THE USE OF SULPHURIC ACID IN THE MINERAL SANDS INDUSTRY AS A CHEMICAL MECHANISM FOR IRON REMOVAL

J Ledgerwood
P van der Westhuysen
NAMAKWA SANDS – EXXARO RESOURCES

ABSTRACT

Namakwa Sands is a mineral processing company based on the West Coast of South Africa and is solely owned by Exxaro Resources. Mineral ore is mined and processed, concentrated and both chemical and mechanically upgraded before being sent for electrostatic separation. The final mineral products report as Zircon, Rutile and Ilmenite.

The requirement for prime Zircon is such that the iron specification is set at less than 0.06% Fe₂O₃. Namakwa is renowned for producing Zircon product with iron levels well below the 0.06%. The leach process whereby iron is removed occurs via the addition of sulphuric acid to mineral at 160 °C contacted in a kiln reactor (HAL). The effective leaching of iron from the surface is imperative to meeting market requirements.

It was found that the major contributors to leaching were the accessibility of acid to the mineral surface and also the feed iron content. The order of dissolution was found to be 0.67. The activation energy for the reaction of iron oxide to iron sulphate was found to be 47 kJ/mol. This is relatively high which indicates a diffusion limitation rather than reaction limitation to the dissolution and that temperature has the greatest influence on rate and with the current plant setup temperature is the only effective variable to change. The results of this study led to a reassessment of the HAL circuit, redesign and implementation of an upgrade whereby iron is effectively leached and subsequently removed from solution.

Keywords – Zircon, Hot Acid Leach (HAL), Kinetics

1 INTRODUCTION

The Namakwa Sands operation is renowned for producing high purity Zircon. The Namakwa Sands operation is owned by Exxaro Limited Resources and forms part of their base metals division. Namakwa Sands produces the highest grade in Zircon product and is one of the largest mineral sands operations in South Africa. Supplying customers from China, Asia and Europe with Zircon, Rutile, Tiokwa®, Zirkwa® and forms of chloride and sulphide slag these products leave via ship from Saldanha. The operation consist of three sites, the mine site located 300 km from Cape Town, the mineral separation plant (MSP) located 320 km from Cape Town and the smelter located 110 km from Cape Town. This report is concerned with the hot acid leach process (HAL) within the mineral separation plant, Figure 1.
Mineral separations plant (MSP)

The mineral separation plant receives feed which is magnetically separated then leached and finally density separated before being fed to the dry mill where electrostatic separations and high force magnetic separation achieve the desired product.

A big problem facing mineral sands in the removal of these iron coatings around Zircon and Rutile particles the reason for this is that customers demand a high purity product to be used in the ceramic industry. Various mineralogical imaging techniques show that the iron oxide must reside on the surface of zircon minerals, while little is contained in the crystal lattice. Iron and calcium oxide coatings covering the minerals are removed via the hot acid leach system, HAL, whereby strong acid is contacted at 160 °C with mineral in a rotary kiln.
Attritioning is used to soften coatings on the mineral surfaces. This mechanical agitation of a high solid density stream leads to a scrubbing action and a subsequent 10 °C increase in discharge temperature. Work compiled by Prinsloo (2006) found that after attritioning of the surfaces another wash stage must be added for further removal of iron in solutions and that a single cyclone wash capability was insufficient. This then led the addition of a second (counter current decantation circuit) wash stage which was designed to remove 99.99% of the iron in solution. Pre-stage 2 the iron removal from circuit was at 80%.

Test work conducted during 1999 concluded that increasing temperature to above 150°C would provide the necessary activation energy. They also concluded that residence times of 30 minutes would be adequate, for reactor A, for that typical feed type. But over the last decade iron content has increased steadily from 1.7 % in 2000 to on average above 2.5 % in 2011 (Figure 2). Iron has been known to make non-magnetic particles behave slightly magnetic and conductive. (Prinsloo, 2006) With increased iron content in the feed the leach load in the reactors has been increased. The impact of increased iron content to the reactors is the reason for the current and future study since it is imperative for proper feed preparation of low iron concentration and high total heavy mineral content for best dry mill separation.

