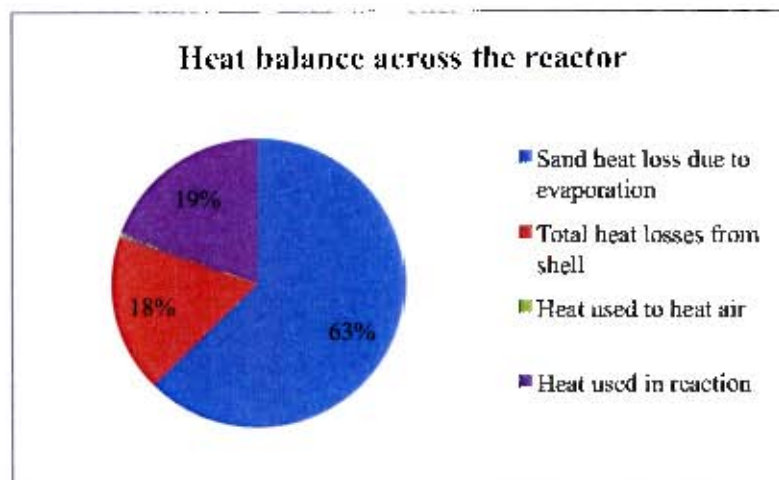


Figure 32: Heat and energy balance across reactor ($T_{\text{discharge}}=100\text{ }^{\circ}\text{C}$, $T_{\text{feed}} = 160\text{ }^{\circ}\text{C}$, discharge moisture 4 %) by Huisamen (2000)

The images also indicated that the heat losses around the discharges (stack column) and the inlet chute were excessive (Figure 33 illustrates the thermal images).

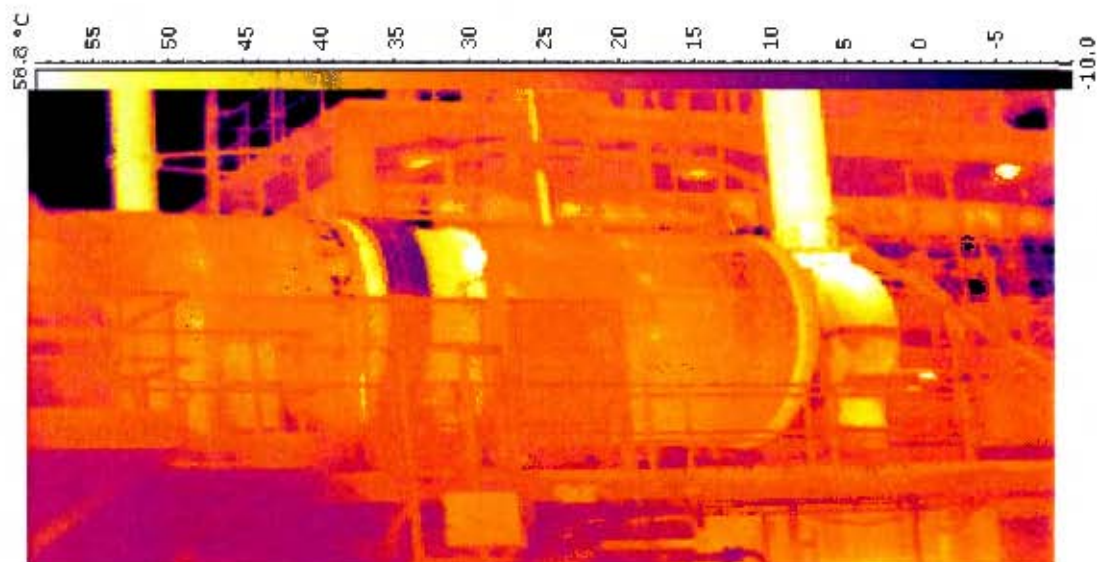


Figure 33: HAI. B discharge thermal image

Thermal analysis images were taken (infra-red detection) which clearly indicated that the majority of the heat losses occurred from the discharge of the kiln, which is due to fact that most of the water escapes through the discharge stack and condenses as it passes, thus releasing energy and subsequently reducing the energy available for the endothermic reaction.

5.1.2. Heat losses and moisture content at discharge

Heat balance calculations were based on the mass and energy assumptions, which take heat losses across the kiln into consideration (this model is a variation of that developed by Huisamen (2000) and is presented in Appendix A). The balance is validated against measured parameters: discharge and inlet temperatures, moisture conditions and S/L ratios. Comparing the moisture conditions calculated to what was measured proved quite successful as a method of validating the mass and energy balance (at a specific feed and discharge temperatures). Figure 34 displays both the calculated values and the measured values. Samples were taken from the reactor discharge under a number of different conditions (small changes in S/L ratios, specifically the concentration of acid in the feed) and feed temperatures (150–160°C).

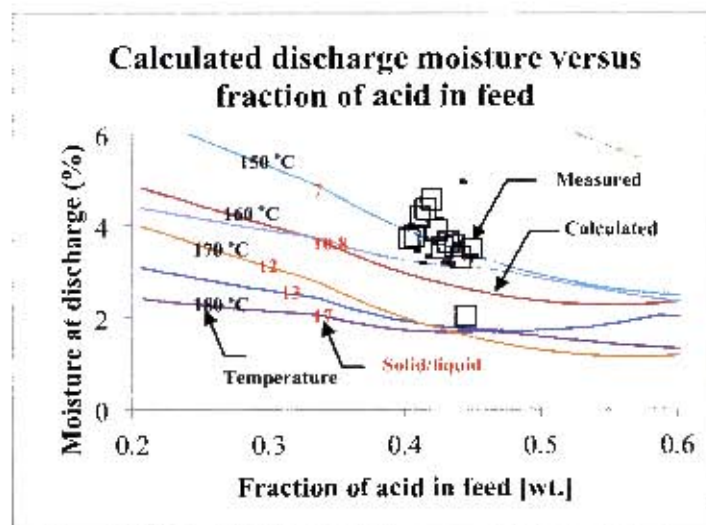


Figure 34: Calculated discharge moisture versus fraction of acid in feed, at 40 ton/hr and initial temperature = 120 – 180 °C, solid/liquid ratio = 7 – 17

The reactors at Namakwa Sands are run at 160 °C feed temperature and at a solid/liquid ratio of 10.8. From Figure 34 above, it is evident that for these conditions the moisture on the discharge, according to the balance, should read between (3 and 4)% which is quite close to the measured values obtained, indicating that the assumptions in the mass and energy balance calculations were close to reality.

The discharge moisture measured values, which are quite similar to the mass and energy balance calculations further support the balances completed in the previous section. This section drives the idea of evaporation and how it affects the heat available for reaction. Also drawn from these analyses is that heat conditions (discharge temperature) tend to be variable with regards to the mass of liquid that evaporates and heat losses across the reactor is largely dependent on the loss to evaporation.

The balance highlights the importance of solid/liquid ratios, Figure 34 illustrates that for a given acid feed (vertical straight line) different solid/liquid ratios are achievable. The complexity of the system is intriguing: the mass of water/moisture at the discharge is highly dependent on the acid/water concentration (according to the V/L diagram – Appendix A) - as the concentration varies, the boiling point of the solution differs and thus the mass of water evaporated differs. The chemistry of the principal ions in solution at different moisture contents and solid/liquid ratios will be presented later as part of the laboratory work. It is clear that if conversion is strongly influenced by the discharge temperature and discharge

temperature strongly influenced by discharge moisture, then, as noted above, the conversion will then also be heavily influenced by the solid/liquid ratio/acid concentration.

5.1.3. Acid concentration on mineral surface

The concentration of acid on the mineral surface can be calculated using the mass and energy balances and then compare to actual free-acid and total acidity measurements at the discharge. Down the length of the reactors it is expected that due to evaporation the concentration of acid will increase. Higher concentrations of acid on the mineral surface is useful for the reaction, however this changes the type of speciation (of metal phases) present on the mineral surface

The free-acid and total acid is determined through a steady state mass balance around the discharge (quench sump) of the reactors. The balance assumes that any free acid in the quench sump will be due to the free acid added by the reactor discharge. During quenching large volumes of make-up (Stream 20 – Figure 35) is added to the sump, which dilutes the true concentration of acid on the mineral surface. It is therefore expected that the true (free-acid and total acidity) concentration would be higher than the measured value. This is illustrated in the Figure 5, this diagram and the streams in the diagram can be found to (see section 2.2. Detailed description of the Hot Acid Leach (HAL) circuit).

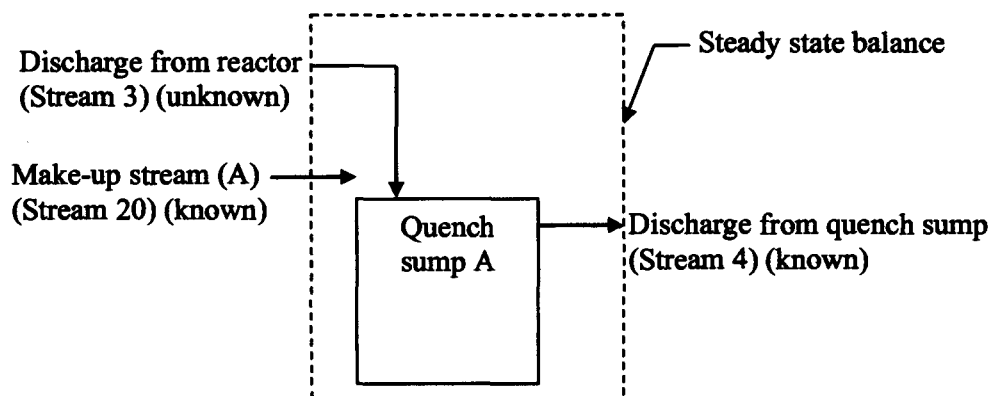


Figure 35: Mass balance across the quench sump post the kiln reactor to determine free acid and total acid (SO_4^{2-} and H_2SO_4) on mineral surface

The measured and calculated acid levels (as a percentage concentration m/m) on the minerals surface (vertical axis) at the discharge of the reactor are displayed in Figure 36, versus the concentration of the feed (horizontal axis) at different temperatures and solid liquid ratios (solid lines).

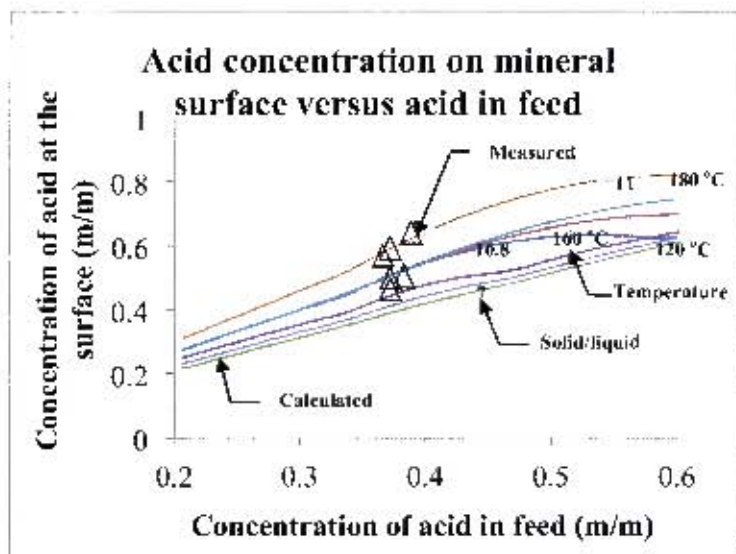


Figure 36: Acid concentration on mineral surface versus acid in feed, feed = 40 ton/hr, initial temperature = 120 – 180 °C, solid/liquid ratio = 7 – 17.

The balance indicates that depending on the extent/conversion of the reaction, the free acid levels vary within the quench sump. This balance revealed that the free acidity on the mineral surface post the discharge varies from 60% to 45 % (m/m). It is evident from this Figure 36 that for any given feed combination (acid/temperature and solid/liquid ratio) the acid concentration on the mineral surface is higher post leaching than what is fed. This Figure confirms the fact that large volumes of water are evaporated across the reactor and thus the concentration of acid increases towards the discharge.

The conclusion that one may draw from Figure 36 is that, under all conditions presented, the acid concentration on the mineral surface always increases towards the discharge end. The same balance also noted that very little acid was consumed in the process.

5.1.4. Reactor residence times (measured)

Mean reactor residence time (MRT) studies were completed by Huisamen (2000) with the help of Blue Cube technologies. The Blue cube unit was tared against the normal HAL feed. Then, after a given time, a slug of ilmentite was introduced into the feed (in addition to the normal feed). The unit of detection is further detailed in the experimental section (see section 4.5.5).

The measured mean residence time (MRT) corresponded well with the calculated value of 20 minutes for HAL A and HAL B (Appendix F). The distinct pattern seen in Figure 37 indicates (for all three tests) an internal recirculation is occurring, which can be explained by the fact that the kiln has a smooth surface on the inside. During a rotation, while most material is displaced axially, 'sticky' particles tend to remain on the inside surface, which represent a dead volume with a slow exchange with the moving charge hence the appearance of recirculation.

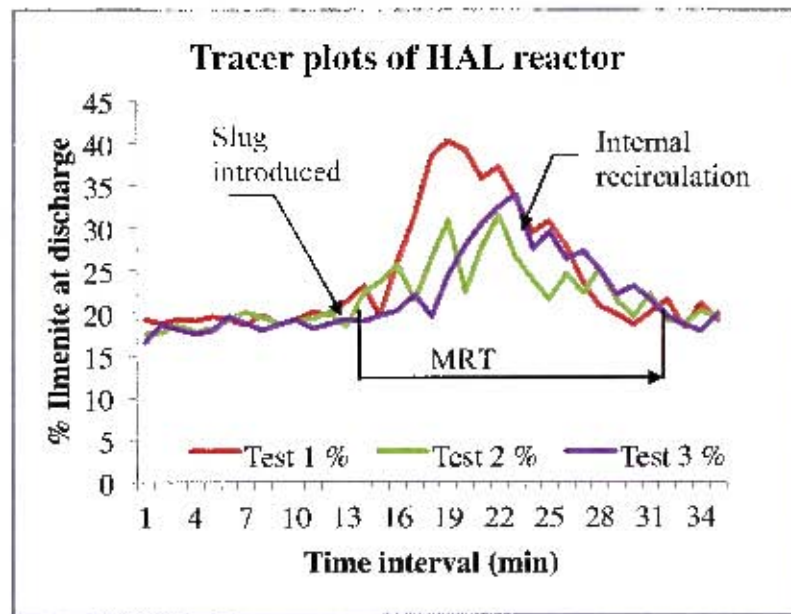


Figure 37: Mean Residence Time of reactors (HAL A&HAL B) is 19 - 30 minutes

It is interesting to point out that both reactors have the same Length/Diameter ratio = 9. While the one is larger than the other, they both exhibit the same residence time at a specific volumetric filling. A number of studies conducted around the reactors revealed that the rotational speed of the reactors does not influence the residence time significantly, due to the low volumetric filling (< 20%). The angle of declination is 2° from the horizontal and is the same for both reactors.

The back-mixing and internal recirculation phenomenon was observed by other authors (Eckehard et al., 2010), (Li et al., 2002) and (Xiao Yan & Eckehard, 2006). Their work suggest that axial transport of solids mainly occurs in the active layer of the bed surface while solids in the stagnant region under the bed surface only turn around the kiln axis without axial

displacement. As rotation speed increases it is expected that the number of particles retained in the active layer increases, which further results in increase in the particles axial displacement per unit time. Their work also suggested that residence time in the kiln-reactor is largely a function of the percentage volumetric fill rather than volumetric flow (Xiao Yan & Echehard, 2006). This was also confirmed again by work Echehard et al. (2010). Work compiled by Li et al., (2002 part 1 & part 2) indicates that with their rotating kiln (L/D ratio of 6, Namakwa Sands HAL A/B ~ 9) an increase in rotational speed from 2 to 8 rpm shows that the mean residence time decreased from 10 to 4 minutes, respectively. It was then suggested that increasing kiln inclination causes the increase of gravitation force in the axial direction of the individual particle during its cascading. One interesting point on the bed height in the kiln is how it relates to the volumetric filling. For Namakwa Sands, the volumetric filling is less than 20%, thus increases in rotation speed from 1 to 2 rpm (limited due to engineering) does not affect the mean residence time. Calculated residence time values agree quite closely to those measured, however it is interesting to note some back-mixing.

5.2. *Experimental results*

As highlighted during the discussion of the plant trials, the effect of discharge temperature was seen to be critical in determining the overall conversion of iron. The experimental results are presented next: the results under laboratory conditions indicate that the plant conditions can be simulated quite closely. These experiments were developed to understand the sensitivity of the conversion to temperature, moisture conditions and evaporation. It was also indicated that higher feed temperatures could result in higher rates of evaporation and thus reduce the available energy for reaction, and thus higher temperatures could result in no change in the iron conversion. Also noted was that the discharge moisture conditions and acid concentration would affect the iron conversion. This section aims to understand why these phenomena exist and what is driving the reaction and finally answer the hypothesis.

- Is the reaction hindered by a solid product layer formed during the rapid evaporation of water and causing the ferric iron in solution to become supersaturated and subsequently precipitate?

5.2.1. Temperature effects on leaching

All the temperature experiments were conducted for 90 minutes (this to establish the full extent of reaction) and at an acid dosing of 23 kg/ton and a 30 % by m/m acid concentration

(S/L ratio of 13). The leachate was then quenched for 30 minutes with ambient (25°C) acid water (pH = 0.6) and the method illustrated in (see section 4.3). Five tests were conducted each at a different temperature (60, 90, 110, 140, 170 °C). These were then repeated three times (see section 4.3.5). The total iron conversion is presented using the LHS axis while the % iron associated with zircon is presented on the RHS axis (Figure 38).

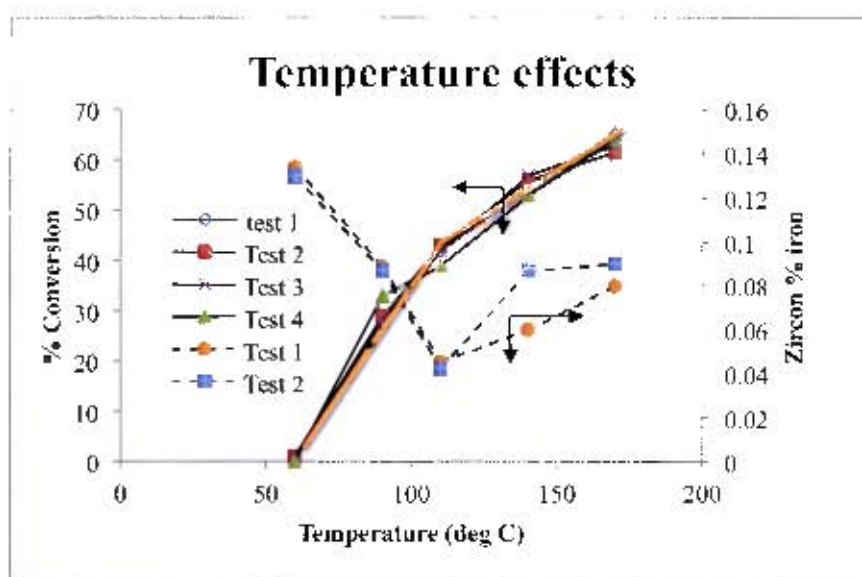


Figure 38: Temperature effects on leaching; 23 kg/ton dosing and 30 % by m/m H₂SO₄ concentration with 90 minutes leaching and 30 minutes wetting

The highest conversion was achieved at the highest temperature, with the biggest change in conversion occurring between 60 °C and 110 °C (the conversion doubles, leaching 50 % of the initial Fe₂O₃). Studying the iron associated with zircon: it is evident that at 90 °C the iron oxide levels are greater than target 0.06 % Fe₂O₃ (Figure 38). Thus to reach the high purity requirement of less than 0.06% Fe₂O₃ the leaching must occur above 90 °C and below 110°C(according to Figure 38), which also points to something interesting; higher temperatures don't translate to greater purity zircon even though greater overall conversions are achieved. This is probably due to the increased leaching of Fe containing minerals at higher temps, and the subsequent precipitate of a ferric-complex onto the zircon particle.

The laboratory analysis indicated that after the 90 minutes of leaching the 90 °C, 110 °C and 140 °C runs resulted in a soft cake, but the 170 °C test showed a hard (moon-rock) discharge cake, owing to the baking environment. The hard-discharged cakes contained no moisture

and would only break if serious force was applied. As expected, the final moisture content of the solid residues was highest for the lowest reaction temperature. It is expected that at higher temperatures, with rapid evaporation of water, the saturation of ferric in solution increases remarkably. This increases the viscosity of the solution, which could change the reaction pathway.

Based on literature and work compiled by Prinsloo (2006), higher temperatures favour the formation of hematite rather than goethite, while others report that jarosite is favoured at higher temperature and acidic environments. The synthesis method for hematite is from ferrihydrate at low pH < 1 and moderate temperatures >90 °C. However, other research (Dutrillac & Monhemius, 1987) reports the formation of jarosite at >120 °C and low pH < 1. Thus the formation of dry solid precipitates at higher temperatures (>140 °C) could be due to re-precipitation of hematite and/or jarosite. Dutrillac and Monhemius (1987) mentioned that various elemental substitutions affect the goethite-hematite stability. It is unclear at this moment what iron complex is formed however this will be studied later during this chapter.

The above experiments indicated that above 140 °C the material potentially underwent solid transformation. The product from high (>140 °C) temperature leach tests is a hardened white cake, while Fe transformation was not substantially improved. This agrees with the literature: Taxiarchou et al. (1997) found that varying temperatures from 90 to 100 °C a maximum leaching yield was 40 %, while at the lower temperature of 80°C a maximum of 30 % was achieved. Also, work compiled by Veglio et al. (1998) showed that leaching at higher temperatures above 100 °C yields a maximum of 45% iron leached after an hour, possible due to a similar phenomenon. Their work also showed that after 1 hour of leaching the quartz particles were clear of iron contaminants – although the solid-liquid ratios in their study were much lower at 2 – 5.

A possible reason why the conversions are all very similar to the reaction at 90 °C maybe due to the fact that at higher temperatures the evaporation of water becomes far more prominent (and occurs rapidly). The evaporation of water and further concentration of sulphuric acid would increase ferric in solution. Then further concentration of ferric occurs, due to evaporation, which results in a supersaturated solution in ferric. Further leaching would allow for a precipitate to form and this slows down the reaction.

5.2.2. Activation energy and residence time dependence

All the temperature (isothermal) experiments were conducted for 90 minutes (this to establish the full extent of reaction) and at an acid dosing of 23 kg/ton and a 30 % by m/m acid concentration (S/L ratio of 13). The leachate was then quenched for 30 minutes with ambient (25°C) acid water (pH = 0.6) and the method illustrated in (see section 4.3). Test 1 was run at a temperature of 90 °C, Test 2 at 110 °C, while Test 3 at 140 °C, while Test 4 was at 170 °C., all reactions occurred in the Pyrex 1L container placed in the oven for the duration of the experiment. The total iron conversion against time is presented in Figure 39.

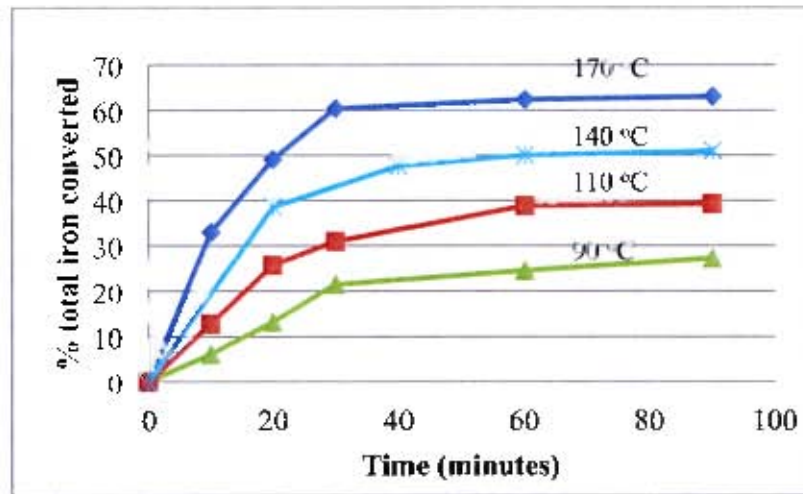


Figure 39: Iron conversion with temperature and time

The first 'segment' of the curve was used to determine the activation energy i.e. from 0 to 30 minutes. The reaction conversions for iron were then plotted against different rate equations provided by Levenspiel (1979); the list can be found in Table 19.

Table 19: Rate equations used ($k[\text{min}^{-1}]$, $t[\text{minutes}]$)

Model	Details	Source	Equation
1	Flat plate Reaction controls		$kt = X$
2	Sphere Reaction controls	(Levenspiel, 1979)	$kt = 1 - (1 - X)^{\frac{1}{3}}$
3	Flat plate Ash diffusion controls		$kt = X^2$
4	n^{th} - order reactions 1 st and n^{th} - order	(Levenspiel, 1979)	$kt = (1 - X)^{1-n} - 1$ or $kt = -\log(1 - X)$
5	Sphere Ash diffusion controls	(Levenspiel, 1979)	$kt = 1 - 3(1 - X)^{\frac{2}{3}} - 2(1 - X)$

Each rate equation was plotted as a function of time - the data presenting in 40. A least squares fit solution was run for each mode versus the experimental data, and then validated by plotting the experimental data, model data versus time using Excel. The choice of the model for determination of the activation energy was based on the greatest statistical significance ($R^2=0.99$ for model 5 versus $R^2=0.96$ for model 4). Figure 40 shows the selected model – a constant spherical particle where the reaction is hindered by diffusion through an ash layer.

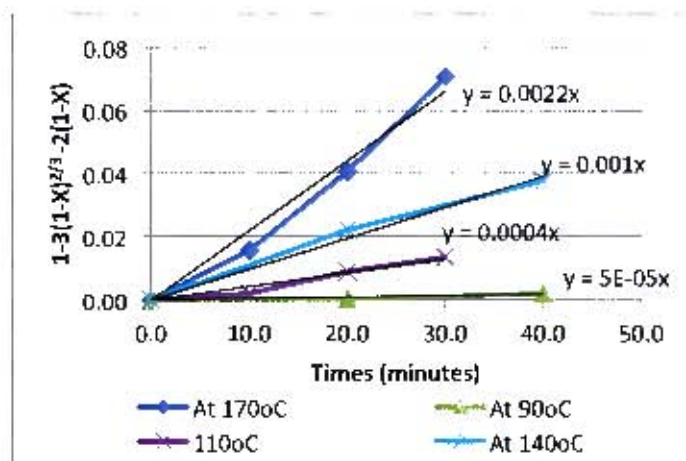


Figure 40: Rates for chemical controlled reaction

The above curve was completed for five different reaction kinetic equations: n-order reaction (model 4), Ash diffusion of spherical particle (unchanging size) controls reaction (model 5), 1st order reaction and chemical controlled reaction (sphere/flat plate). The straight-lines (best-fits) plotted in Figure 40 provide the rate constants at each temperature. The gradient of each line (are then plotted against temperature to form (Figure 40) an Arrhenius plot. Arrhenius plots relate activation energy to rate equations for different temperatures at different times (Figure 41). The log of the gradient represents, the rate of reaction, versus the reciprocal of the temperature provides the activation energy. It was found that the model that most accurately describes the reaction according to statistics ($R^2=0.99$) was: the ash-diffusion model for a particle of unchanging size.

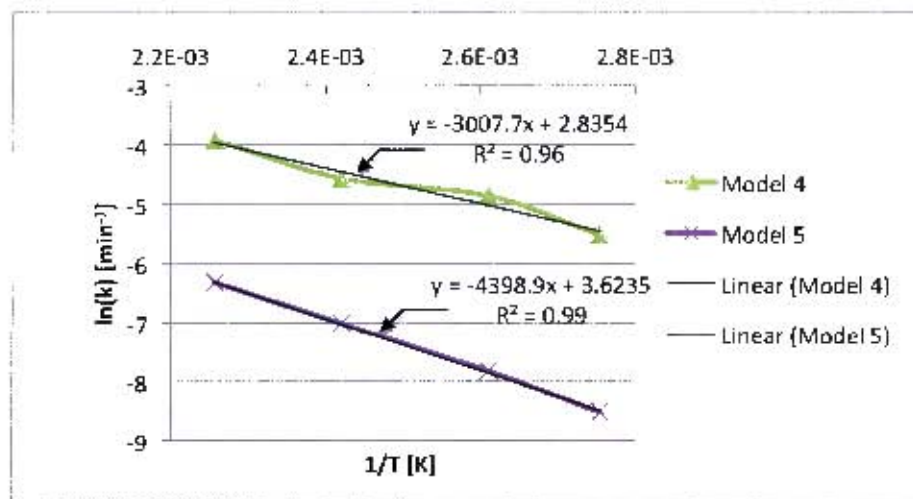


Figure 41: Arrhenius plot for reaction conversions

The Arrhenius equation is used to determine the activation energy:

$$\ln(k) = \ln(-A) - \frac{E}{R} * \frac{1}{T}$$

The gradient of the lines in Figure 41 represent the activation energy. The two models produced different activation energies: for model 4; 24 kJ/mol while for model 5; 38 kJ/mol. It is interesting that the rate model that best fits describes a reaction hindered by diffusion (for a sphere) and the high activation energy indicates a reaction-limited pathway, which may seem like a contradiction. The appropriateness of the Shrinking core diffusion model for this case, regardless of whether it gives the best results can't conceptually be represented by a spherical leach model and the therefore the flat plate model would have been more conceptually appropriate. However, this phenomenon is not unique to this reaction; a number of studies have been conducted on known reaction-limited reactions, where high activation energies were found, however the best-fit model was a diffusion-controlling one.

The first 30 minutes was taken for the high temperature test, while 40 minutes was taken for the test at 140 °C, while 60 minutes was taken for the remaining two tests. This is because the gradients of the straight lines post this (30 minutes) indicates a change in mechanism (this will be discussed later; it has to do with the dehydration of the mineral and the initial S/L ratio). As seen in Figure 42, for each experiment the change in mechanism does not occur at the same moment. The driving force for the change in mechanism is thought to be evaporation (as evaporation occurs rapidly at high temperature gradients).

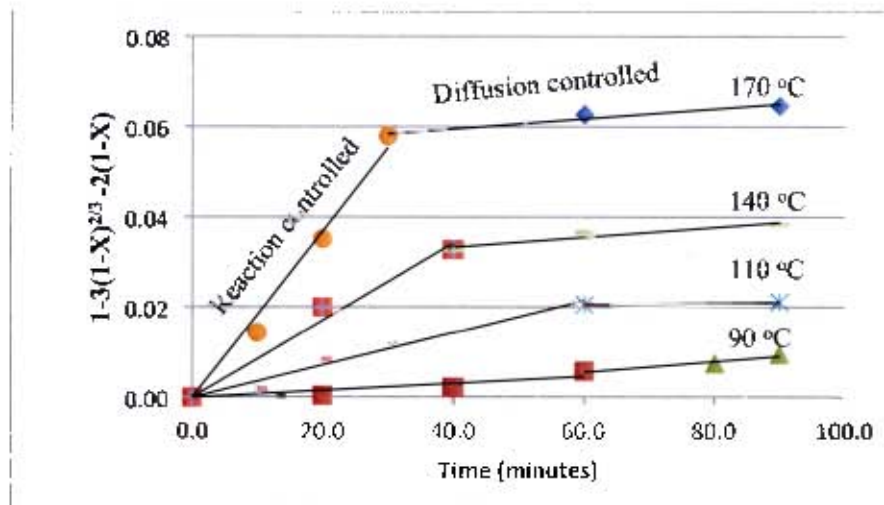


Figure 42: The change in reaction mechanism

Some well-known diffusion-controlled reactions yield high activation energies (i.e. activation energy contradicting the model – Table 20). Most of the ilmenite dissolution reactions indicate that the reaction is highly dependent on temperature, with the activation energies determined here ranging from 39 kJ/mol to 75 kJ/mol (Zhang & Nicol, 2010), while for hematite and magnetite dissolution the activation energy was also high at 54.2 kJ/mol (Chastukhin et al., (2003)). However both sets of authors used diffusion models to describe the leaching mechanisms. Their argument is that the reaction was somewhat limited by a combination of the two; first reaction controlled and once the passivation layer is formed the reaction becomes diffusion controlled.

Chastukhin et al., (2003) did not present individual leach rates of each iron oxide specie. However their work indicated that hematite leaching occurred faster than that of magnetite. Their conclusion was that the rate of dissolution was very much an active site phenomenon and that the reaction was predominately limited by diffusion. The dissolution of goethite is subject to high activation energies: 50.1 kJ/mol to 68.2 kJ/mol (as the work completed by Abdus-salam and Adekola (2006) indicates). They further state that the activation energy was very dependent on the relative phases of the iron-oxides and the presence of impurities. Their analysis does make sense because the activation energy is defined as the energy required to break chemical bonds within the crystal structure. Their research showed that a passivation layer (O-Fe film) was formed after a very short period, which was thought to slow down the reaction rate (Biber et al., 1994), hence the reason why a diffusion model was fitted. They propose a combination of first reaction-limited then diffusion-limited pathways.

Table 20: High activation energies reported for some diffusion-controlled reactions

Diffusion controlled reaction	Source	Activation energy (kJ/mol)
Ilmenite and H ₂ SO ₄ under SO _x	(Zhang & Nicol, 2010)	39.1 - 75.0
Ilmenite in Caustic (NaOH)	(Amer, 2002)	72.1
Fe ₂ O ₃ and Fe ₃ O ₄ in sulphuric acid	(Chastukhin et al., 2003)	54.2
Raw laterite leaching	(Olanipekun, 2000)	71.7
Goethite in HCl	(Abdus-salam & Adekola, 2006)	50.1 – 68.2
Hematite dissolution in Sulphuric acid	(Lee et al., 2006)	140.0
$1-(\frac{2}{3})x-(1-x)^{2/3}$	Current study	38
$kt = -\log (1 - X)$	Current study	24

The reactions between hematite on the mineral surface and the other gangue around the mineral surface require that Fe-O bonds are first broken to produce ferric in solution. Ferric then complexes with -SO₄²⁻ (and SO₄²⁻ with Ca²⁺), forming an insoluble jarosite-gypsum-complex. As evaporation occurs, the ferric becomes supersaturated and more visous, thus making the theory of diffusion through a porous layer plausible. The high activation energy required in this case is probably due to the complex Fe-O mix of elements that reside on the mineral surfaces and in the gangue. However, after a very short period of time, a solid precipitate forms which changes the mechanism to a primarily diffusion controlled reaction. The formation of a solid product layer due to evaporation is what favours the use of the diffusion limited model. This could explain why can be described by a rate-based equation that describes a reaction hindered by a solid product layer and also possesses a high activation energy.

5.2.3. Evaporation effects at different S/L ratios

The solid/liquid ratio has an influence on two fundamental aspects, the availability of acid for reaction and the extent of water that can be evaporated from the solution. The evaporative tests studied two distinct regimes; the first test (low S/L regime Test 1) was run at a S/L ratio of 8 and the second test regime (high S/L ratio Test 2) at a S/L ratio of 13 - Figure 44. All

these test were done with the solids being preheated to 120 °C and then contacted with acid and water (at different concentrations) for a total reaction time of 90 minutes in the Pyrex vessels with the lid being placed on and the reaction maintained in an oven set to 120 °C. The concentration of acid has a significant impact on the boiling point of the solution (see Appendix A). The decision to run the tests at a fixed temperature of 120 °C was based on the V/L diagram, which indicated that for the acid concentration of 20% to 40% (m/m), within an evaporative environment, the solution will become more concentrated in acid, while the vapour will be close to 99% water.

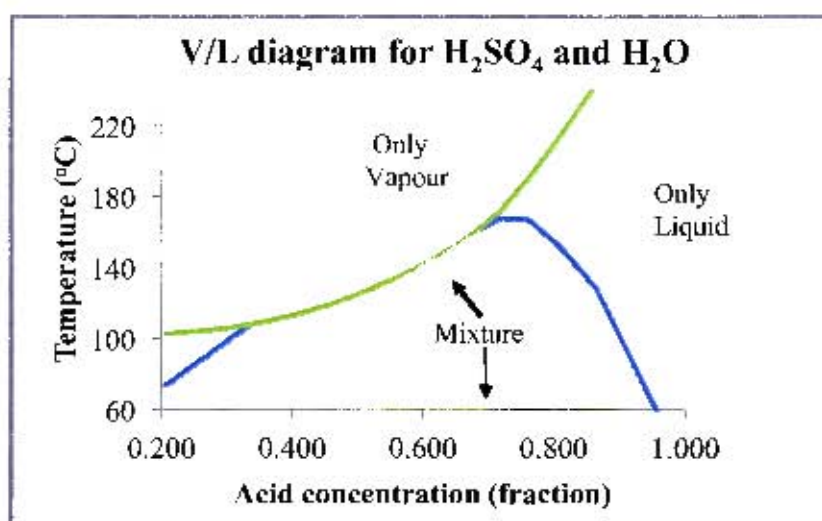


Figure 43: Vapour/Liquid diagram for sulphuric acid and water at 1 atm

The test also involved changing the acid concentration while keeping the S/L ratio the same. Water was used to make up the difference so as to maintain the S/L ratio. The results are presented in Figure 44. Lower acid concentrations versus high acid concentrations at different S/L ratios were tested.

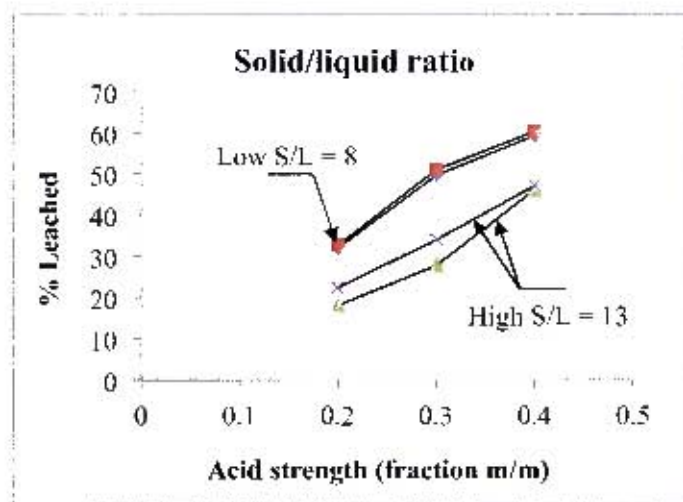


Figure 44: Solid/liquid ratio effect on leaching (feed preheated to 120 °C, high S/L = 13, while low S/L = 8, with increasing acid concentration, 90 minutes)

From the analysis it is evident that the lower the solid liquid ratio, the better the conversion achieved for any concentration of acid. For both tests, higher acid concentrations are preferable above lower acid concentration. A combination of higher acid concentrations and low S/L ratios provide highest leaching conversions.

It was observed during this experiment that the leach residues were hard for both tests (agitation was applied initially, however as the residues became drier agitation was stopped), even when running at different solid liquid ratios, indicating the formation of moon-rocks, this is peculiar as the formation of moon-rock is usually caused by low moisture conditions. The solid formation indicates that the reaction probably slowed down quite rapidly at the higher S/L ratios – this due to the high evaporation rates.

The only work in the literature that considered S/L ratios was that compiled by Veglio et al. (1998), which indicated that solid/liquid ratios between 0.5 – 1 did not play a large role in leaching of iron oxide from the surface of quartz particles. However, S/L ratios between 1 and 5 negatively affected the percentage of iron leached. This work, shown in Figure 45, didn't indicate, however, at what concentration of acid the solid-liquid ratios were kept. Nor did they provide an explanation for the observed decrease in leaching efficiency at higher solid/liquid ratios.

Work by Agtzini-Leonardou et al. (2008) shows that at higher acid concentrations of 20 – 60 % H_2SO_4 and solid liquid ratios of between 0.5 and 0.05, better leaching results were

achieved. The highest extent of leaching of the red-mud residual occurred at 46.7 %; this was achieved at 60% acid concentrations and a solid/liquid ratio of 0.2. This work is in agreement with that compiled by Olanipekun (2000), which indicated that solid/liquid ratios were to an extent more important than acid concentration.

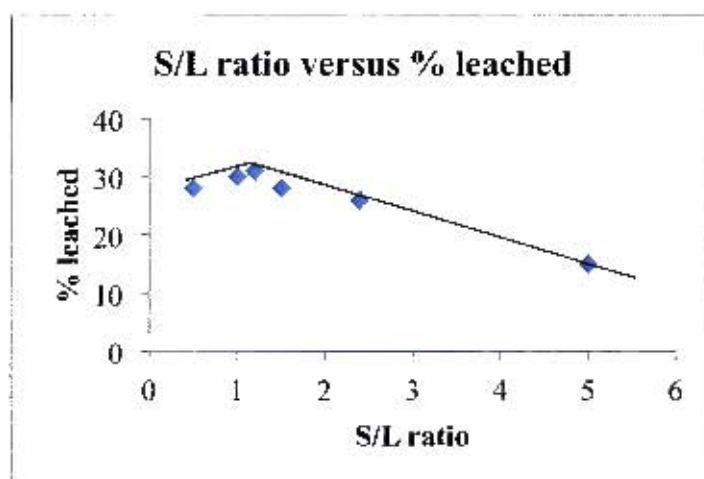


Figure 45: Solid/liquid ratio versus reaction conversion (Veglio et al., 1998)

This experimental data does suggest that lower S/L ratios favour higher iron conversion. This is because the total available mass of water that would readily evaporate is greater at lower S/L ratios. The low S/L ratio experiments take a longer time to reach the relative supersaturation point, where dissolved species precipitate from the solution. This experiment illustrates that even though more water is evaporated at lower S/L ratios, the solution dynamics dominate and are very critical in determining the final conversion. This is similar to what was observed by Olanipekun (2000).