![Figure 2: % Iron in feed to HAL and subsequent discharge % Iron and removal efficiency](image)

2 BACKGROUND TO THE HAL REACTORS

Leaching of mineral sands is often referred to as a solid – liquid multiphase reaction. The mineral surfaces covered in iron oxide in the most stable form – Fe₂O₃ are contacted with sulphuric acid. This reaction involves sulphuric acid removal of the surface and the formation of iron sulphate – Fe₂(SO₄)₃. The feed is received from a HAL bin which feed two reactors A, B at 12 t/hr and 27 t/hr respectively. Before entering the reactor the feed is preheated to 160 °C through a fluidized bed and gravity fed to the feed chute where sulphuric acid is added at 35 – 40 wt%. The mixing dynamics of acid/water and solids aren’t well understood but thought to occur quite turbulently due to the violent acid (98 %wt) – water reaction. The solution is added above the mineral sands. This deviates from the initial design of adding solution under
the solids. The subsequent changes in design led to the addition of fumes fans to the reactors as feed tended to accumulate near the feed chute due to the slight angle of the kiln, gravity and the general rotation the mineral tends to follow a plug flow type reactor. Residence time distribution of the reactors haven’t been determined but are thought to be close to ideal with little back mixing occurring (Nauman, 2002).

![Diagram of reactor](image)

Figure 3: Namakwa Sands Hepworth - Hot Acid Leach reactor, the flow patterns within the reactor can be noticed

Test work was conducted in 2005 which confirmed the work conducted in 1999 and indicated that reactor A compared to B contained on average 4 % more moisture and the discharge was on average 5 – 8 °C cooler.

### 2.1 REACTOR DESIGN DETAILS

Fer-Min-Ore found the following details on reactor A and B,

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Reactor A</th>
<th>Reactor B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Throughput (t/hr)</td>
<td>12</td>
<td>12</td>
</tr>
<tr>
<td>Rotation (rpm)</td>
<td>1.3</td>
<td>1.29</td>
</tr>
<tr>
<td>Retention time (min)</td>
<td>30</td>
<td>28</td>
</tr>
<tr>
<td>Reactor volume (cum)</td>
<td>16</td>
<td>15.9</td>
</tr>
<tr>
<td>Slope (degrees)</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Design Current</td>
<td>Design</td>
<td>Current</td>
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<td>Design Current</td>
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<td>Current</td>
</tr>
<tr>
<td>Throughput (t/hr)</td>
<td>12</td>
<td>27</td>
</tr>
<tr>
<td>Rotation (rpm)</td>
<td>1.3</td>
<td>2</td>
</tr>
<tr>
<td>Retention time (min)</td>
<td>30</td>
<td>90</td>
</tr>
<tr>
<td>Reactor volume (cum)</td>
<td>16</td>
<td>46</td>
</tr>
<tr>
<td>Slope (degrees)</td>
<td>2</td>
<td>2</td>
</tr>
</tbody>
</table>

Fer-Min-Ore also produced curves that display increasing % fill with increasing throughput and decreasing rotational speed. At current operating conditions a throughput of 27 t/hr and a rotational speed of 1.9 rpm translate to a 10% fill. The residence time is subsequently 40 minutes. The details that an increase of residence time would support the leaching process would ultimately increase the recovery of zircon. Tables of residence time versus throughput and % fill can be used to adjust the revolutions per minute which would allow for a slower/faster residence time without
much adjustment to fill% in reactor. Also if the throughput of the reactors are increased
the relative adjustments can then be matched for the same residence times. But this is
not operationally viable as the motor attached to the kilns are fixed speed. So the only
variable that maybe adjusted is the feed rate.

3 THEORY

Thermodynamic data on reaction 1 is based on Gibbs free energies. As the reaction
involves solid – liquid and occurs at high temperatures, real Cp values and equations of
states are used for determining the heating energies.

\[ \text{Fe}_2\text{O}_3(s) + 3\text{H}_2\text{SO}_4(\text{g}) \rightleftharpoons 3\text{H}_2\text{O}(\text{g}) + \text{Fe}_2(\text{SO}_4)_3 \quad K = 10^9 \text{ at } 160 \degree C \ldots (\text{Rxn 1}) \]