5.2.4. Evaporation dynamics at the constant S/L ratios

The effect evaporation has on the leaching conditions is also of great concern and there is evidence that the reaction conversion is affected by evaporation, as presented in section 5.1.2. The final moisture conditions also influences the rate of leaching inside the kiln reactor. However it is interesting to note that the S/L ratio test work indicated that final discharge moistures were not as important as initial S/L ratios.

The next experiment was set up to answer whether the rate of evaporation influences the rate of reaction and the final conversion. The study looked at two different scenarios:

- (a) high rate of evaporation at same temperature yields lower conversion
- (b) lower rate of evaporation at same temperature yields higher conversions

To test the effect of evaporation on leaching at a constant S/L ratio, the laboratory leaching conditions were changed in such a way as to simulate either an initially very moist environment (moisture contained in closed reaction vessel) or a rapidly evaporative drying environment (evaporating to atmosphere in an open reaction vessel), while maintaining a constant temperature (120 °C), acid concentration (30% m/m), acid dosing (35 kg/t) and S/L ratio (10.8). Figure 46 shows a plot of the evaporation effects.

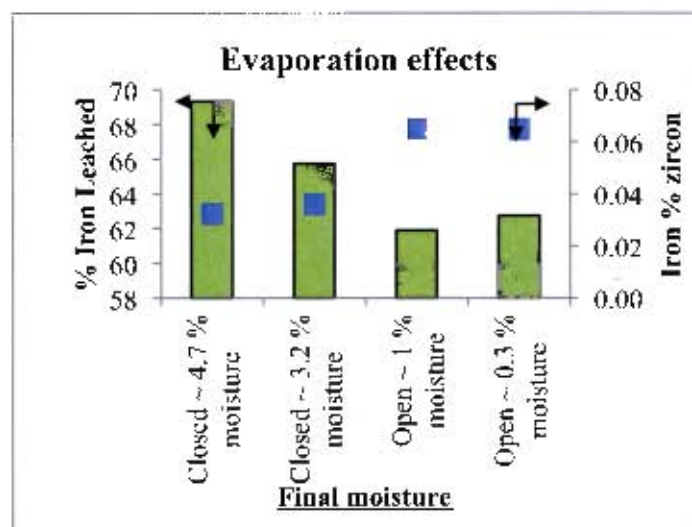


Figure 46: Evaporation effects on leaching; leached at 120 °C, 30 % acid concentration, 35 kg/ton acid dosing, leached for 90 minutes (S/L ratio ~ 10.8)

According to Figure 46, under high final moisture (4.7 and 3.2 % H₂O) conditions, the extent of leaching in a closed environment is far greater than that under open conditions. It would appear, that initially the reaction would prefer to be moist, however once it progress past a certain point it is irrelevant if the environment its moist or not as the reaction rate is now hindered by diffusion, possibly due to super-saturation and precipitation and is thus very slow. This gives some insight as to what is actually happening.

Also, the conversion of solid iron to dissolved ferric on zircon surface is greater under initially higher moisture environments compared to the dryer, open environment scenario. The results presented suggest that discharge moistures are important, however what is more important is that the environment is moist during the initial rapid leaching phase, and that

conversion is heavily dependent on this initial phase. To illustrate this, Figure 47 was constructed. This figure shows two systems: the development of moisture content with time in an open system and a closed system. Over time both systems reach the relative dehydration stage where the moisture content is the lowest. However each system takes a very different route.

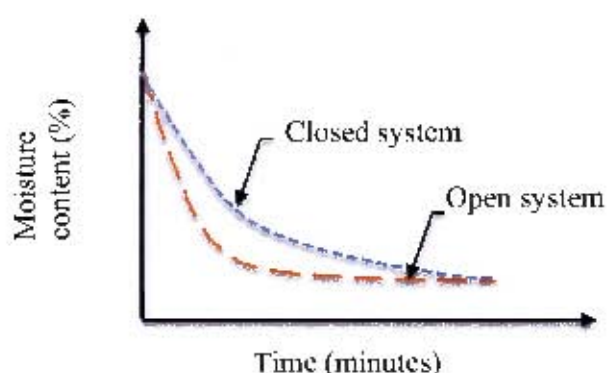


Figure 47: Evaporation happens faster for open systems

This experiment illustrates that the rate of evaporation is critical in determining the final iron conversion. For very fast rates the super-saturation limit is approached faster, while slower rates allow further leaching to continue before super-saturation is reached.

5.2.5. Wetting effects on leaching (both concentration and dosing)

Wetting effects on leaching were tested, this was done to understand which played the greater role: the acid concentration or the mixing dynamics in leaching. Either the dosage (kg/ton mineral) or the concentration of sulphuric acid was changed, while the other was kept constant (the S/L ratio remained the same). The experimental setup was similar to the previous experiments and Table 21 shows the test variables that were changed to understand the effects of strength and dosing rates on overall iron leaching.

All leach residues were hard and brittle after leaching for 90 minutes. The leach residues were then processed via the usual laboratory method (see section 4.3). All tests were conducted at a temperature of 170 °C, in a closed environment i.e. with the Pyrex lid placed on top of the vessel. This experiment was run to understand why higher temperature within the kiln didn't translate into higher conversion and thus the maximum temperature achievable by the laboratory oven was chosen. Note that at temperatures of above 160 °C no improvement in iron conversion was noticed on the plant.

Table 21: Wetting rate tests and solid liquid ratios

Test no	Strength % (m/m)	Dosing rate kg/t	S/L ratio (unit)
A	20	23.0	8.7
B	30		13.0
C	40		17.4
D	30	36.2	8.3
E		23.0	13.0
F		16.3	18.4
G	20	14.6	13.7
H	30	23.0	13.0
I	40	32.4	12.3

Figure 48 shows the conversion obtained when the acid concentration and acid dosage were changed. The S/L ratios for each test are displayed in Figure 48.

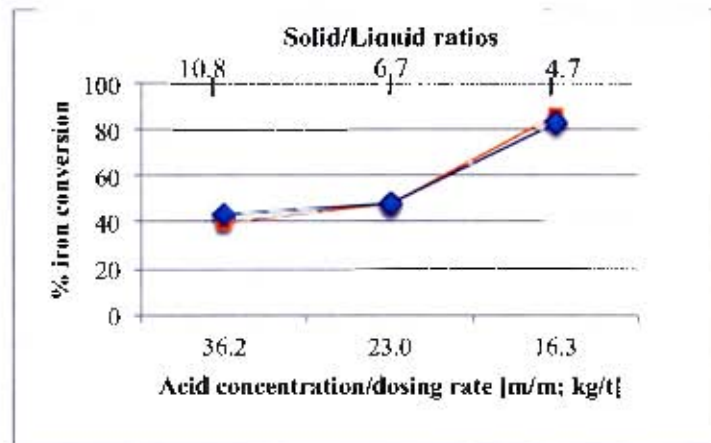


Figure 48: Leach kinetic envelope shows the relationship between dosing and strength; at 170°C while leaching for 90 minutes and agitation for 30 minutes, strength/dosing varies from 16 – 36 (%)/(kg/t).

From the results presented in Figure 48, the tests appear to show that low acid strength and low S/L ratios are far preferred over higher acid concentrations, or even higher dosing, this is also noticed in section 5.2.3. As already discussed, it is clear that higher acid concentrations and dosage clearly influence the leaching to the extent of that S/L ratios affect conversion. For all experiments it would seem that higher dosings or higher acid strengths lead to lower conversion. This not only confirms that acid volumes being fed to the reactor are sufficient for high conversion, but also the idea that precipitation following super-saturation slows down the reaction.

5.2.6. Ferric solution dynamics in sulphuric acid

The super-saturation dynamics that occur in an acid bake environment involve the precipitation of ferric from solution. To understand this, a series of experiments were run to determine the ferric, calcium and moisture in solution. The free acidity of the solution was also determined. The leach tests involved a fixed temperature in an oven at 110°C, contacted for a fixed period of time (from 0 to 90 minutes). For each test the initial acid (40% H₂SO₄ and 40 kg/ton) concentration and dosing remained the same (the same HAL feed sample was taken). A test was run for a fixed period of time and after that period the samples were processed according to laboratory procedures (see section 4.3). Ferric and calcium concentrations were determined using ICP, while free acidity was determined using titration. A duplicate test was completed. Figure 49 illustrates the results obtained: the LHS axis represents the concentration in (g/L) for both calcium and ferric, while the RHS represents the percentage moisture remaining on the particle surface. The results are plotted over time. The conversion was shown in in Figure 39: Iron conversion with temperature and time for 110 °C.

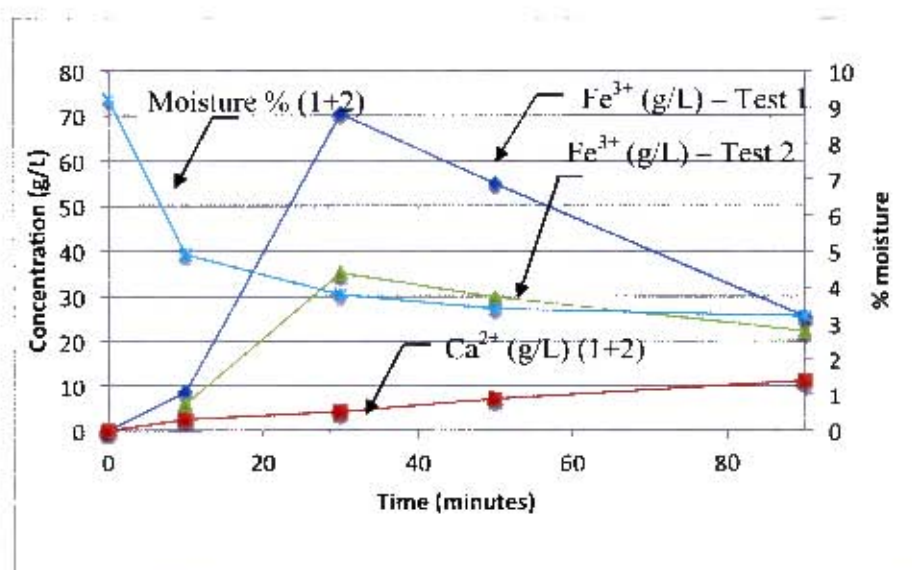


Figure 49: Solution Iron concentration

It is clear from Figure 49, that initially the concentration of ferric in solution builds up very quickly to a maximum, after which the concentration starts decreasing. This appears to happen for the first test at 70 g/L Fe³⁺ and 35 g/L Fe³⁺ for the second test. For calcium the concentration increases quite slowly and reaches a maximum after 90 minutes at 11 g/L (it

seems as though calcium is slightly more soluble as the dehydration process continues). The moisture contained in the minerals starts off at 9% and very quickly dehydrates to just below 4% from where it continues to dehydrate, however not as rapidly as before. The concentration of sulphuric acid versus time is displayed in Figure 50. The concentration of sulphuric acid as previously discussed does increase on the mineral surface. The reason for this is due to evaporation and dehydration of the minerals during baking.

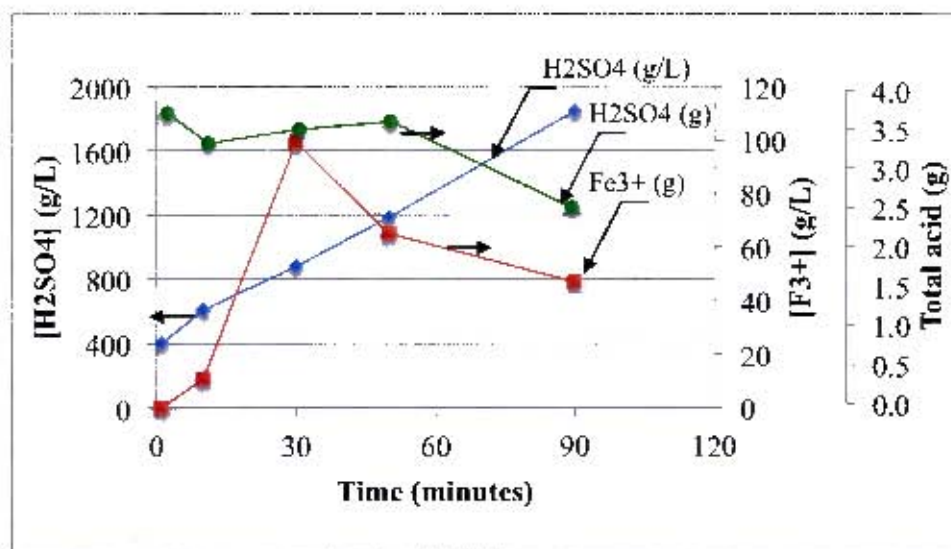


Figure 50: Ferric concentration and free acid concentration versus time

The initial concentration of acid is merely 40% or 400g/L. However after a very short time the acid concentration increased to effectively 600 g/L while the total amount of acid decreased to 3.3 g. This gives an indication that the acid was consumed while the mineral was being dehydrated. The consumption of acid is what produced ferric in solution, hence the ferric concentrations rapidly increased. At some point the ferric concentration starts decreasing, first very rapidly and then slowly. The total acid mass (in solution) decreases due to consumption and then increases slowly, but finally decreases. Figure 51 – combines the moisture content of the solids with ferric and free acidity in solution.

- The first 30 minutes of the experiment is where leaching of ferric into solution occurs. This part of the reaction is limited purely by the reaction-rate. The conversion of hematite to ferric is very quick here and this conversion reaches a maximum after 30 minutes.
- After this the ferric concentration starts dropping indicating precipitation. It is also noticed that the concentration of sulphuric acid increases continuously with the

dyhydration of the minerals. Here the total amount of sulphuric acid is also decreasing,

- (c) Finally the dehydration further decreases the moisture and with this the sulphuric acid slowly start decreasing again. However this can not be due evaporation of sulphuric acid as the boiling point of >60% wt/wt solution is 144°C, while the temperatures of the oven were set at 110 °C).

Ruiz et al., (2007) completed research on hematite precipitation from ferrous sulphate solutions via high-pressure (>700kPa) oxidation of ferrous to ferric. The main objectives of their study were to determine the effect of high ferric and acidity concentrations on the extent of iron precipitation as well as the particle size distribution of the precipitates. Their experiments were all conducted at temperature similar to the dry baking environment (170 to 220 °C), concentration of sulfuric acid (1 to 10 g/l), initial iron concentration (1 to 15 g/l).

Ruiz et al., (2007) results revealed the following:

- (a) an increase in the temperature produced precipitates with smaller particle sizes and lower sulfur contents.
- (b) an increase in sulfuric acid concentration and initial iron concentration produced precipitates with larger particle sizes and lower sulphate concentrations

With regards to the present study: it is postulated that the first decrease in sulphuric acid is due to the conversion of hematite into ferric, which consumes acid (revised reaction 1 illustrates). The slow increase post the first minimum is then due to the precipitation of ferric-hydroxide sulphate, which produces acid according to Reaction 2.



Ferric precipitates once it reaches super-saturation levels in solution. It will preferentially precipitate according to Reaction 2 until acid levels rise to levels where precipitation via this pathway is no longer supported. This helps explain why acid levels start rising just before the peak in both conversion and ferric concentration is noticed. Precipitation as FeOHSO₄ produces acid and the equilibrium of Reaction 2 is limited by a maximum concentration of acid in solution, and driven further backwards under low moisture environments (Reaction 3 requires water to proceed). Once the level of acid reaches a maximum, such that Reaction 2

stops the precipitation of ferric proceeds via reaction pathway 3; presented below. Reaction 3 is the production of a ferric-sulphate in a very high acidic, high sulphate but dry environment.



Reaction 3 consumes excess acid, sulphates and ferric ion in solution to produce a ferric-hydrate-sulphate complex. The reaction is driven by high ferric concentrations, high sulphate concentrations and high proton concentrations (in a very low moisture environment). Casas et al. (2007) studied these systems and defined them quite accurately for the temperature range from 50 °C, high acidic environments > 55 g/L H_2SO_4 and in excess of 24g/L ferric concentrations and found that the preferred precipitate under these conditions was $\text{FeH}(\text{SO}_4)_2$ rhomboclase (Casas et al., 2005). Reviewing the experimental data obtained and combing the observations of Ruiz et al., (2007) and Casas et al., (2005) Figure 51 is constructed.

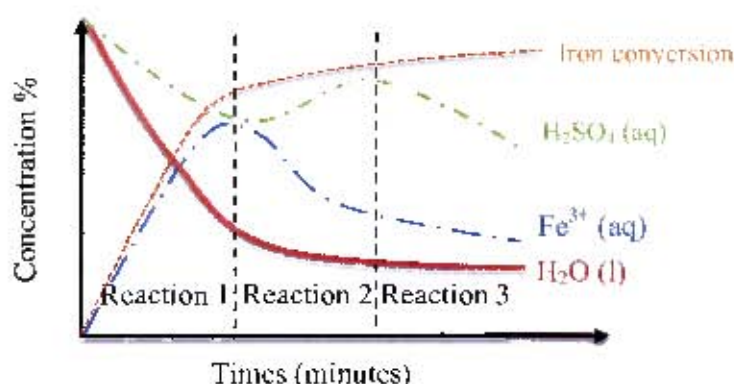


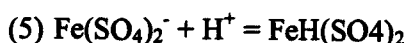
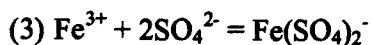
Figure 51: Reaction dynamics (as per Ruiz et al., (2007) observations)

Figure 51 indicates the following equilibriums govern the extent of the overall iron conversion.

- The progression from Reaction 1 to Reaction 2 is driven primarily by saturation of Fe^{3+} due to rapid dissolution and rapid dehydration.
- Progress from Reaction 2 to Reaction 3 is governed by the saturation of sulphuric acid and specifically free acid concentration.

According to Casas et al., (2005) it is further postulated that the following equilibria govern the various endpoints for each reaction:

- $\text{H}_2\text{O} + \text{H}^+ = \text{H}_3\text{O}^+$
- $\text{Fe}^{3+} + \text{SO}_4^{2-} = \text{Fe}(\text{SO}_4)^+$



The precipitation pathways mentioned above are not completely new to the hydrometallurgical industry and have been somewhat studied by various authors. Ruiz et al., (2007) studied the precipitation of ferric from sulphate solutions, Langova et al., (2007) studied the precipitation of goethite from ferric sulphate solutions, further work on charactering of ferric and ferrous precipitates was completed by Frost et al., (2005), Casas et al., (2005) and again Casas et al., (2007) studied the solubility of ferric in a number of different sulfate solutions at different temperature and found ferric solubility increased with temperature for solutions from (25 °C to 50 °C).

It is reasonable to conclude that the precipitates formed in the process contain sulphate(s) (SO_4^{2-}), ferric ions (Fe^{3+}) and protons (H^+). The exact characteristics and make-up of these solid precipitate(s) are beyond the scope of the present study. However, caution must be taken to make an absolute conclusion on what the solid-precipitates are because the make-up of these precipitates are also consistent with a range of iron-complexes: hydronium-jarosite ($\text{H}_3\text{OFe}_3(\text{SO}_4)_2(\text{OH})_6$), rhomoclase ($\text{FeH}(\text{SO}_4)_2$), FeOHSO_4 (ferric-hydroxide sulphate) – all contain sulphur, ferric and protons. The reaction is therefore thought to proceed during the later period of leaching very slowly and this is hindered by the solid product layer of such ferric-hydroxi-sulphates.

5.2.7. Images of leach residues

At each stage in the leaching process, leached residue samples were taken and photographed under a microscope. The photos clearly indicate that after 5 minutes hardly any leaching had occurred, after 10 minutes the leaching approached higher values, while between 25 and 60 minutes only those 'hard-to-get' unleached particles remain. However after 60 minutes the yield in leaching hardly increases. It is difficult to ascertain if precipitation back onto the particle occurred, as, to achieve the images, the samples needed to be washed and attritioned. However this does indicate an important point (Figure 52): after 60 minutes there is no visible change in the percentage of leached particles.