Other reactions occuring on the side line involve,

\[ \text{FeSO}_4^+ + 2\text{H}_2\text{O} \rightleftharpoons 3\text{H}^+ + \text{FeO}^\cdot\text{OH} + \text{SO}_4^{2-} \quad K = 10^{-3} \text{ at } 160 \degree C \ldots (\text{Rxn 2}) \]
\[ \text{FeTiO}_3(s) + \text{H}_2\text{SO}_4 \rightleftharpoons \text{FeSO}_4 + \text{TiO}_2 + \text{H}_2\text{O} \quad K = 10^{11} \text{ at } 160 \degree C \ldots (\text{Rxn 3}) \]
\[ \text{FeO}(s) + \text{H}_2\text{SO}_4 \rightleftharpoons \text{FeSO}_4 + \text{H}_2\text{O} \quad K = 10^{14} \text{ at } 160 \degree C \ldots (\text{Rxn 4}) \]
\[ \text{FeAl}_2\text{O}_4(s) + 4\text{H}_2\text{SO}_4 \rightleftharpoons \text{Al}_2(\text{SO}_4)_3 + \text{FeSO}_4 + 4\text{H}_2\text{O}, K = 10^{28} \text{ at } 160 \degree C \ldots (\text{Rxn 5}) \]

The kiln receives varying amounts of Ilmenite and Leucoxene in addition to the
unleached Zircon and Rutile. Ilmenite and Leucoxene are both iron base titanium
metals both find themselves at concentrations of between 2 – 5 % and 3 – 6 %
respectively. According to the thermodynamic constants, leaching the above 1 – 5
reactions will yield iron sulphates in either the ferric or ferrous form. Leaching of iron-
based alumina would be highly leachable, though the kinetics show little will be
formed. Second to reaction 4 is reaction 3, leaching of oxidized iron oxide to ferrous
sulphate followed by the leaching of Ilmenite. In total the iron content in the feed
system rarely exceeds 3.5 % Fe$_2$O$_3$. For thermodynamic considerations all 4 reactions
were considered.

First the heat of reaction is calculated as a function of temperature, the following
assumptions are made,

- Excess H$_2$SO$_4$ at (40 wt % H$_2$SO$_4$)
- Solids have inert properties
- Solids activity = 1
- Water is in vapour form

3.1 HEAT OF REACTION

Heat of reaction is calculated using the known energies of formation for reactants and
products. The reference point is set at 25 °C. Throughout the operating range from 25
°C to 300°C the reaction follows an endothermic nature. With specific consideration to
the conditions at 160 °C the heat of reaction is 253 kJ/mol – Fe$_2$O$_3$ reacted.
3.2 EQUILIBRIUM CONSTANTS AT VARYING TEMPERATURES

The reaction dynamics in the HAL reactors are not well understood and there seems to be diffusion limitations to the rate of dissolution. The reason for this is that the reaction occurs via a solids bake scenario. Acid is added (40% wt), with a solids liquid ratio of (10:8), and water provides the required mixing. This occurs at 160 °C and the reaction is thought to be endothermic rather than exothermic and promptly stops at 105 °C. The reasons for this are thought to be the related to activation energies. Figure 4 demonstrates the reaction curves of species present, Modelling the reaction using Figure 4 it can be noticed that at temperatures greater than 160 °C the reaction is at 99% of the equilibrium meaning at this temperature mostly all the iron oxide will be reacted to form iron sulphate, provided a reactor can operate along this horizontal line. But the reactor in question is a plug-flow semi-adiabatic reactor with a temperature profile that drops from 160 °C at 0 m to 95 °C at 45 m – the length of a single reactor. Therefore 99 % iron removal is not realisable with the type of reactor and reaction considered here (endothermic) unless energy were added at the same time as it were removed. This would then allow the reaction to proceed vertically straight up the 160 °C line and achieve 99 % equilibrium.

However in industrial type leaching the above is not possible and represents a somewhat ideal situation. Since industry requires a product of high purity (Fe removal = 99%), Zircon must contain Fe₂O₃ < 0.06 % a two or three stage reactor system may be implemented. Discharge from the first reactor at 60 % leached are reheated and then sent to the second reactor at 90% leached and then reheated once again and finally sent to the last reactor where the overall iron leached is at 95 %.