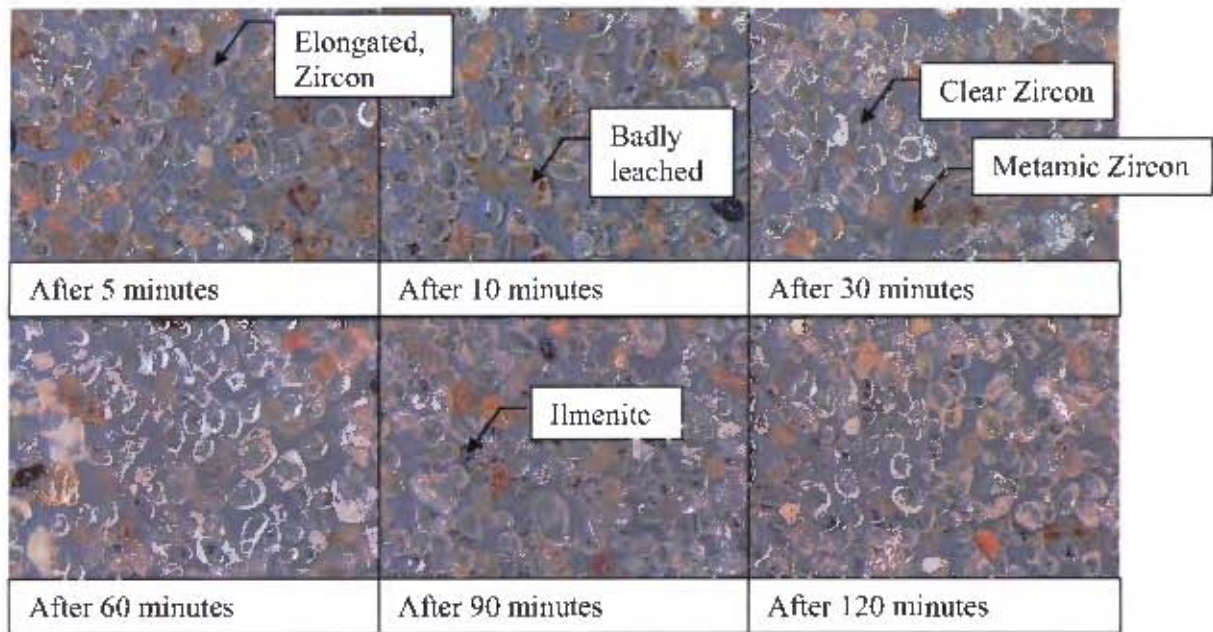


Figure 52: Post leach microphotographs at each stage (10 - 120) minutes

SEM images of the leached residue were also taken in order to understand what the coatings around the heavy minerals look like straight after leaching and then after attritioning. The iron oxide coatings are hard outer surface-based shells (A - post leaching no-attritioning) and (B - post leaching with attritioning). Image (A) indicates that the precipitates are spherical agglomerates and the agglomerates stick to the outer shell of the particles. The outer shells seem rather like a crust (Figure 53), which retains its shape after detaching from the mineral surface post attritioning, which further justifies the attritioning argument. The images also offer evidence of pitting on the mineral surface (b), which occurs due to high acid strength and abrasive attritioning.

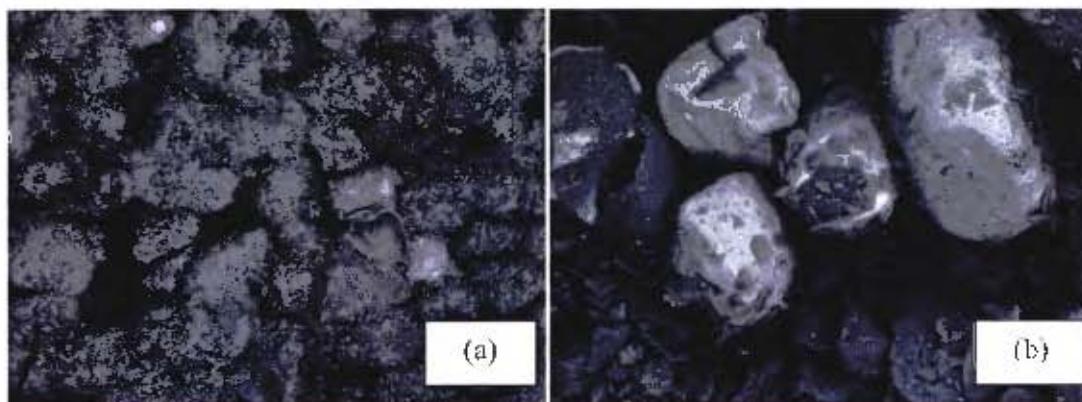


Figure 53: Reactor discharge - SEM images

5.3. Summary of experimental and plant data

The variance noticed in zircon production was previously shown to be due to three main reasons, viz insufficient leaching, reattachment issues and insufficient attritioning. This thesis aimed to understand the variance brought about by leaching. A plant survey was first conducted to understand the extent of ineffective leaching. The survey was very informative, as it provided evidence to support the mass and energy balance and also paved the way forward with regards to what dynamics should be investigated in the laboratory work.

A survey revealed that conversion across the reactors is very inconsistent and that the conversion can vary by as much as 30% for a given day. The mean residence time of the reactor was determined both by tests and by calculation. Both the calculated and measured values agree quite closely with each other, some back-mixing was observed towards the discharge part of the reactor. It was concluded that the back-mixing wouldn't have a significant impact on skewing conversion results because the temperatures towards the discharge end are somewhat 50% lower than at the feed end. Further work demonstrated that the reactor discharge temperature and moisture conditions are functions of external temperature, and when correlated to conversions showed that lower conversions are noted during hotter conditions. Infra-Red images of the reactors were used to demonstrate that the majority of heat is lost at the discharge of the reactor. The reason for this was due to the higher bed-level (which at the discharge end is 0.35m compared to the feed end at 0.2m) towards the discharge end and the bad insulation at the discharge. The mass and energy balance revealed that 63% of the fed heat was lost due to evaporation and that the moisture content of the mineral decreases down the reactor, while the concentration of acid increases. The fact that evaporation accounts for such a high percentage of the heat lost indicates that solid/liquid ratios may heavily affect the reactor conversion.

The laboratory work aimed to understand the dry baking environment and specifically the theory on super-saturation as the main driver for insufficient leaching and reduced conversions.

Temperature studies in an acid bake environment noted that under all conditions the highest conversion corresponds to the highest temperature. However it was also discussed that the increase in conversion beyond 110 °C was not as rapid as below 110 °C (gradients of the two lines). It was discussed that this may be due to the fact that at higher temperatures the

evaporation of water becomes far more prominent (and occurs rapidly), which further increased the concentration of ferric and which then resulted in a supersaturated solution in ferric. Further leaching would allow for a precipitate to form and thus subsequently slow down the reaction.

Rate based test work related the temperature curves to different rates. Four tests were conducted at different temperatures, with the highest temperature being at 170 °C; producing the highest conversion, while the lowest temperature produced the lowest conversion. All tests were run for 90 minutes. There were two major dynamics, which were observed during the rate based experiments:

- (1) Rapid initial reaction from (0 – 30 minutes)
- (2) Reaction rates all slowed after 30 minutes

Using a least-squares method to determine the rate equation, the experimental work was fitted to known rate equations developed by Levenspiel (1979), which related the conversion over time. It was found that the rate fit was best for the diffusion through a solid-ash-layer for a sphere of unchanging size. It was also noted that the model could only be used to predict the reaction conversion for times from 0 – 30 minutes. However it was interesting to note that the activation energy as determined, by the Arrhenius equation, to be 38kJ/mol. While for a single first order kinetic model (which was also statistically significant $R^2=0.96$) showed a activation energy of 24 kJ/mol.

The high activation energies have also been reported for other diffusion-limited leaching cases; leaching of ilmenite, hematite, goethite and magnetite using sulphuric acid all revealed high activation energies, while being known to be diffusion limited reactions. It is thought that the reason why the high activation energy is prevalent (in iron-oxide reactions) is due to the breaking of Fe-O bonds, which require significant energy to initiate the reaction. The diffusion limitation is brought about due to a solid product layer around the mineral surface during evaporation.

The stability of ferric in this sulphate environment was determined to be every sensitive to the mass of water evaporated. The dissolution of hematite happens very quickly, and during this period it is very dependent on the temperature. Also during this period, evaporation of water occurs very quickly with the moisture content of the solids decreasing rapidly. The

evaporation of water increases the concentration of ferric on the mineral surface. Once the point of super-saturation occurs, precipitation of ferric happens back onto the mineral surface. However this does not stop the dissolution of hematite reaction from occurring, but rather slows it down. The phase of iron that precipitates is known to contain sulphates, ferric and protons. It is therefore postulated that the reaction post super-saturation proceeds very slowly because of solid product layer, which hinders the diffusion of protons to the mineral surface.

CHAPTER 6

MATLAB MODEL DEVELOPMENT

The primary objectives of the chapter:

- Consolidate both plant and laboratory data
- Demonstrate a validated model
- Illustrate different scenarios

The following chapter will detail the model developed using MATLAB and show how it was validated against plant data and laboratory data. The model was then also used for optimization studies across the reactor.

6 Introduction

The data collected during the laboratory work helped in the development of the various models for activation energy and the energy balance around the reactor and the residence time influences of the material inside the reactor. From this a dynamic reactor model can be developed. The reactor is a multi-phase system, which consists of a gas phase where water vapour is in equilibrium with water in solution around the mineral surface. While the solid phase represents the minerals, which is where the reaction of hematite to ferric occurs and later also the precipitation of ferric from the solution in the form of $\text{FeH}(\text{SO}_4)_2$. Figure 54 illustrates the conceptual model set-up to determine the conversion of ferric, the mass of water evaporated, the change in acid concentration, the temperature of both the solid and gas at different segments across the length of the reactor. Heat is lost due to evaporation, the endothermic reaction and heating of air within the kiln.

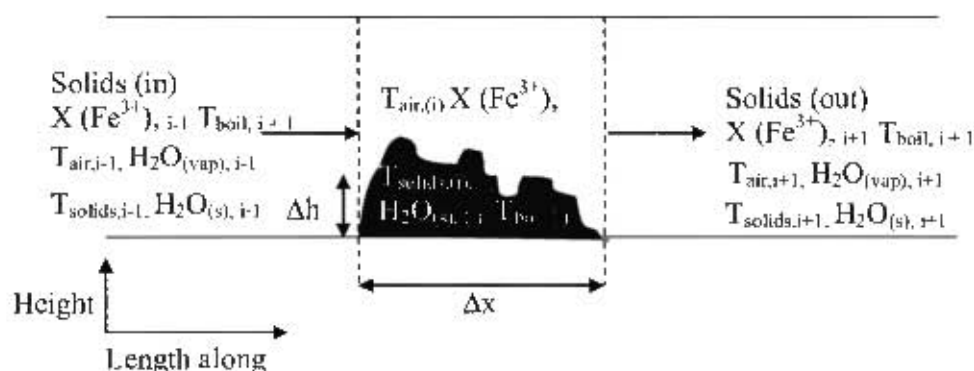


Figure 54: Model for reaction across the kiln

6.1. MATLAB model

The MATLAB model is centered on a mass and energy balance. The balance incorporates the endothermic nature of the hematite reaction, it also accounts for heat losses to the air and heat losses to evaporation. MATLAB version 7.8 was used to both compile and edit the source code. The physical constants are explained in the next section.

The rate equation:

Experimental work demonstrated that the best-fit rate equation that correctly predicted the rates (over the period 0 to 30 minutes) was the ash-diffusion controlled rate for a constant spherical particle by Levenspiel (1979). The mean residence time of the kiln was also determined during plant trials to be 20 - 30 minutes. The rate equations developed during the experimental section provided the reaction conversion over time for hematite leaching.

$$kt = 1 - \frac{2}{3}(x) - (1 - x)^{\frac{2}{3}} \quad \text{Equation 6(a)}$$

To solve for the conversions, a Newton-Raphson method is used (Equation 6(b)), which solves for a root in the range $X = [0,1]$, while the rate is calculated using the rate curve developed from the kinetic data presented as Equation 6(e), which is dependent on temperature. The rate is measured as $[\text{min}^{-1}]$ while t is time $[\text{min}]$. Equation 6(a) is only valid from 0 to 30 minutes.

$$X(i) = X(i - 1) - \frac{f(x)}{f'(x)} \quad \text{Equation 6(b)}$$

The Newton-Raphson method uses $X(0) = 0$ as the initial estimate, while Equations 6(c) – 6(d) are inputs into the iterative function.

$$f(x) = 1 - \frac{2}{3}(x) - (1 - x)^{\frac{2}{3}} - kt \quad \text{Equation 6(c)}$$

$$f'(x) = -\frac{2}{3}(x) + \frac{2}{3}(1 - x)^{-\frac{1}{3}} \quad \text{Equation 6(d)}$$

The method for calculating roots of polynomial equations is well known and the iteration number was taken as 10. Tests over the range of $X = [0,1]$, $t = [0,30]$ and $T = [60, 180]$ all convergence to solutions within 7 iterations, thus taking 10 is a safe option for convergence.

Rate variance with temperature:

The reaction activation energy was obtained from the temperature studies conducted during the laboratory test work (from 0 to 30 minutes). The Arrhenius equation development was discussed previously and will not be further detailed now. This equation was used to calculate the temperature variance in the kinetic rate.

$$k[\text{min}^{-1}] = 37.47 \exp\left(-4604 * \frac{1}{T[\text{K}]}\right) \quad \text{Equation 6(e)}$$

Mass and energy balance for the kiln system:

A mass and energy balance around the system was developed. Which takes into account the fact that the reactor behavior is much like a plug-flow reactor. As presented in Figure 37: Mean Residence Time of reactors (HAL A&HAL B) is 19 - 30 minutes. The back-mixing dynamics were considered to have a negligible effect on the balance (this project scope is limited to studying a pure plug flow system).

The heat and mass balances are constructed along the length of the reactor, for each Δx (Figure 54) of the reactor, the heat loss to environment, the amount of water evaporated and the energy used in the reaction is determined and the change in the solids temperature is determined. These can be summarised as such:

- 1) Endothermic nature of reaction
- 2) Heat loss to environment (air specifically)
- 3) Water evaporates only for a temperature if a temperature difference between air temperature and solid temperature exists

The energy balance assumed a steady-state system, the general form is presented as Equation 6(f), each term is a function of temperature: heat of reaction is a function detailed as Equation 6(g) and was linearized for simplification, the real curve however does seem to be more or less linear for the temperature range [60; 250], the enthalpies can be developed further for phase changes. The enthalpy associated with mixing is also excluded from these calculations, such that the partial enthalpies become equal to the enthalpies of the pure components.

$$\dot{Q} - \dot{W} - F_{A0} \sum_{i=1}^n \Theta_i (H_{i0} - H_i) - \Delta H_{Rx}(T) F_{A0} X = 0 \quad \text{Equation 6(f)}$$

For a system that does not include a specie that is reacting or phase changing (i.e. hematite) the following formula was developed:

$$\dot{Q} - \dot{W} - F_{A0} \sum_{i=1}^n \Theta_i \left(\int_{i=1}^n C_{pi} \right) - \Delta H_{Rx}(T) F_{A0} X = 0 \quad \text{Equation 6(g)}$$

The heat capacity of the hematite was assumed constant at 0.8 kJ/kg.K (. The evaporation of water in the process was added to as another loss to environment (in the place of W) such that the equation 6(g) is transformed to 6(h).

$$\dot{Q} - Q_{evap} - F_{A0} \sum_{i=1}^n \Theta_i \left(\int_{i=1}^n C_{pi} \right) - \Delta H_{Rx}(T) F_{A0} X = 0 \quad \text{Equation 6(h)}$$

1) Endothermic nature of reaction:

The endothermic nature of the reaction 1 has already been discussed. The kiln reactor operates over a temperature range of 80 °C to 200 °C. For this range the ΔH_{rxn} was linearized to simplify the calculations. The resulting linearized is equation 6(d).

$$\Delta H_{rxn}[\text{kJ/kg Fe}_2\text{O}_3] = 7.5422 * T + 625.8 \quad \text{Equation 6(i)}$$

2) Heat losses from kiln reactor:

Heat losses from the kiln to the air were calculated using the following equation:

$$\dot{Q} = -Ua(T - T_0) \quad \text{Equation 6(j)}$$

A heat-transfer coefficient of 80(W/m²K) was taken as the forced convection coefficient due to the high velocities of evaporating air within the kiln and due to the fact that air is blown into the kiln (Perry et al., 1969). The a in Equation 6(j) is the heat-transfer area per unit volume (Equation 6(k)):

$$a = \frac{A}{V} = \frac{\pi DL}{\frac{\pi D^2 L}{4}} = \frac{4}{D} \quad \text{Equation 6(k)}$$

3) Evaporation of water:

The evaporation of air is assumed to be a linear function, and heat transfer from the solid to the air is thought to occur via convection. All the minerals present within the kiln are non-hygroscopic and therefore their surfaces will remain saturated with the water/acid mixture. The drying rate is by diffusion of water from the surface of the minerals through a stagnant film layer. The mineral surface temperature will approach that of the air temperature (which would be just less than the wet-bulb temperature. The partial pressure of water is taken from

Figure 55. The influence of acid on the boiling point curve for H_2SO_4 was modeled by fitting a least squares 4th order polynomial fit through a number of different concentrations. The curve for this is $T_{\text{boil}}[K] = (1455.7 X^4) - (2495 X^3) + (1763 X^2) - (485.2 X) + 420.65$.

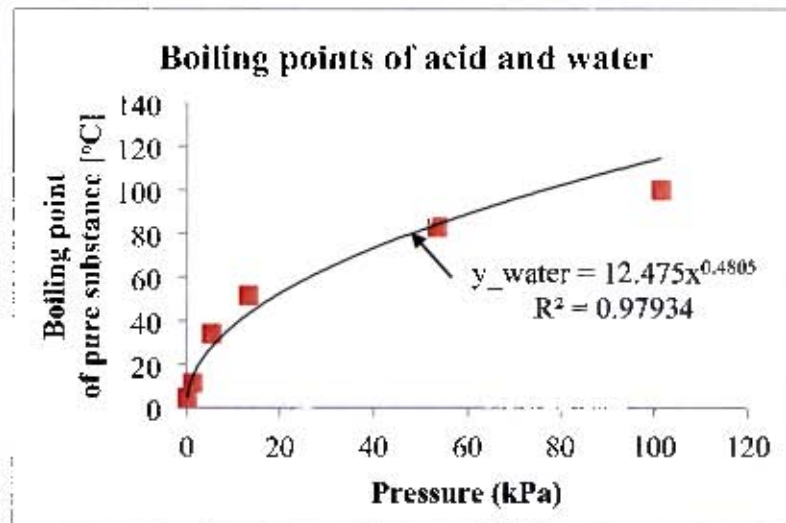


Figure 55: Boiling points of acid and water at various pressures (Sandler, 1997)

The model used to calculate the mass of water evaporating was developed and taken from Perry et al. (1969) and follows the following form [kg/min], it has two forms, either the partial pressure form or the temperature difference form (this MATLAB model uses the temperature difference previous):

$$\frac{dW}{d\theta} = \frac{60 \cdot Ua(T - T_a)}{H_{\text{evap}}} = k_g \cdot A \cdot \Delta p \quad \text{Equation 6(j)}$$

The change in temperature for the cooling air was calculated using formula (Equation 6.j), which accounts for the change heat-transfer between the air and solids and uses a heat-transfer coefficient of $1W/m^2.K$ (Perry et al., 1969), while the C_p of air was taken as $1kJ/kg.K$ and m_{air} the flowrate of air was taken at $600 m^3/min$.

$$\frac{dT_a}{dV} = \frac{Ua(T - T_a)}{m_{\text{air}} C_{p_{\text{air}}}} \quad \text{Equation 6(k)}$$

Using the relationship between the differential of a unit volume of a cylinder and it side length, the following formula can then be substituted into Equation 6.k:

$$dV = dx \cdot \frac{1}{2} \cdot \pi \cdot r^2 \quad \text{Equation 6(l)}$$

Substituting Equation 6.k into Equation 6.1 gives the following:

$$\frac{dT_a}{dx} = \frac{Ua(T-T_a)}{m_{atr}Cp_{atr}} * 2 * \frac{1}{\pi} * \frac{1}{r^2} \quad \text{Equation 6(k)}$$

The final energy balance for the reactor is computed using the following model, which incorporates heat lost to (a) the incoming air (b) to evaporation (c) to the endothermic reaction:

$$\frac{dT}{dx} = \frac{X*[-\Delta H_{rx}(T)] + Ua*(T_a - T) - H_{evap}*M_{moisture}}{\sum_1^m F_{Fe_2O_3} * Cp_{Fe_2O_3}} \quad \text{Equation 6(m)}$$

Residence time across reactor:

To model the residence time distribution, literature data on residence time distributions for kilns were studied; the model is based on a differential equation developed by Eckehard et al. (2010). The model allows for the flow of granular solids in a horizontal drum without any lifters and discharge-end constrictions (much like Namakwa Sands kiln reactors). The model results obtained compared well with their experimental data (Eckehard et al. ,2010). The key benefit of using this model is that it can be used to derive the bed height within the kiln at any point. The bed height together with the cross-sectional area and a small Δx ; the fraction of mass inside the reactor for that Δx length can be calculated, hence the residence time to this mass element can be calculate. This is the key to the MATLAB model:

a

b

$$\frac{dh}{dx} = 3 * \frac{\tan(\eta)}{4 * \pi * n} * v * (R^2 - ((h - R)^2)^{\frac{3}{2}} + \frac{dR_i}{dx} - \frac{\tan\beta}{\cos\theta} \quad \text{Equation 6(n)}$$

Equation 6(e) takes into account (a) the axial transport of solids, while (b) takes into account that there exists some constriction towards the discharge end of the kiln (dam). For the Namakwa Sands reactors this term is set to zero because the R_i (the internal radius of the kiln) does not vary significantly with length. This also simplifies the calculation of the bed height, which Equation 6(d) can not provide. The whole MATLAB model depends on being able to determine the time that the particle has spent in the kiln and thus Equation 6(n) is critical in the calculation as a whole.