3.3 REACTOR ADIABATIC LEACH LINES

The current Namakwa Sands – reactor system is setup in the following way. Feed temperatures at 160 °C with a 60 % maximum leachable iron and a discharge of below 90 °C due to adiabatic nature of the kiln and endothermic reaction – water also evaporates and thus the temperature drops even further. At best the iron is leached at a maximum of 40 – 50 %.
Using the ideas behind the thermodynamic data, it is possible to calculate the relative equilibrium that will be reached in the reactor at each temperature (Figure 4). This gives a good indication as to current reactor performance. The reactors are well insulated and the total heat loss is less than 10 %. From this data if the reactor was to leach 60% of the iron the feed has to be greater than 160 °C while the discharge may be no less than 95 °C. If the reactor discharge temperature decreased even further this would be due to heat loss from evaporation rather than reaction which would ultimately cause a lower % of iron being leached.

3.4 REACTOR DISCHARGE TEMPERATURE VS. FEED TEMPERATURE

To confirm this thermodynamic theory Figure 5, below shows plant data obtained during plant trails conducted in 2005. This data was constructed after changing the feed temperature of the reactors from 130 °C to 140 °C then 150 °C on separate days. The peaks seen in the temperatures are due to mid day temperatures being mid-days being hotter than morning or afternoon temperatures. This deviation is reported at +/-4 °C during this period.
Figure 5: Discharge temperature data from reactors A and B, shows reactor A has a lower discharge temperature compared to reactor B. Also reactor A has a higher in moisture content compared to reactor B, (Kuhn A., 2005)

The performance of reactor A vs. reactor B can be monitored in terms of temperature and moisture in discharge, from Figure 5, both reactors are fed at 160 °C both have the same S/L rations therefore both have the same concentration of water. But reactor A has a lower discharge temperature and a higher concentration of water. This could only make sense if the following were true: The only difference is the residence times; Reactor A is at 28 minutes while B is at 40 minutes. Both have air blowing into the feed. The reason for reactor A’s lower temperature compared to B can be attributed to the blowing in of air.

3.5 THERMODYNAMIC REACTION MECHANISMS

Based on the thermodynamic modelling the following proposed mechanism and reactions take place,

- Initially it is noticed that the iron sulphate is not produced at recognisable concentrations till temperatures are above 60°C.
- FeSO$_4^+$ present at 25 °C decreases rapidly at 60 °C. Above 60 °C the decrease rate becomes very rapid.
- FeO*OH is formed at very low temperatures and gradually increases till 60 °C where the concentration then starts to decrease again.
- Ferric concentration is initially moderate and decreases as temperature increases.
- With the dissociation of sulphuric acid, high proton concentrations are present initially but as temperature increases the level of protons increases till a maximum at 90 °C.
- The predominant iron product at above 170 °C is iron sulphate.
Based on the above points the following can then be concluded. The production of iron in forming the sulphate occurs via intermediates and that at 60 °C an observable change in leaching is observed. This is also confirmed by work conducted in Jan 2000, (Anglo Research, 2000). The formation of an insoluble product layer hindering the dissolution of Ilmenite which showed the formation of TiO₂ and Ti₂O₃ (Olanipekun, 1999)

4 RESULTS AND DISCUSSION

4.1 PLANT TRIALS

Plant trials performed during 2000 conducted on reactor A

1. The rate of dissolution seems to be faster initially, from 0 to 60 minutes,
2. The rates increase rapidly thereafter
3. It tends to slow down and levels off slightly after 150 minutes at a maximum iron leached at 30 %.

Plotting gradients for the two rates it is obvious from the two lines drawn in Figure 6, that two mechanisms exists and that the diffusion limitations might be slowing the second rate down. At 60 minutes the relative deviations from the average became quite apparent. Due to this, the subsequent high standard deviation could be the result of a change in mechanism. This could be due to slow product removal from the surface of zircon particle.