6.1.1. MATLAB Structure and programming algorithm

The calculation method for the loss of energy from the particle is detailed below, for further details refer to Appendix B – MATLAB code. The MATLAB program calculates heat losses across the reactor at each length, using initial conditions as inputs into the program – as depicted by Table 22. The ODE 45 solver in MATLAB uses a 4th and 5th order Runge-Kutta method to integrate the differential equations. The program is initialised by running the main file. A high level algorithm is displayed in Figure 56.

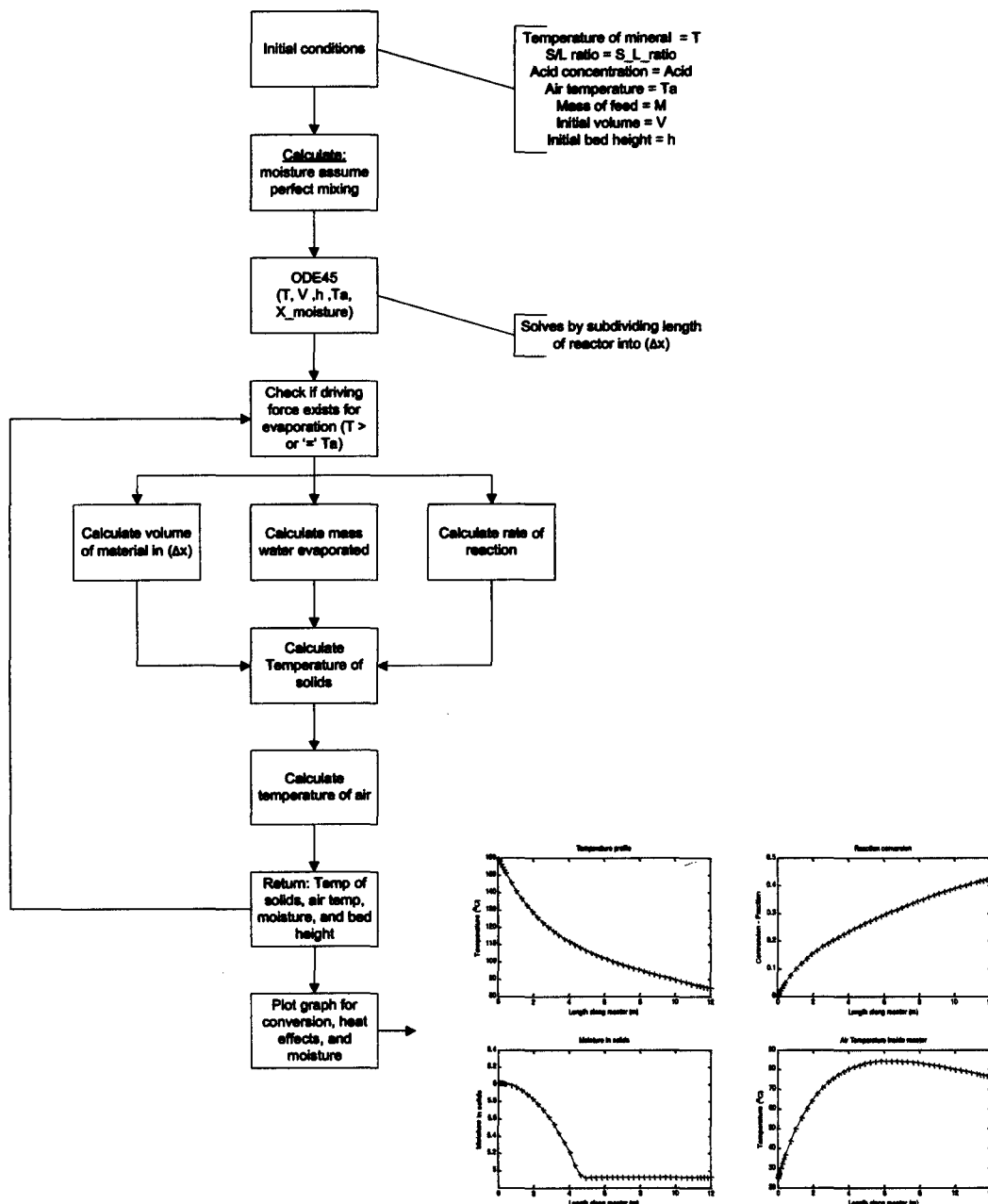


Figure 56: MATLAB algorithm for the NS kiln model

6.1.2. Assumptions and validation

The assumptions used to develop the model were based on physical observations on the plant, while others are heuristics-based (such as the heat-transfer coefficients). The solution-speciation was not part of this MATLAB model (due to the high complexity of such models, which goes beyond the scope of the present work), and thus an assumption on the value of the moisture content was made at which the solution becomes over-saturated and the reaction rate slows down. This simplified the calculation procedure. The following list details the various assumptions made:

1. Driving force for evaporation:
 - a. Temperature difference between air and particle/evaporating surface
2. No acid evaporates relative to water
3. Reaction rate occurs at the temperature of the particle (or bulk mass)
4. Bed height at feed end is close to zero (0.1 m)
5. The reaction rate slows down, and super-saturation is reached, once the moisture content in the solids drops below 3% (Figure 49), while the reaction rate slows to an appreciated zero when moisture is <1%.

A number of parameters were fixed during the validation process. These parameters were physical measured parameters such as the physical dimensions of the kiln; the heat-transfer coefficients were assumed based on Perry et al. (1969).

Table 22: MATLAB Constants

Parameter	Details	Value and [unit]
R	Kiln diameter	1.5m
U _{air}	Heat-transfer coefficient for air to water	1 W/m ² .K (assumed)
U _{water}	Heat-transfer coefficient for water to solid	80 W/m ² .K (assumed)
Density	Density of solids (includes a porosity of 20%)	3.6 t/m ³
Beta	Kiln rotational speed	2 RPM (measured)
n	Angle of declination	2° (measured)
Eta	Angle of solids repose	53° (assumed)
v	Mass flow of solids	12 t/hour
N _{air}	Volumetric flow of air (wet air)	10 m ³ /s (assumed)
L	Kiln length	12 m

Further assumptions in the calculations:

- (a) The air becomes saturated towards the discharge end of the reactor and could be over-saturated at the discharge, as noticed on the plant. The stack drawing the off-gas from the reactor shows significant condensation of water as it cools flowing up the stack, indicating that the air must be saturated at the discharge temperature.
- (b) The assumption that no acid evaporates relative to water is based on the V/L-diagram for H_2SO_4 and H_2O systems (Appendix A) – from the diagram it is reasonable to assume no sulphuric acid evaporates.
- (c) The overall heat transfer coefficient of $80 \text{ W/m}^2\cdot\text{K}$ is somewhat higher (double) than what would be expected for this scenario (typically $40 \text{ W/m}^2\cdot\text{K}$ for boiling water). This is motivated by the fact that the solution contains sulphuric acid, and particles stick together.
- (d) The bed height was measured to be close to 0.01m at the feed end the reactor and 0.1 – 0.2 m at the discharge.

6.2 Model results versus actual plant data

The MATLAB model was first validated for conditions experienced on the plant using the reaction rates and data from the laboratory work. Firstly plant conditions are tested as shown in Figure 58. The two scenarios observed by Namakwa Sands personnel are the following:

- (a) On hot days the zircon production is lowered due to it being off-specification on iron
- (b) Lower temperatures, higher solid/liquid ratios produced on-specification zircon

6.2.1 HAL performance as seen on day-to-day (air temperature fluctuations)

First the model can be used to compare the current leaching effectiveness with the data shown in Figure 29: Reactor performance during 2011 ($T_{\text{feed}} = 160^\circ\text{C}$, $S/L = 10.8$, 40 wt% H_2SO_4). The variance was thought be brought about by the change in feed air temperatures. The model scenario was then run where the temperature of the air was adjusted from 5 to 45°C and the other variables were fixed (see Table 23) the reaction conversions were then plotted versus data obtained during plant sample campaign as seen in Figure 29.

Table 23: Input variables for changes in feed air temperatures

Variable	Details	Value [Unit]
T _{feed}	Solids feed temperature	160 °C
S/L ratio	Solid/liquid ratio	10.8
C _{acid}	Sulphuric acid concentration	40% wt.
h	Discharge solids bed height	0.1 m
T _{air}	Air temperature	Ranged from 5 – 45 °C

The phenomenon demonstrated here is what has been noticed by plant personal, whereby zircon products become off-specification after a hot day. The results from the model will be presented in such a way as to compare to actual data taken from the plant (samples) during four periods:

- (a) on a hot day where the mean day temperature was 45 °C
- (b) on a warm day where the mean day temperature was 27 °C
- (c) on a cold day where the mean day temperature was 16 °C
- (d) on a very cold day where the mean day temperature was 5 °C

The results are presented in Table 24 and compared to actual plant samples taken during the same test conditions (measured air temperatures, discharge temperatures, discharge moistures and reaction conversions-EXP). The MATLAB model this correlated to the experimental variables can also be matched to a R^2 , giving an indication of how well the model predicted that value compared to the actual value obtained from experimental data.

Table 24: MATLAB Model versus experimental results

Test	Conversion (%)		Discharge temp (°C)		Moisture (%)	
	MATLAB	EXP	MATLAB	EXP	MATLAB	EXP
Feed air temp. 5°C	30	31	81	81	2.2	4.5
Feed air temp. 16°C	23.1	23	85	87	1.3	3.6
Feed air temp. 27°C	24	26	88	89	1.5	3.15
Feed air temp. 45°C	24	22	92	100	1.2	2
R^2	0.86		0.94		0.78	

It is clear that the model does reasonably well to predict the discharge temperature ($R^2=0.94$), however it does seem to be fairly off-course with the discharge conversion ($R^2=0.86$) and discharge moisture ($R^2=0.78$), which the model calculated consistently lower than the actual experimental values. The reason why the model fails in predicting the temperature at the discharge is because of over-predicting the evaporation of water, which is also why the moisture levels on the discharge are lower. The model does not account for a condensing phase at the discharge, which would result in less water being evaporated overall. Further tweaking of the heat-transfer coefficients could also solve this problem. However, what is of importance to this study is that we understand the dynamics occurring along the length of the reactor. This will help to develop an explanation as to why colder days lead to higher zircon yields and higher conversions as seen in Table 24. Figure 57 is developed using the results obtained by running the feed air temperature scenarios as presented in the previous paragraph and instead of just final data points presenting the data along the length of the kiln.

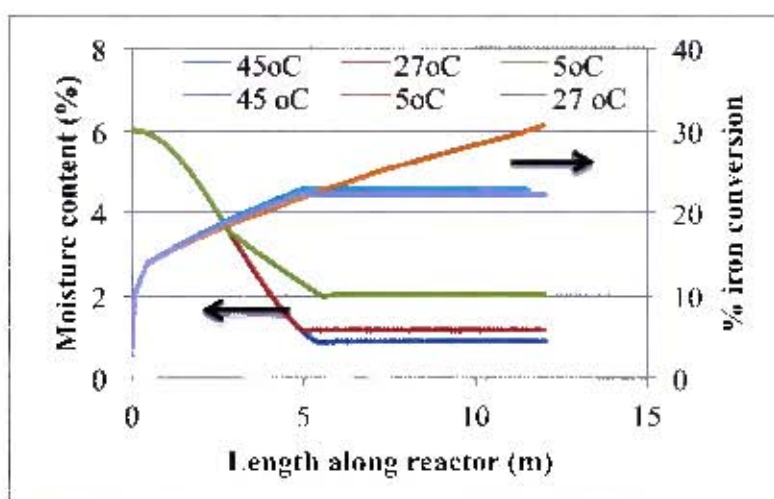


Figure 57: Reactor performance under feed air temperature changes and moisture contents along the reactor length

It is also interesting, that between 5°C and 16 °C, the greatest conversion improvement occurs, however after this there seems to be very little change in the conversion at higher ambient air temperatures. Between 5°C and 16 °C, it appears as though there is a critical ambient air temperature, where further increases result in moisture content within the kiln to drop. A brief sensitivity analysis on this revealed that for the feed conditions specified, feed-air temperatures above 8°C result in lower conversion.

These observations are consistent with what was noticed in the plant tests, cold weather produced on specification zircon products, while really hot weather resulted in poor leaching or iron coatings. Different evaporation rates are thought to drive the reaction.

Evaporation:

Also of note are the different evaporation rates, for all air feed temperatures the initial evaporation rates are all similar. However, 2.5 m down the length of the reactor, the rate of evaporation for the 8°C air temperature slows down. The reason why all the evaporation rates are similar initially is thought to be the mixing effect of sulphuric acid and water (which produces water vapour). This effect is more dependent on the concentration of acid in solution. Once the change in enthalpy of mixing has occurred, the process of evaporation of the remaining water in solution starts. The slowing down of the rate noticed, 2.5m down the kiln reactor for the lower temperatures, is thought to be due to the fact that at lower temperatures the relative carrying capacity of air for water is much lower than at higher temperatures. Therefore at higher temperatures the air is far more likely to evaporate due to the fact that air can carry more water.

6.2.2 HAL performance as at higher solids feed temperatures

The performance of the HAL reactor has been questioned, specifically when it was noticed that after increasing the temperatures (moving from 160 °C to 180 °C) on the fluidized bed driers which are feeding hot minerals into the HAL reactors, no significant increase in reaction conversion was noticed. The MATLAB model was adjusted to account for hotter minerals as feed as illustrated in Table 25, while the other variables were kept constant.

Table 25: Input variables for changes in feed air temperatures

Variable	Details	Value [Unit]
T_{feed}	Solids feed temperature	Ranged from 60°C - 180 °C
S/L. ratio	Solid/liquid ratio	10.8
C_{acid}	Sulphuric acid concentration	40% wt.
h	Discharge solids bed height	0.1 m
T_{air}	Air temperature	25 °C

Similar work as what was completed in the previous section where the reactors were sampled under similar conditions to the MATLAB model and the plant data (EXP) was collected,

samples were taken of the reactor discharge (moisture, iron conversion and temperatures). This data is then compared to the MATLAB model data as presented in Table 26.

Table 26: Model predictions for increasing solids temperature

Solids temp.	Conversion (%)		Discharge temp. (°C)		Moisture (%)	
	MATLAB	EXP	MATLAB	EXP	MATLAB	EXP
120	19.80	22	58.11	70	5.59	5.6
140	27.92	27	70.85	78	3.93	4.2
160	28.77	26	96.82	96	1.04	3.15
180	28.05	27	99.82	100	1.04	2
R ²	0.92		0.81		0.92	

The results compare well to the actual plant data in terms of measured discharge temperatures, measured discharge moisture and conversions. It is also interesting to note that with increasing solid temperatures the conversion increases. This was noticed in the experimental (laboratory) work, although after 140 °C there seems to be little improvement in the actual conversion. The reactor dynamics can be further illustrated using Figure 58, where the the discharge temperatures, iron conversion and the moisture content are plotted against the mineral feed temperature

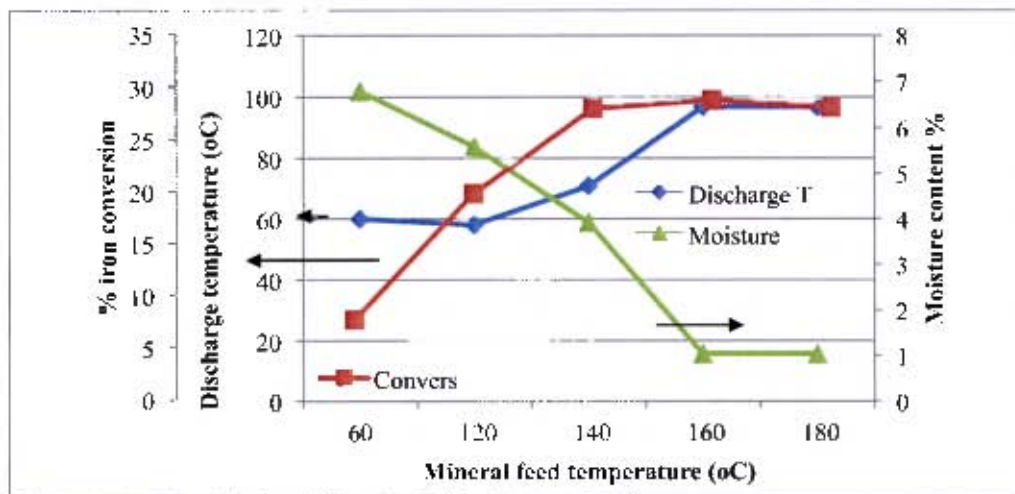


Figure 58: Reactor performance under varying solids temperatures

An important observation was that increasing the temperature over 140 °C doesn't drive the reaction to higher conversions. Comparing conversions for feed temperatures of 140 °C versus those at 160 and 180 °C it is interesting to note that the conversions at these

temperatures are very similar and that the differences are negligible. The reason for this is related to the rate of evaporation, which at high temperatures is so rapid (this due to the higher temperature difference) that the solution reaches a super-saturated point long before that of the colder solids. The point of super-saturation thus occurs at an earlier point within the kiln for the high temperatures than for the lower temperatures. The super-saturation of the solution results in a slower rate reaction at these higher temperatures, effectively slowing the reaction down to a bare minimum. The result is that the reaction reaches the same conversion at 140 °C as compared to 180 °C because the reaction rate now slows down. This could be due to precipitation as indicated in previous sections; it is clear that moving temperatures higher does not directly translate into higher conversions. This information also points to possible energy saving. Running the kiln reactors at 160 °C previously showed the best results and therefore this temperature was chosen as the preferred running condition. However the MATLAB model has demonstrated that the conversion at these higher temperatures is no better than running at 140 °C.

6.2.3 Solid/liquid ratio and its effect on reaction conversion

During the experimental section it was seen that the S/L ratio also influenced the conversion of hematite within the reactor. The experimental section detailed the lower S/L ratios produced lower conversions. Reports by Huisamen (2000) detail that during an iron excursion (the excursion had lasted for more than four days), a trial period was run on the reactors, where they were set at lower temperatures and very high S/L ratios ($S/L = 17$); the result was on-specification zircon product within 12 hours. Huisamen (2000) could not explain this phenomenon and suggested that it may have been caused by a significant change in the feed. In 2011 however, work by Ledgerwood (2011) confirmed Huisamens observations, yet again little evidence could support this theory. The present MATLAB model can be used in an attempt to answer why this happens. The main explanation is attributed to the fact that at lower S/L ratios more water is present in the solution (for a fixed volume of solids) and thus the result is that baking at lower S/L ratios shows higher conversions than at higher S/L ratios.

This was tested using the MATLAB model by adjusting the S/L ratio of feed material into the kiln. The other parameters were fixed as listed in Table 27.

Table 27: MATLAB model parameters

Variable	Details	Value [Unit]
T _{feed}	Solids feed temperature	160 °C
S/L ratio	Solid/liquid ratio	Ranged from 5 - 17
C _{acid}	Sulphuric acid concentration	40% wt.
h	Discharge solids bed height	0.1 m
T _{air}	Air temperature	25 °C

MATLAB model data is presented in Table 28, which details the output from the model in terms of S/L ratio, discharge temperature, moisture content and also the relative saturation point within the kiln (at a certain distance from the feed-end) and the associated time spent in the kiln.

Table 28: High S/L ratio effects on conversion

S/L ratio	Conversion (% Fe ³⁺)	Discharge Temperature (°C)	Moisture (%)	Saturation temperature (°C)	SP (Length from feed (m))	Calculated MRT (minutes)
5	23.75	89.45	4.52	109.31	5.83	9.72
11	30.17	91.20	3.93	110.06	4.93	8.22
13	31.22	110.55	1.24	110.50	4.79	7.98
17	32.21	112.32	1.04	110.54	4.59	7.66

It is evident from Table 28 that there is no significant difference in the conversions for S/L ratios from 11 to 17. However from 5 to 11 a significant change in conversion is noticed, favouring higher S/L ratios. The reason for this is that under lower S/L ratios large amounts of water are evaporated, which results in further temperature drops before the reaction has time to proceed far at high temperatures. Small changes are noticed: higher discharge temperatures for higher S/L ratios – this makes sense as with lower S/L ratios less water is evaporated. That the saturation points are all different points to an interesting phenomenon: the lower the S/L ratio, the longer it takes to reach super-saturation within the kiln. This explains the reason why lower temperatures and higher S/L ratios produce higher conversions. Thus the plant observation on the lower temperature and higher S/L ratio can be

computed using the MATLAB model. The model was run for normal operating conditions and then for lower temperature and higher S/L ratio.

Table 29: Higher S/L ratio and lower temperature

S/L ratio	Feed temperature (°C)	% Moisture	% Conversion
10.8	160	3.93	30.17
17	140	2.71	31.2

The results in Table 29 don't indicate a major increase in conversion for the one scenario compared to the other. It is interesting to compute the energy associated with evaporation within the two different scenarios. Table 30 indicates the results.

Table 30: Energy used for evaporation at different S/L ratio

S/L ratio	% heat used in evaporation of heat supplied
10.8	89%
17	45%

As indicated, the higher the S/L ratio is, the less energy is used in evaporation. This is due to the availability of water. The energy left once the evaporation process has taken its course is left for the reaction. In the present case it is shown that it is possible to achieve similar conversions running the reactor at 140 °C, compared to running the reactors at 160 °C. This results also suggests that a possible energy saving could come from running at lower temperatures while yielding the same conversion.

6.3. Sensitivity analysis on reactor

A sensitivity analysis can be run on the MATLAB model to understand what the largest contributor to conversion is within the reactor system. Changing a single variable at a time and leaving the others unchanged was core to the sensitivity analysis. The same percentage change was made on each variable, i.e. $\pm 15\%$ change from normal operating conditions for each. The different scenarios that were computed are listed in Table 31.

Table 31: Sensitivity analysis (input variables changes)

Variable	15% change upwards	Normal conditions	15% change downwards
Solids feed temperature (°C)	136	160	184
S/L ratio	9.18	10.8	12.42
Air temperature (°C)	21.25	25	28.75
Acid concentration	34	40	46

Figure 59 represents a graph illustrating the percentage change effect each variable has on the conversion, which will provide sufficient information as to what variables can be manipulated for optimization of the kiln bake environment. The respective gradients give an idea of how much of a relative effect that particular variable has on the conversion.

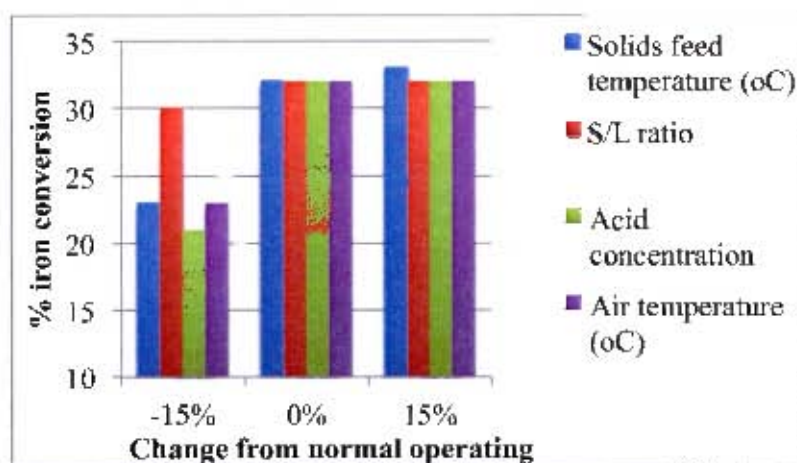


Figure 59: Sensitivity analysis on kiln reactor system

It is evident from Figure 59, that the conversion is very sensitive to three variables:

- Feed-air temperature
- Solids feed temperature
- Acid concentration
- Over this (S/L = $\pm 25\%$ of 10.8) range also the S/L ratio does seem to have an effect, however as noticed in the previous section, S/L ratio has the most profound effect

It is interesting to note that the conversion is not very sensitive to S/L ratios as the gradient of this line is very flat compared to the other three gradients. It must be reiterated that the above

analysis does not account for changes in two variables at one time. Three of the four variables are controlled using a PLC system and monitored by plant personal, however the one that Namakwa Sands has least control of is that of feed air temperature. As the kiln reactor is placed outside it is very susceptible to day-night temperature fluctuations, which already makes for a dynamic system due to a changing air temperature.

6.4. *Summary of MATLAB model*

The MATLAB model was developed from the laboratory work, which extended the kinetic data, completed a mass and energy balance together with evaporative rates. The model successfully describes the conversion achieved across the reactor and the discharge temperature. However it failed to properly calculate the moisture content at the discharge. This is possibly because of the heat-transfer coefficient ($80 \text{ W/m}^2\cdot\text{K}$) and the assumption that air volumetric flow rate was $10\text{m}^3/\text{s}$, which, if the true flow-rate/coefficient is much smaller than the assumed values, would result in much higher evaporation rates.

The validity of the MATLAB model was done by running different HAL reactor scenarios, whereby the air temperatures were changed or the solid-feed temperatures were adjusted, or the acid concentration changes were made. The specific scenarios were chosen such that they matched specific data, which had been collected over the previous year (2011). The plant data, which was in the form of discharge moisture conditions, discharge temperatures and conversions, was compared to the MATLAB model output. For all the cases the model was able to predict quite accurately what the plant survey data was. The assumption that the reaction becomes hindered (caused by super-saturation) after a moisture of $< 1\%$ proved quite successful in developing the conversions as these values agreed quite closely with the observed iron conversion.

The MATLAB model also answered a major question: why with does the conversion remain unaffected by temperatures above 160°C . The model suggests that the reason for this is primarily related to evaporation rates. At higher ($>160^\circ\text{C}$) temperatures the relative saturation point is reached at a very similar location (in terms of meters from the feed-end) within the reactors as when running at 160°C . The model was also able to explain, why on hotter days the conversion of iron across the reactors drop; this was said to be due to the higher heat capacity of water at higher temperatures. The higher heat capacity drives further water off the

surface of the particle and thus brings the relative super-saturation point even closer to the start of the reaction.

The actual reactors could have been quite a bit shorter – based on the model it is suggested that on average the reaction runs for 5m along the length of the reactor. Further energy savings maybe implemented, if the reactors were run at higher S/L ratios (13) while at lower temperatures 140 °C, as these conditions produce the same conversion as temperatures of 160°C and S/L ratios of 10.8 which are currently employed

It is also clear from the model that greater residence times won't improve conversion and that the reaction itself is completed during the first half of the kiln.

It does appear, however that the conversion in the reactor is set at a maximum of around 30%, higher conversions will not be achievable using the kiln system at any choice of operating variables. Namakwa Sands will have to look at a different reactor system to enable it to further enhance its bottom-line.

CHAPTER 7

CONCLUSIONS AND RECOMMENDATIONS

The aim of this project was to develop an understanding of the leaching process occurring in the Namakwa Sands HAL reactors. Based on the results and discussion presented in Chapter 5 and Chapter 6 the following conclusions and recommendations will be made.

7.1 Conclusions

The main objectives of the study were met in the following ways:

Based on plant surveys conducted:

- External weather conditions were shown to affect the conversion of hematite (iron) across the reactor. The plant survey results indicated that during hot days the HAL reactor conversion is a lot less than compared to colder days, while the discharge temperatures were colder for colder cold days and hotter for warmer days.
- Moisture conditions within the reactor affect ferric conversion across the reactor. The final discharge moisture content was thought to be driving the conversion, however the MATLAB model clearly showed that the moisture content at the discharge is unimportant but rather at the very beginning of the kiln.
- Residence times of the reactors were calculated and confirmed to be 20 minutes.
- Higher reactor feed temperatures don't translate into higher iron conversions.
- Mass and energy balances indicated that evaporation accounted for 63% of energy lost (currently). The results also indicated that the acid concentration along the reactor length increases due to evaporation. The mass and energy balance successfully predicted the acid concentrations and moistures at the discharge, indicating that the assumptions to the energy balance were correct.

- The seasonal effects noticed from winter to summer months, day to night maxima and minima all affect the discharge moisture content and consequently the temperature. The difference between a maximum and a minimum can be as much as 20 °C.

Based on laboratory work:

- The initial reaction rate is very fast, however it quickly reaches a maximum after 30 minutes of contacting with acid-solution. The reaction-rate beyond 30 minutes is appreciably slower. It was argued that the rate described a reaction hindered by diffusion, while the activation energy describes a rate hindered by the reaction. The activation energy was determined to be 38 and 24 kJ/mol (Fe_2O_3). The rate is thought to be initially reaction driven, but after a short period (due to the evaporation of water) the concentration of ferric becomes saturated, which upon further leaching/dehydration the solution becomes super-saturated. The laboratory data suggested that the reaction does not stop at this point, but continues at a slower rate. This suggests that the reaction is limited via both the reaction and diffusion conditions.
- The transition between the two mechanisms is marked by thermodynamic stability of ferric in solution. The mechanism was shown to change when ferric starts precipitation from the solution.
- The formation of a solid product layer explains why higher temperatures don't translate into higher conversion. Which is driven by evaporation, where as leaching proceeds ferric ions become supersaturated within solution, upon further leaching, the ferric precipitates as a ferric-complex back onto the zircon minerals. This causes the product layer formation.
- The exact ferric specie that precipitates is not known, however based on the relative solution measurements and the data presented during the laboratory work, the specie is likely to be a complex of ferric, sulphates and protons.

Based on reactor modeling:

- The HAL reactor model was accurate in describing the conversions achieved across the reactor. The model was validated against plant survey data.. The model accurately predicted discharge solid temperatures and conversions; however it predicted consistently lower discharge moisture conditions. The assumptions on air flow-rates is thought to be skewing the model (i.e. actual air flow-rates are much lower than assumed).
- The percentage contribution of feed heat to evaporation relative to reaction can be manipulated through the S/L ratios, and in this way conversion may always be maximized.
- The model indicates a peak in air/internal gas temperature, indicating that saturation of vapour occurs at this point, beyond which the moisture water is in equilibrium with the vapour.
- The conversion of the reactor is greatly affected by solid/liquid ratios, air feed temperature, solid temperature and the acid concentration.
- The model also shows that the discharge moisture condition is not a good indicator of reactor performance, and cannot be used as a control measure to monitor the reactor performance.
- The model also shows that similar conversions can be achieved by running at lower temperatures (140 °C) and higher S/L ratios (13), as compared to running at higher temperatures (160 °C) and lower S/L ratios (10.8) currently practiced. This highlighted a potential energy saving on the fluidized bed drier.

Based on the evidence:

The discussion on whether HAL reactors can be used to obtain ceramic grade Zircon is controversial, nothing seemed to improve leaching efficiency, whether it was increases in solids temperature or changes in acid concentration. The impact these changes had on the conversion of hematite to ferric-complex was negligible.

7.2 Recommendations

The following recommendations are made based on the preceding conclusions:

- Further research into developing the right technology for the operation. The formation of a product layer during the baking environment is noticed to reduce the leaching across the kiln. A CSTR type reactor would be far better suited for this type of leaching operation (the typical solid/liquid ratio would be 1/100), where a steam-injection could provide the required heat and a CCD type leach circuit could be employed. Another form of agitation mentioned in this project was that of sonic attritioning, which could also be investigated to improve conversions. The benefit of running CSTR CCD reactors would be that of real-time iron control. Currently the iron conversion across the kiln is very difficult to control. This would present a significant possible acid saving and excess acid can be recycled.
- House the kiln in its own building - if the development of a new circuit is impossible the next alternative would be to house the kiln in a building type environment, this will allow for far more stable operation and will reduce the observed variance influenced by external conditions and seasonal affect, moreover the following recommendations are made:
 - a. The air-blower must be either decommissioned or the air fed into the blower is pre-heated. This would enable the air to be fed at a constant temperature and in this way reduce the variance associated to heat loss caused by evaporation.
 - b. Scrolls must be installed on the inside of the kiln to dive the solids further down the kiln and in this way reduce the amount of air required.
- The leaching conditions clearly indicate that running at temperatures $>140\text{ }^{\circ}\text{C}$ don't result in higher iron conversions and therefore Namakwa Sands should consider running their reactors at lower temperatures. The results clearly indicate that the conversion does not change significantly above $140\text{ }^{\circ}\text{C}$ and therefore a running at higher temperatures is not necessary. The potential benefit from running at lower temperatures can be significant, especially considering the current fuel shortages.

REFERENCES

- Abdus-salam, N. & Adekola, F.A., 2006. Comparative Dissolution of Natural Goethite Samples in HCl and HNO₃. *Journal of Applied Science and Environmental Managment*, 2(10), pp.11 - 17.
- Agtzini-Leonardou, S., Oustadakis, P., Tsakiridis, P.E. & Markopoulos, C., 2008. Titanium leaching from red mud by diluted sulfuric acid at atmospheric pressure. *Journal of Hazardous Materials*, 157(1), pp.579 - 586.
- Amer, A.M., 2002. Alkaline pressure leaching of mechanically activated Rosetta ilmenite concentrate. *Hydrometallurgy*, (67), pp.125 - 133.
- Azimi, G. & Papangelakis, V.G., 2011. Mechanism and kinetics of gypsum - anhydrite transformation in aqueous electrolyte solutions. *Hydrometallurgy*, 108(1), pp.122 - 129.
- Bao, L. & Nguyen, A.V., 2010. Developing a physically consistent model for gibbsite leaching kinetics. *Hydrometallurgy*, 104(1-2), pp.86 - 98.
- Bentley, M.D., 1989. Namakwa Sands Project. Memo. Vredendal: Memo Anglo American Corporation of South Africa Limited.
- Biber, M.V., Afonso, M.d.S. & Stumm, W., 1994. The coordination chemistry of weathering: IV. Inhibition of the dissolution of oxide minerals. *Geochimica et Cosmochimica Acta*, 58(9), pp.1999 - 2010.
- Casas, J.M., Crisóstomo, G. & Cifuentes, L., 2005. Speciation of the Fe(II)-Fe(III)-H₂SO₄-H₂O system at 25 and 50 °C. *Hydrometallurgy*, 80, pp.254-64.
- Casas, J.M., Crisóstomo, G. & Cifuentes, L., 2007. Solubility of sodium-jarosite and solution speciation in the system Fe(III)-Na-H₂SO₄-H₂O at 70 °C. *Journal of Geochemical Exploration*, 92, pp.111-19.
- Chastukhin, A.E., Izotov, A.D., Gorchev, I.G. & Kutepov, A.M., 2003. Analysis of Fe₂O₃ and Fe₃O₄ Dissolution kinetics in Terms of the Chaim Mechanism Model. *Theoretical Foundations of Chemical Engineering*, 37(4), pp.398 - 406.
- Cigan, J.M., Mackey, T.S. & O' Keefe, T.J., 1980. Lead-Zinc-Tin. In TMS-AIME world symposium on metallurgy and environmental control., 1980. The metallurgical Society of AIME.
- Cservenya'k, I., Kelsall, G.H. & Wang, W., 1996. Reduction of Ti(IV) species in aqueous sulfuric and hydrochloric acids: I. Titanium speciation. *Electrochimica Acta*, 41(4), pp.563 - 572.
- de Villiers, C., 2011. Characterisation of heavy mineral sands and soils by radiometry and its use in mineral beneficiation and agriculture. PhD Thesis. Stellenbosch.
- Dobney, S.J., 1988. Magnetic separation. *Industrial Minerals*, (7), pp.50-53.

- Du, F., Li, J., Li, X. & Zhang, Z., 2011. Improvement of the iron removal from silica sand using ultrasound-assisted oxalic acid. *Ultrasonics Sonochemistry*, 18(1), pp.389 - 393.
- Dutrizac, J.E. & Monhemius, A.J., 1987. Mineralogical overview of iron control in hydrometallurgical processing. *Iron control in hydrometallurgy*, pp.19 - 46.
- Eckehard, S. et al., 2010. Experimental investigation of solid bed depth at the discharge end of rotary kilns. *Powder Technology*, 1(197), p.17–24.
- Englebrecht, C., 2011. Dry mill leaching diagnostic. Progress report. Namakwa Sands.
- Farmer, A.D., Collings, A.F. & Jamerson, G.J., 2000. Effect of ultrasound on surface cleaning of silica particles. *International Journal of Mineral Processing*, 60, pp.101 - 113.
- Freyer, D. & Voigt, W., 2003. Crystallization and Phase Stability of CaSO_4 and CaSO_4 - Based salts. *Chemical Monthly*, 134(I), pp.693 - 719.
- Frost, R.L. et al., 2005. NIR spectroscopy of selected iron(II) and iron(III) sulphates. *Spectrochimica Acta Part A*, 62, pp.42-50.
- Gous, M., 2006. An overview of the Namakwa Sands Ilmenite Smelting Operations. *South African Institute of Mining and Metallurgy*, pp.189-202.
- Guimares, S.J.F., De Olivera, N. & De Salles, F.L., 1987. Purification of registro kaolin by magnetic separation. *Minerals and Metals*, 51(485), pp.13 - 17.
- Hind, A.R., Bhargava, S.K. & Grocott, S.C., 1999. The surface chemistry of the bayer process solids: a review. *Colloids and Surfaces*, 146(1), pp.359 - 374.
- Huisamen, F., 2000. HAL reactor. commissioning Report. Namakwa Sands.
- Hussein, M.K., Kolta, G.A & El-Tawil .S.Z., 1976. Removal of iron from Egyptian ilmenite. *Egyptian Journal of Chemistry*, 19(1), pp.143-52.
- Ismael, M.R.C. & Carvalho, J.M.R., 2003. Iron recovery from sulphate leach liquors in zinc hydrometallurgy. *Minerals Engineering*, 16(1), pp.31- 39.
- Jackson, J.S. & Wadsworth, M.E., 1976. A kinetic study on the dissolution of Allard Lake ilmenite in hydrochloric acid. *Light Metals*, 1(1), pp.481 - 540.
- Jansen, F., 2001. Relocation of the Blue Cube MQi units for the benefit of measuring the wet gravity feed stream and Hot Acid Leach Feed (HAL). Proposal. Stellenbosch: Blue Cube Systems (Pty) Blue Cube Systems (Pty).
- King, R.P., 2003. Modeling and simulation of mineral processing systems. Article. Utah: Butterworth University of Uta.
- Kosmulski, M., Maczka, E., Jartych, E. & Rosenholm, J.B., 2003. Synthesis and characterization of goethite and goethite-hematite composite: experimental study and literature survey. *Advances in colloid and interface science*, 103(1), pp.57 - 76.

Kruger, A., Focke, W.W. & Kwela, Z., 2002. Effect of ferrous and ferric iron impurities on the crystallisation of gypsum and sludge formation in wet-process phosphoric acid. *Chemical Engineering Communication*, (189), pp.684 - 694.

Langová, Š., Riplová, J. & Vallová, S., 2007. Atmospheric leaching of steel-making wastes and the precipitation of goethite from the ferric sulphate solution. *Hydrometallurgy* , 87, p.157–162.

Ledgerwood, J., 2010. Namakwa Sands Mill circuit optimisation project. Optimisation Report. Vredendal: Namakwa Sands.

Ledgerwood, J., van Zyl, W. & van der Westhuyzen, P., 2011. The effect of particle size distribution in electrostatic and magnetic separation – the big picture; recovery and yield. Heavy Minerals Conference , I.

Lee, S.O. et al., 2006. Study on the kinetics of iron oxide leaching by oxalic acid. *International Journal of Mineral Processing*, I(80), pp.144 - 162.

Levenspiel, O., 1979. *Chemical Reaction Engineering*. 2nd ed. New York: Losu.

Levenspiel, O., 1979. *The Chemical Reactor Omnibook*. 2nd ed. New York: Losu.

Li, S.-Q. et al., 2002. Axial transport and residence time of MSW in rotary kilns Part I. Experimental. *Powder Technology*, I(126), p.217– 227.

Li, S.-Q. et al., 2002. Axial transport and residence time of MSW in rotary kilns: Part II. Theoretical and optimal analyses. *Powder Technology*, I(216), p.228– 240.

Lindley, K.S. & Rowson, N.A., 1997. Feed preparation factors affecting the efficiency of electrostatic separation. *Magnetic and Electrical Separation*, 8(1), pp.161-74.

Lui, Y., Chuxia, L.F. & Wu, Y., 2007. Characterisation of red mud derived from a combined Bayer process and bauxite calcination method. *Journal of Hazardous Materail*, 146(1 - 2), pp.209 - 223.

Manning, T. & Grow, W., 1997. Inductively Coupled Plasma Atomic Emission Spectrometry. *The chemical educator*, 2(I), pp.1 - 19.

Nauman, B.E., 2002. *Chemical reactor design, optimization and scale up*. New York: McGraw-Hill.

Oderinde, R.A. & Olanipekun, E.O., 1992. Kinetics of hydrochloric acid leaching of laterite. *Pakistan Journal of Scientific and Industrial Research*, 35, pp.77 - 80.

Olanipekun, E.O., 1999. A kinetic study of the leaching of a Nigerian ilmenite ore by hydrochloric acid. *Hydrometallurgy*, 53(1), pp.1 - 10.

Olanipekun, E.O., 2000. Kinetics of leaching laterites. *International Journal of Mineral Processing*, 60(1), pp.9 - 14.

Papangelakis, V.G. & Rubisov, D.H., 2000. Sulphuric acid pressure leaching of laterites — speciation and prediction of metal solubilities at temperature. *Hydrometallurgy*, 1(58), pp.13 - 26.

Perry, R.H., Green, D.W. & Maloney, J.O., eds., 1969. Drying fundamentals. In *Perry's Chemical Engineers Handbook*. 7th ed. McGraw Hill. pp.12.3 - 12.15.

Petersen, J., 2010. Introduction to Hydrometallurgy. Lecture notes. Cape Town: Chemical engineering department University of Cape Town.

Philander, C. & Rozendaal, A., 2009. Mineral intricacies of the Namakwa Sands mineral resource. *The Southern African Institute of Mining and Metallurgy*, pp.99-106.

Pitzer, K.S., 1980. Thermodynamics of Aqueous Systems with Industrial Applications. *American Chemistry Society*, (133), p.451.

Prinsloo, A., 2006. The formation of chemical precipitates in the HAL process and its impact on electrostatic separation of zircon and rutile minerals. MSc. Thesis. Stellenbosch: University of Stellenbosch.

Richards, J., 2011. XRD Analysis of a 4 Samples from Namakwa Sands. Memorandum. Pretoria: Exxaro R&D Exarro.

Rozendaal, A., Philander, C. & C., C., 2010. Characteristics, recovery and provenance of rutile from the Namakwa Sands heavy mineral deposit, South Africa. *The Journal of The Southern African Institute of Mining and Metallurgy*, pp.67 - 74.

Ruiz, M.C., Zapata, J. & Padilla, R., 2007. Effect of variables on the quality of hematite precipitated from sulfate solutions. *Hydrometallurgy*, 89, p.32–39.

Sandler, S.I., 1997. Chemical and Engineering Thermodynamics. 3rd ed. New York: John Wiley & Sons, Inc.

Santona, L., Castaldi, P. & Melis, P., 2006. Characteristics and separability of red mud and heavy metals. *Journal of Hazardous Material*, 136(2), pp.324 - 329.

Sinha, H.N., 1984. Hydrochloric acid leaching of ilmenite. In AusIMM, ed. *Proceeding of the Symposium on Extractive Metallurgy AusIMM*. Melbourne (Australia), 1984. The Australasian Institute of Mining and Metallurgy.

Solymar, K., Sajo, I., Steiner, J. & Zoldi, J., 1992. Characteristics and separability of red mud. *Ligh Metals*, 146(1-2), pp.209 - 233.

Styriakova, I. et al., 2010. Dissolution of iron from quartz sands by basin bioleaching under static in-situ conditions. *Hydrometallurgy*, 104(1), pp.443 - 447.

Sukla, L.B. & Das, R.P., 1987. Kinetics of nickel dissolution from roasted laterites. *Transactions of the Indian Institute of Metals*, 40(1), pp.351 - 353.

Svoboda, J., 1993. Separation of particles in the corona-discharge field. *Magnetic and Electrical Separation*, 4(1), pp.173-92.

Taxiarchou, M. et al., 1997. Removal of iron from silica sand by leaching with oxalic acid. *Hydrometallurgy*, 46(1), pp.215 - 227.

Tindall, G.P. & Muir, D.M., 1998. Effect of E_h on the rate and mechanism of transformation of goethite into hematite in a high temperature acid leach process. *Hydrometallurgy*, 47(1), pp.377 - 381.

Tremaine, P.R., Trevani, L.N. & Rudolph, W.W., 2004. Acid-base ionisation and metal complexation under hydrothermal conditions by UV-visible and Raman spectroscopy. In Collins, M.J. & Papangelakis, V.G., eds. *Pressure Hydrometallurgy*. Alberta, Canada, 2004. CIM.

TZMI, 2010. Zircon. Annual Zircon report. TZMI.

Ubaladini, S., Piga, L., Fornari, P. & Massidda, R., 1996. Removal of iron from quartz sands: A study by column leaching using a complete factorial design. *Hydrometallurgy*, 40(1), pp.369 - 379.

van Dyk, J.P., Nanna V. & Pristorius, P., 2002. Kinetics of ilmenite dissolution in hydrochloric acid. *Hydrometallurgy*, 65(1), pp.31 - 36.

van Santen, R., 1984. The Ostwald Step Rule. *Journal of Physical Chemistry*, (88), pp.5768 - 5769.

Veglio, F. et al., 1998. Drum leaching test in iron removal from quartz using oxalic and sulphuric acid. *International Journal of Mineral Processing*, 54(1-2), pp.183 - 200.

Welham, N.J., Malatt, K.A. & Vukcevic, S., 2000. The stability of iron phases presently used for disposal from metallurgical systems - A review. *Minerals Engineering*, 13(8 - 9), pp.911 - 931.

Wollmann, G., Freyer, D. & Voigt, W., 2008. Polyhalite and its analogous triple salts. *Monatsh Chemistry*, (139), pp.739 - 745.

Xiao Yan, L. & Eckehard, S., 2006. Mean residence time and hold-up of solids in rotary kilns. *Chemical Engineering Science*, p.5176 - 5181.

Zhang, S. & Nicol, M., 2010. Kinetics of the dissolution of ilmenite in sulfuric acid solutions under reducing conditions. *Hydrometallurgy*, 1(103), pp.196 - 204.

APPENDIX A to F

Contents:

Appendix A: (a) V/L system for sulphuric acid and water mixture
(b) Excel heat balance calculation method

Appendix B: (a) Schematic of MATLAB model
(b) Source code for MATLAB model

Appendix C: (a) Laboratory equipment and further methods

Appendix D: (a) Thermo-photo graphs of HAL A
(b) Thermo-photo graphs of HAL B

Appendix E: Kiln reactor mass and energy balance

Appendix F: Kiln reactor mean residence time

Appendix G: Data on CD-ROM

Appendix A: V/L system for sulphuric acid and water mixture

Determining the theoretical boiling point of a mixture of sulphuric acid and water:

Develop Antoine equation for pure substances:

The Antoine equation is first established for both pure substances across the concerned temperature range (0 – 200) °C. This is then plotted to find the least squares fit to the equation.

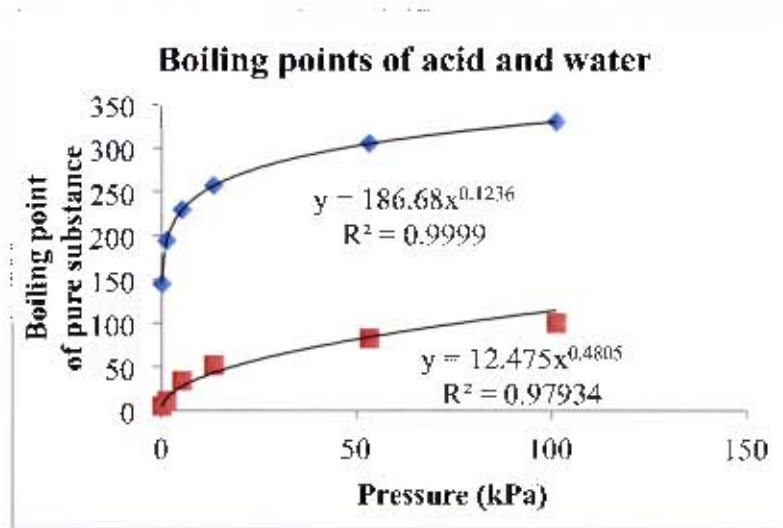


Figure 60a: Boiling points of acid and water at various pressures (Sandler, 1997)

Then approximate the heat of evaporation over a small temperature range using the approximated integrated Clausius-Clapeyron equation.

$$\ln \left(\frac{p^{vap}(T_2)}{p^{vap}(T_1)} \right) = - \frac{\Delta H^{vap}}{R} * \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

For the case of sulphuric acid:

$$\ln \left(\frac{1.332895}{0.133289} \right) = - \frac{\Delta H^{vap}}{(8.314)} * \left(\frac{1}{(273.15 + 194.5)} - \frac{1}{(273.15 + 145)} \right)$$

$$\frac{\Delta H^{vap}}{1} = \frac{- \ln \left(\frac{1.332895}{0.133289} \right) * (8.314)}{\left(\frac{1}{(273.15 + 194.5)} - \frac{1}{(273.15 + 145)} \right)} * \frac{1}{98}$$

$$\Delta H_{H_2SO_4}^{vap} = 771.71 \frac{kJ}{mol.K}$$

This can then be used to construct the phase equilibrium curve for the mixture of sulphuric acid and water:

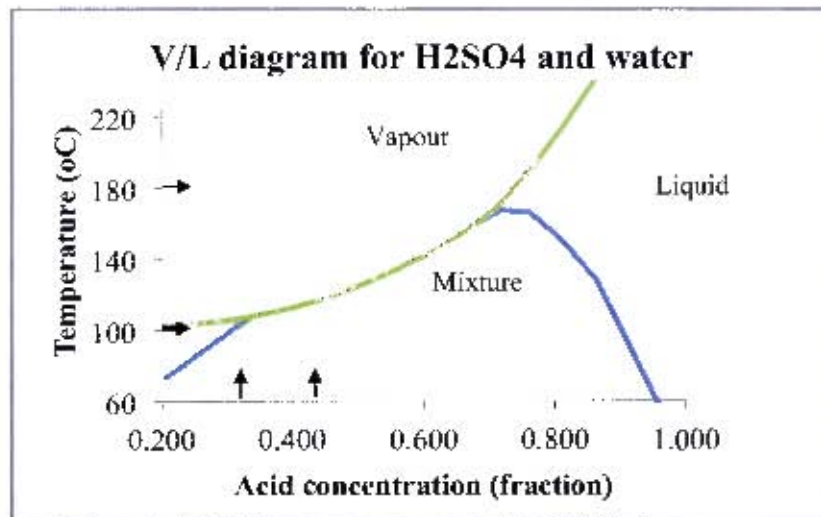


Figure 1b: Vapour/Liquid diagram for sulphuric acid and water at 1 atm.

Steady state - energy balance around reactor:

Assumptions:

1. Heat loss across reactor is negligible.
2. Heat lost inside reactor initially is only due to the evaporation of water.
3. Mixing heat caused by (Acid + water) happens 20 cm from reactor entrance and due to the thermal insulation around expansion piping no energy is lost here.

Energy calculations:

- (a) Is provided from (Figure 1a + Figure 1b)
- (b) Is provided by Cp of mineral and final temperature

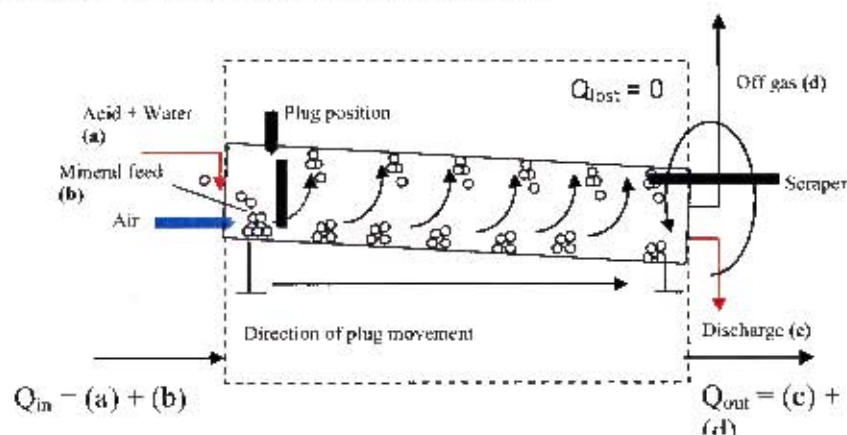


Figure 61: Heat balance around HAL reactor

Excel programming behind heat balance (similar to MATLAB model):

- Specify the T_{sand} and the X_{acid} , Solid/Liquid ratio
- Calculate boiling point of mixture of acid and water (T_{boil} and X_{acid})
 - If $T_{\text{sand}} > T_{\text{boil}}$ /// evaporation will occur
 - Compute evaporation (kJ, T_{solution})
 - Else return 0 /// evaporation will not occur
- Compute Enthalpy of evaporation for (mixture acid + water)
 - Use this to determine the amount of water evaporated ($\text{Water}_{\text{evaporated}}$)
- Recompute the acid concentration on the mineral surface by using S/L ratio, X_{acid} and subtract water evaporated,
- Calculate energy lost due to reaction
- Calculate discharge energy and moisture %
- Appendix E

Appendix B: MATLAB model for HAL reactor

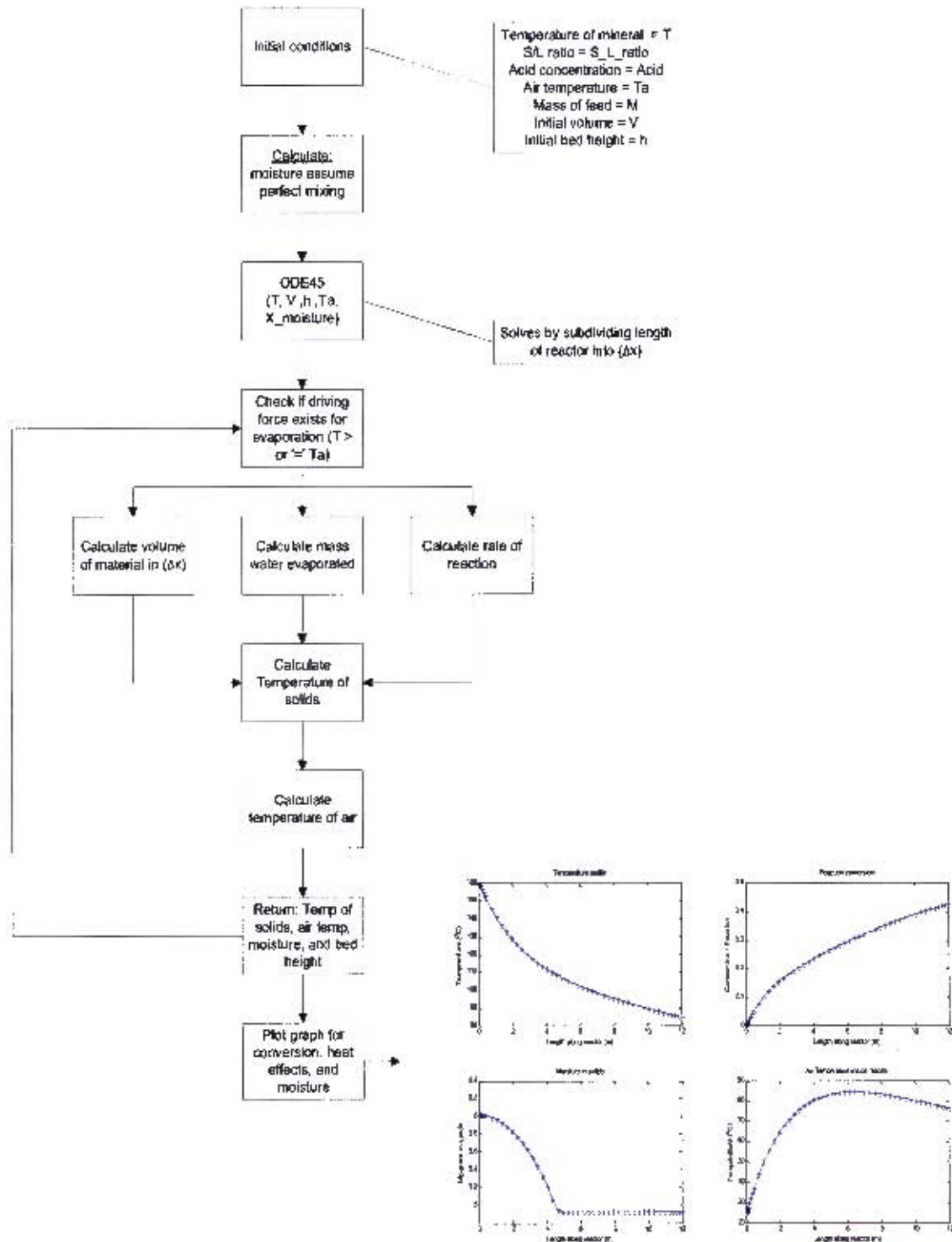


Figure 1B: MATLAB programming procedure

FILE 1: ODEFUN – This file is the one containing the deferential equations.

```
function dYfuncvecdx = ODEfun(x,Yfuncvec)
```

```
T = Yfuncvec(1);
V = Yfuncvec(2);
h = Yfuncvec(3);
Ta = Yfuncvec(4);
Moisture = Yfuncvec(5);
```

```
% intial conditions for iron oxide (%) and mass flow t/hr
C0 = 1;
MassFlow = 12;
```

```
% kiln dimentions
R = 1.5;
```

```
% constants gas and pi
R_ = 8.314;
pi = 3.141592;
```

```
% overall heat transfer coefficients
Ua_air = 1;
Ua = 80;
```

```
density = 4; % density of solids
Cp = 0.8; % cp of solids
v = MassFlow / density / 3600; %volumetric flow rate of solids
eta = 2 / (180 / 3.141592); % ange of repose
n = 2/100;
beta = 2; % rpm of kiln
Hevap = 2700; % of water
Acid_conc = 35/100; % acid strength wt. %
MassFlow=12;
S_L_ratio = 5;
Dosing = (MassFlow/S_L_ratio*1000*Acid_conc)/(MassFlow);
```

```
Mass_water_intial = Dosing * v * density / Acid_conc * (1 - Acid_conc); % dosing of acid (kg/ton)
```

```
T_boil = 1455.7 * Acid_conc ^ 4 - (2495.1 * Acid_conc ^ 3) + 1763 * Acid_conc ^ 2 - (485.26 * Acid_conc) +
147.5 + 273.15;
```

```
if (T < Ta)
    T = Ta; % No driving force for heat transfer if temperatures are the same
end
```

```
theta = 2 * acos((R - h) / R); % angle for area determination is a function of the height of material
```

```
Area = 1 / 2 * R ^ 2 * (theta - sin(theta)); %Area of arc this is dependant on the angle above
```

```
if ((T+273.15) >= T_boil)
    dWdx = v/density*Mass_water_intial-V/density*Mass_water_intial; % no evaporation occurs if the
temperature is below the boiling point of the solution
else
    dWdx = 0;%% for drying the straigth line
end
```

```
DeltaH = 7.5422 * T + 625.8; %kJ/kg Fe2O3
```

```

t = Area/(v*60); % time in reactor is a function of the residence time of unit mass

% Mass flow of water through bed, i.e. moisture
dMdx = 100*(MassFlow*Dosing/Acid_conc*(1-Acid_conc)*dWdx)/(MassFlow*Dosing/Acid_conc*(1-
Acid_conc)*dWdx + MassFlow*Dosing + MassFlow*1000);

if (Moisture <= 2)
    k = 0;
else
    k = 14.283* exp(-22200 / ((T + 273.15) * R_)) ;
end;

N_air = 224.5/800; %% 5cum/hr ~ 5000l/hr/22.4l = 224.5 mol

Cp_air = 1; % Cp of air

X = (1-(1-t*k)^3);

dVdx = Area; % volume of area.bed height

% temperature profile of solids
dTdx = Area * (Ua*Area*(Ta-T) -(DeltaH*(X)/1e2*v*1e3*density) -
Hevap*(dMdx/100))/(v*1e3*density*Cp);

%height of solids in kiln
dhdx = 3 * tan(eta) / (4 * 3.141592 * n) * v * (R ^ 2 - ((h - R) ^ 2)) ^ (-3 / 2);

%Temperature profile of air
dTadx = Area*Ua_air*(T-Ta)/(N_air*Cp_air)-5;

% function ends
dYfuncvecdx = [dTdx; dVdx; dhdx; dTadx; dMdx;];

```

FILE 2: This file is the main file containing all the initial conditions

```
clear;
clc;

Acid_conc = 35;
MassFlow = 12;
S_L_ratio = 10.8;
Dosing = (MassFlow/S_L_ratio*1000*Acid_conc/100)/(MassFlow) % in kg/ton mineral

tspan3 = [0 12.]; % Range for the independent variable
y3 = [160.; 0; 0.1; 40; MassFlow*Dosing/(Acid_conc/100)*(1-Acid_conc/100)/(MassFlow*1000)*100;]; %
Initial values for the dependent variables

[T3,V3] = ode45 (@ODEfun,tspan3, y3);

R_ = 8.314;
n3 = length(V3);

density = 4; % density of solids
Cp = 0.8; % cp of solids
v = MassFlow / density / 3600; %volumetric flow rate of solids
t3 = V3(1:n3,2)/v/60;

i=1;

while i <= n3 % to switch the mechanism from forward reaction to reverse reaction

    if (V3(i,5) < 2)
        k3(i) = 0;
        X3(i) = (1-(1-t3(i)*k3(i))^3);
    else
        k3(i) = 14.283* exp(-22200./ ((V3(i,1) + 273.15) * R_));
        X3(i) = 1-(1-t3(i)*k3(i))^3;
    end;
    i = i+1;
end;

Figure(1);
subplot(2,2,1),
plot(T3(1:n3),V3(1:n3,1), '-+'), ylabel('Temperature (^0C)'),xlabel('Length along reactor (m)');
title('Temperature profile');
subplot(2,2,3),
plot(T3(1:n3),V3(1:n3,5), '-+');xlabel('Length along reactor (m)'), ylabel('Moisture in solids');
title('Moisture in solids');
subplot(2,2,2),
plot(T3(1:n3),X3(:), '-+');xlabel('Length along reactor (m)'), ylabel('Conversion - Fraction')
title('Reaction conversion');
subplot(2,2,4),
plot(T3(1:n3),V3(1:n3,4), '-+');,xlabel('Length along reactor (m)'),ylabel('Temperature (^0C)')
title('Air Temperature inside reactor');
```

Appendix C: Laboratory equipment and methods

Reagents and equipment

The following procedure was followed for each experiment; values in (brackets) were changed depending on what experiment and what conditions were being tested:

- a. Weigh out 100g of mineral sand sample
- b. Preheat sample to (160 °C), oven
- c. Preheat Pyrex tube (160 °C),
- d. Add solids to Pyrex tube, weigh this and record mass
- e. Place solids in Pyrex tube on top of bench top heater in fume (wear gloves)
- f. Add acid to Pyrex tube at (7) S/L ratio
- g. Prepare filter paper insert for draining solids
- h. Measure the mass remaining in the Pyrex tube
- i. Add 100ml of acid water (pH < 1) to Pyrex tube under fume C.
- j. Take sample off bench top heater for analysis and pour sample into filter paper
- k. Wash solids out from Pyrex tube using 20 ml of distilled water
- l. The solution remaining in volume metric flask should be ~ 120ml
- m. Mark sample and measure mass No. liquid and dry solid sample
- n. Send sample for electrostatic separation (Corona-stat) refine the non-conductors to produce a clean non-conductor for magnetic separation (repeat non-conductor recycling 5 times)
- o. Use the non-conductors produced in step (n) for magnetic removal step, refine the non-magnetic fraction produced till a clean non-magnetic product is produced using the Mag-Roll (repeat non-magnetic material recycling 5 times)

Equipment used.

- | | | |
|------------------------|---|---|
| - Pyrex beakers | - | Used as the reaction vessel |
| - Glass rod | - | To gently agitate the mixture. |
| - Hot plate | - | To control the temperature in the vessel |
| - (316 SS) Thermometer | - | To measure the temperature fluctuations |
| - Test tubes | - | To hold iron assay solution. |
| - Weighing balance | - | To accurately measure out the reactants needed. |

- | | |
|----------------------|---|
| - pH meter | - To measure pH of some reactants |
| - Rubber tubing | - To transport air for aeration. |
| - Filter paper | - Filtering solids from solution |
| - Spray bottle | - Washing of solids |
| - Vacuum generator | - Provides vacuum for filtering solids |
| - Measuring cylinder | - To measure out exact volumes of solutions |
| - Osmosis unit | - Provided de-ionized water (MilliQ) |
| - Hand gloves | - Protect hands against acid rashes |
| - Fume cupboard | - Fume extraction system |
| - Eye wear | - Protect eyes from acid |

Reagents used.

- Mineral sands ore
- Concentrated Hydrochloric acid (32 % wt.)
- Oxygen (in air)
- Sodium chloride (NaCl)
- De-ionized water (H₂O)
- Concentrated Sulphuric acid (98 % wt.)
- Hydrofluoric acid (40 % wt.)

Appendix D: Thermal images of HAL A and HAL B

HAL A reactor thermal images

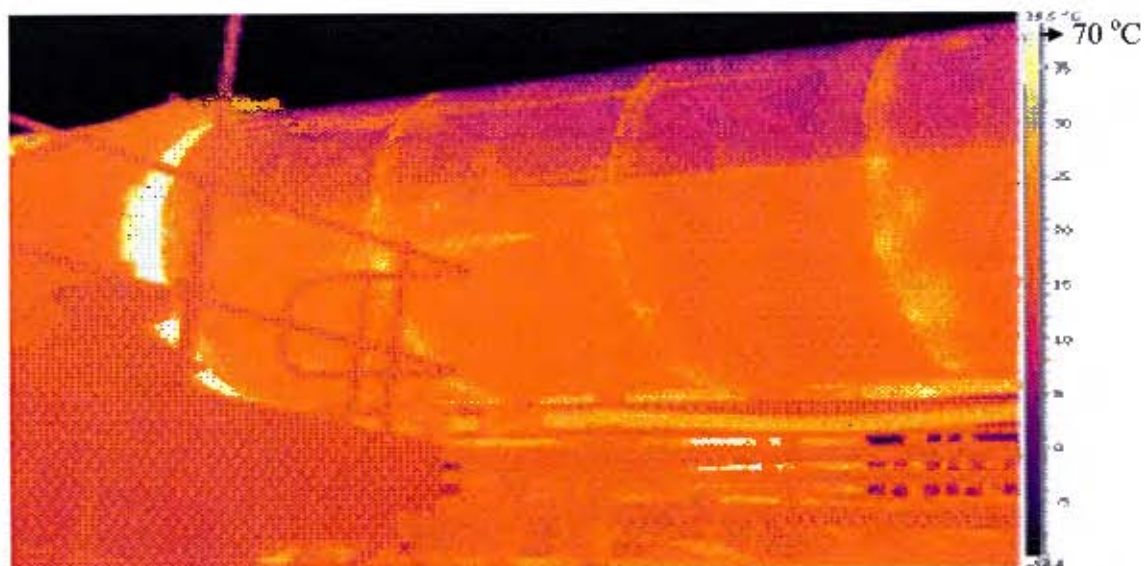


Figure D1: Coupling of HAL reactor A

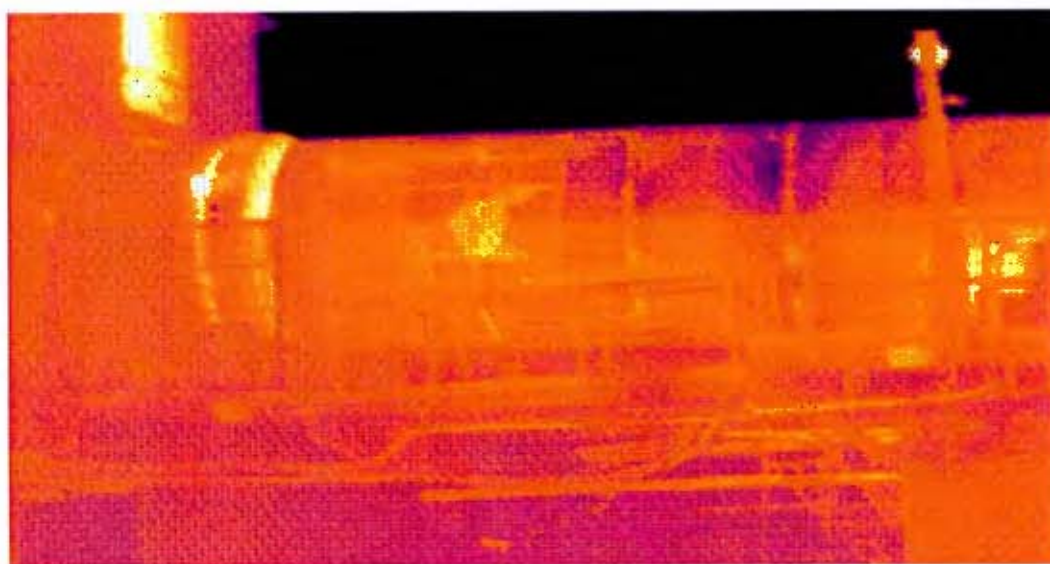


Figure D2: Discharge end of HAL A

HAL B reactor thermal images

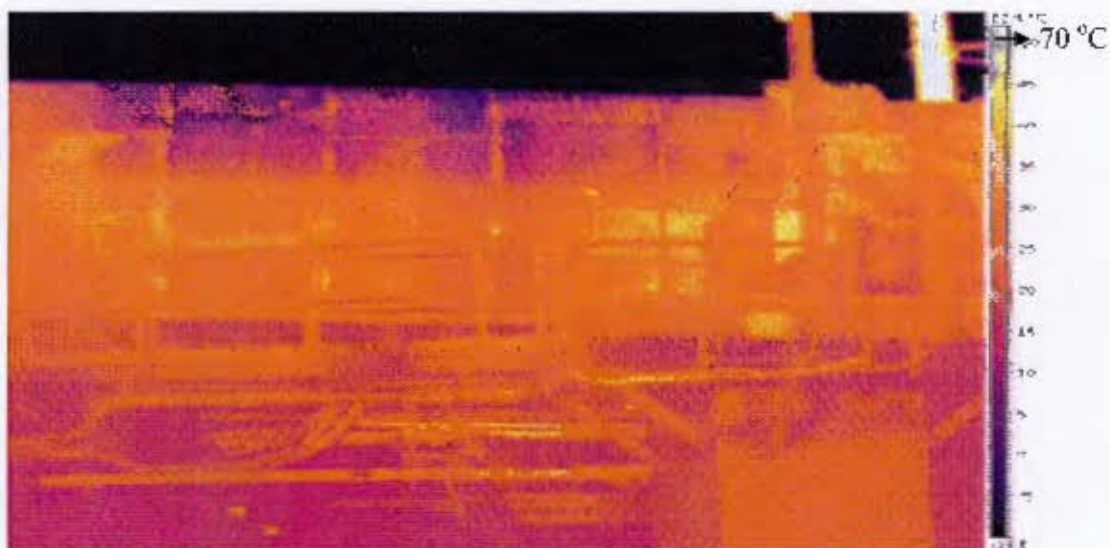


Figure D3: Coupling of HAL reactor B

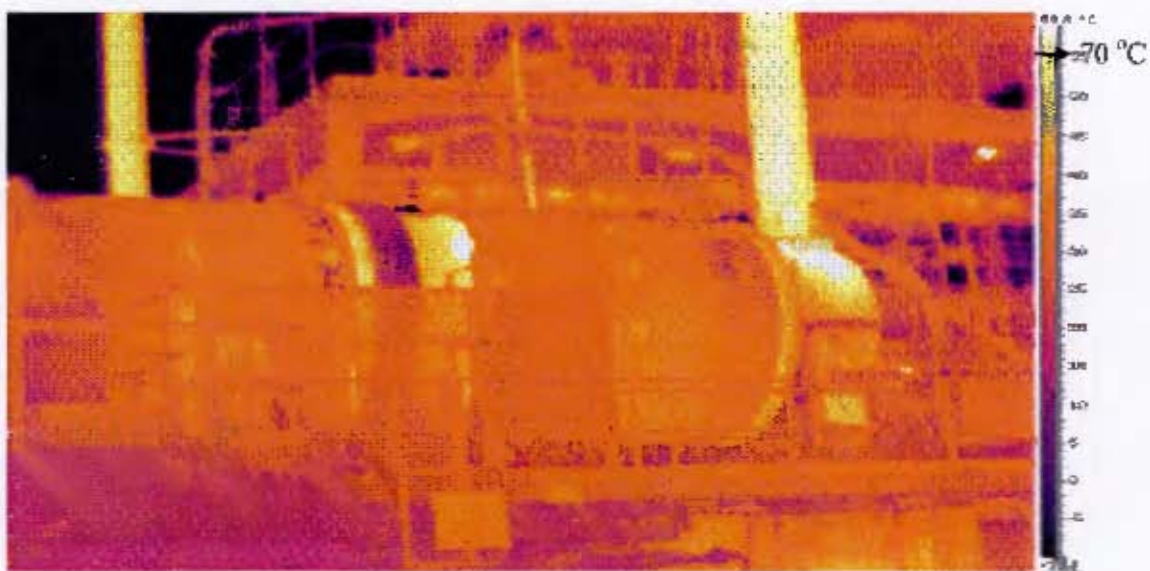


Figure D4: Discharge end of HAL reactor B

Appendix E: Kiln reactor Excel mass balance (Huisamen, 2000)

<u>Heat balance over reactor</u>	
Heat loss by sand = Latent heat gain by steam + Thermal heat gain by air + Heat losses over reactor	
Assuming : Acid solution inlet temp approx 100 degrees, bed temp constant at 100 degrees	
Latent heat (J/h) = Sand heat loss - Air heat gain - Heat losses	
Sand heat loss due to evaporation	722400000
Total heat losses from shell	1.52E+08
Heat used to heat air	3.88E+06
Heat lost due to reaction	4.39E+08
Heat available to vaporise water with losses and air intake	5.66E+08
Heat available with no heat losses from shell	7.19E+08
Heat available with no heat losses from shell, and no air intake	7.22E+08
<u>Mass of water vaporised with heat losses and air intake</u>	251.0
<u>Mass of water vaporised without losses from shell</u>	318.5
<u>Mass vaporised without losses and no air intake</u>	320.2

<u>Evaporative heat consumed at reactor inlet</u>		
Solids flow (t/h)	12	Input
Solids flow (kg/h)	12000	Calc
Acid strength (% m/m)	38	Input
Acid addition rate (kg/t)	35	Input
Acid flow (kg/h)	420	Calc
Acid density (kg/l)	1.84	Literature
Acid flow, 98 % (l/min)	3.8	Calc
Water flow (kg/h)	685.3	Calc
Water flow (l/min)	11.4	Calc
Total acid solution (l/min)	15.2	Calc
Total acid solution (kg/h)	1105.3	Calc
Acid solution density (kg/l)	1.21	Calc
Latent heat of vaporisation of water (J/kg)	2.256E+06	Literature
Specific heat of sand (J/kg.K)	860	Measured, Literature values: Diatomaceous earth 840, Brick 838, Concrete 880, Asbestos 1050
Sand inlet temperature (deg C)	160	Input
Sand final temperature (deg C)	90	Input
<u>Thermal heat lost by sand (J/h)</u>	M.C.dT	7.224E+08
<u>Mass of water vaporised at inlet (kg/h)</u>	M.L = M.C.dT	320.2
		Calc, ignore heat losses through shell, and air heating
<u>Mass of water remaining as liquid (kg/h)</u>		365.1
Bed percent moisture (% m/m) excl acid		3.0
		Calc

<u>Heat losses from reactor surface due to radiation</u>		
Reactor length (m)	12.0	Input
Reactor diameter (m)	1.32	Input

Surface area (m2)	$A = \pi \cdot d \cdot l$	49.76	calc
Outside temp (deg C)		50	Input
Outside temp (deg K)	T	323	Calc
Emissivity	e	0.95	
Stefan-Boltzman const (W/m2.K4)	a	5.67E-08	Literature
	$Q = e \cdot a \cdot A \cdot T^4$		
<u>Radiative heat loss rate (J/h)</u>		2.92E+04	Calc
<u>Heat losses from reactor surface due to natural convection</u>			
<u>Calc film heat transfer coeff using empirical relation for natural convection from horizontal pipes</u>			
Shell temp (deg C)		50	
Shell temp (deg F)		147.6	
Air temp (deg C)		25	
Air temp (deg F)		102.6	
Temp diff (deg F)	dt	45	
Shell OD (in)	do	52.0	
	$h = 0.50 \cdot (dt/do)^{0.25}$		
Film heat transfer coeff (Btu/h/ft^2/degF)		0.48	Calc - Kern Pg 215
Film heat transfer coeff (W/m^2/degC)		2.7	
<u>Film heat transfer coeff (J/h/m^2/degC)</u>		9860	
Reactor surface area (m2)	A	49.76	Calc
Film heat transfer coeff (W/m2.K)		50	Literature: 5-50 typical range, use max value
Film heat transfer coeff (J/hm2.K)	h	180000	
Shell temp (deg C)		50	Input
Air temp (deg C)		33	Input
	$Q = h \cdot A \cdot dt$		
<u>Convective heat loss rate (J/h)</u>		1.52E+08	Calc
<u>Total heat losses from shell (J/h)</u>		1.52E+08	Calc

<u>Volumetric flow of vapour generated in reactor</u>			
Pressure (1 atm) (Pa)	P	1.01E+05	Input
Temperature (deg C)		100.0	Input
Temperature (deg K)	T	373.0	Calc
Universal gas const (J/mol.K)	R	8.314	Literature
Mass of water vaporised(kg/h)	MH2O	320	Calc
Molecular mass of water (g/mol)	mH2O	18	Literature
Molar flow of steam (mole/h)	$n = M \cdot 1000/m$	17790	Calc
<u>Volume steam generated (m3/h)</u>	$V_{st} = n \cdot R \cdot T/P$	546	Calc
<u>Calculation of air flow into reactor based on scrubber velocity measurement</u>			
Scrubber flow velocity (m/s)	v	8.7	Measured by G Kuhn
Scrubber diameter (m)	d	0.5	Measured
Scrubber cross sectional area (m2)	$A = \pi/4 \cdot d^2$	0.20	Calc
Scrubber inlet temp (deg C)		65.0	Measured
Scrubber discharge temp (deg C)		60.0	Measured
Ave scrubber temp (deg C)	Tscr	62.5	Calc
Reactor discharge temp (deg C)	Tout	90.0	Measured
Ambient temp (deg C)		33.0	Input

<u>Scrubber volumetric flow (m3/h)</u>	$V_{scr} = v.60.A$	102.5	Calc	
				Adjust flow for temperature difference, assume all steam condenses in cooler box
<u>Reactor outlet air flow (m3/h)</u>	$V_{air.out} = V_{scr}.T_{out}/T_{scr}$	153.7	Calc	
<u>Reactor outlet steam flow (m3/h)</u>	V_{st}	546.2	Calc	
<u>Reactor outlet total vapour flow (m3/h)</u>	V_{out}	700.0	Calc	Combine air and steam flows
				Adjust air flow for temp difference between reactor outlet and ambient air temp
<u>Air flow into reactor entrance (m3/h)</u>	$V_{air.in} = V_{air.out}.T_{in}/T_{out}$	54.1	Calc	
To calc mass flow of air:				
Vol % O2 in air		20	Assume	
Oxygen flow (m3/h)	$VO_2 = V_{air}.Vol\%O_2$	11	Calc	
Moles O2 (moles/h)	$nO_2 = P.VO_2/R.T$	353	Calc	
Mass O2 (kg/h)	$MO_2 = nO_2 * 32 / 1000$	11	Calc	
Vol % N2 in air		80	Assume	
Nitrogen flow (m3/h)	$VN_2 = V_{air}.Vol\%N_2$	43	Calc	
Moles N2 (moles/h)	$nN_2 = P.VN_2/R.T$	1410	Calc	
Mass N2 (kg/h)	$MN_2 = nN_2 * 28 / 1000$	39	Calc	
<u>Total mass flow of air (kg/h)</u>	$M_{tot} = MO_2 + MN_2$	51	Calc	
Calc air mass flow from literature air density:				
Density of air (kg/m3)	$D = M_{tot}/V_{air}$	0.94	Calc	
Quoted density at 0 deg C, 1 atm (kg/m3)		1.3	Literature	
Check: Calc density at T and P (kg/m3)	$D1.T1 = D2.T2$	0.95	Calc	
Check mass flow of air (kg/h)	$M = D.V$	51	Calc	
Heat used to raise inlet air temp				
Specific heat of air (J/kg.K)	C_{air}	1005.4	Literature	
Air inlet temp (deg C)	$T1$	24	Input	
Air outlet temp (deg C)	$T2$	100	Input	
Total mass flow of air (kg/h)	M_{tot}	51	Calc	
		3.88E+0		
<u>Heat consumed by heating air (J/h)</u>	$Q = M.C.(T2-T1)$	6	Calc	

<u>Heat of reaction for the conversion of Iron (III) oxide to iron (III) sulphate</u>			
Reaction:	$Fe_2O_3 + 3.H_2SO_4 = Fe_2(SO_4)_3 + 3.H_2O$		
Stoichiometric reaction ratio:	1 mole Fe_2O_3 reacts with 3 mole H_2SO_4		
<u>Heats of formation:</u>		<u>kcal/mole</u>	
Fe_2O_3		-198.5	Literature
H_2SO_4	(liquid)	-193.69	Literature
H_2SO_4	(aq, 400)	-212.03	Literature
$Fe_2(SO_4)_3$	(aq, 400)	-653.3	Literature
H_2O	(liquid)	-68.317	Literature
Heat in (kcal/mole)		-834.59	Calc
Heat out (kcal/mole)		-858.25	Calc
Heat released (kcal/mole)		800.00	Calc
Solids tonnage (t/h)		12	Input
Average % Fe_2O_3 in reactor feed		1.46	Sept actual
Average % Fe_2O_3 in wet gravity feed		0.73	Sept actual
Change in Fe_2O_3 %		0.73	Calc
Mass rate Fe_2O_3 conversion (kg/h)		87.6	Calc
Molar mass Fe_2O_3 (g/mole)		159.7	Literature
Reaction rate (moles Fe_2O_3 /h)		548.5	Calc
<u>Total reaction heat generated (J/h)</u>		4.39E+08	Calc

Appendix F: Kiln reactor mean residence time

Three methods were used to determine the mean residence time in the reactor; the following is a list of them:

Method 1 (Perry et al., 1969)		
$t = 0.23 \cdot L / (SN0.9D) + \text{or} - 0.6 \cdot BLG / F$		
$B = 5 \cdot (Dp) - 0.5$		
t = residence time (min)		? min
L = dryer length (ft)		12.3 m
S = slope (ft/ft)		0.0349 ft/ft
N = speed (r/min)		1.8 rpm
G = air-mass velocity (lb/(h.ft ²))		0.529 kg/(s.m ²)
D = dryer diameter (ft)		1.3 m
Dp = average particle size (um)		110 um
F = feed rate (lb/(h.ft ² cross section))		4.79 kg/(s.m ²)
B	0.476731295	
term1	20.41546993	
term2	-0.388413326	
t =	20.0	min

Method 2 (Perry et al., 1969)		
$t = 0.19 \cdot L / (NDS)$		
t =	28.6	min

Method 3 (Eckehard et al., 2010)		
$t = V \cdot \% \text{fill} / \text{volumetric flow}$		
% fill	12% ->	15%
Volumetric rate	3.63	(m ³ /hr)
t =	25.9 min	to 32.3 min
t =	26.7	min

Appendix G: Laboratory data and plant survey data

CONTENTS OF CD-ROM

1. Lab data (for all test)
2. Plant survey data
3. Plant tracer studies data
4. MATLAB model
5. Excel temperature model
6. Excel MRT for kiln model