![Leached kinetics for iron oxide at 140°C](image)

**Figure 6: Leach kinetics for iron oxide at 140 °C - plant**

4.2 DETAILED MECHANISM STUDY

To explain this idea of slow product removal from the surface due to diffusion the following mechanism is posed,

1. The relative size of the hydrogen proton molecule makes it very accessible to the Zircon particle where iron oxide resides (Fe – O) – 2 protons reacts with oxygen to form two hydroxides and in this process 1 iron molecule is released
2. Hydroxide ions are very close to the surface of particle and with a very negative polar side will be attracted to ferric iron ions in nearby vicinity. Iron will not move too far from the surface because of its very large particle size, so diffusion from the surface will be very slow.

3. Hydroxide ions will react with iron causing a slightly higher concentration of protons in solution.

4. Iron hydroxide will then react further from the surface with sulphate iron. The hydroxide then forms water and protons that are sent back to the surface to continue the reactions.

5. Proton cyclic reaction

Interpreting the two mechanisms of dissolution displayed in Figure 6: the initial dissolution occurs faster than that of the latter showing a slight change in mechanisms. This was observed by when leaching of Ilmenite occurred and the conclusion was based on the formation of a diffusion barrier, caused by the formation of polynuclear [Ti(OH)]^{3+}, [Ti(OH)]^{2+}, [(TiO)(OH)]^{2+} which formed on the unleached particle inhibiting/slowing the reaction. (Olanipekun, 1999) The fact that iron also behaves much like titanium forming polynuclear iron hydroxide and the tri-hydroxides Fe(OH)$_2^+$, Fe(OH)$_3^+$, Fe(OH)$_4^-$, Fe(OH)$_5^{-2}$ leads to the believe that this causes slower diffusion of the products from the surface to the solution. (Liang et al., 2000) The increased concentration of iron closer to the surface slows the reaction of iron oxide to ferric iron. With fast diffusion of H$^+$ to the surface and rapid reaction till the formation of iron hydroxides around the surface of the particle, this slows down the reaction rate and produces the observed trend - Figure 6.

### 4.3 ORDER OF REACTION

To determine the order of the reaction an empirical approach was taken. Knowing what the concentration of the feed and discharge iron is; a relationship can be established to determine the kinetic order of reaction. The approach is based on statistics – best fit case, rather than on hard science.
The two equations are based on concentration % Iron oxide present in feed and discharge, a plot of concentration ratio vs. time will provide the order

$$\left( \frac{[C(t)]}{[C(0)]} \right)^n = kt \quad (8)$$

Results from this plot can be found in Figure 8 below. For orders not equal to 1 the following equation is used,

$$\left( \frac{[C(t)]}{[C(0)]} \right)^{1-n} - 1 = kt \quad (9)$$

$$[C(t)] = \left( (kt + 1) \ast C(0)^{1-n} \right)^{\frac{1}{1-n}} \quad (10)$$

The statistical analysis indicated that the actual order of the reaction was 0.656 with a $R^2 = 0.992$. This compared to the single order reaction with a $R^2 = 0.9413$. The overall rate constant was determined as $0.0047 \text{ m}^2/\text{minutes}$. An order less than 1 indicates that the reaction is not only governed by the concentration of reactants but also other factors.

![Reaction rates for iron oxide acid bake at 140 °C](image)

**Figure 8: Reaction rates for iron oxide acid bake at 140 °C, determination of reaction order and Arrhenius constant at 140 °C, (Visser, 2006)**

### 4.4 DETERMINING THE ACTIVATION ENERGY

Tests conducted at different temperatures were used to determine the constant at the individual temperatures. This was based on final products with reactor A residence time set at 17 – 21 minutes, and a reaction order = 0.645. This was then used together with the Arrhenius equation (Towler & Sinnot, 2008) for determining the concentration at a given time which was correlated. The actual plant data can be seen in Figure 9. The activation energy was found to be 48.77 +/- 7 kJ/mol. From this value it may seem that it is chemically limited but after a literature review and chemical mechanisms consideration it is clear that the reaction is limited by iron diffusion. It is clear that for
the diffusion limited bauxite reaction high activation energies were found varying from 38 kJ/mol to 79 kJ/mol. It is clear that the predominant source of iron is Fe$_2$O$_3$ but it must also be mentioned that iron in Ilmenite, garnets and leucoxene are also leached to a small extent. Again for the diffusion controlled experiment of Ilmenite leaching in sulphuric acid produced activation energy of 62.4 kJ/mol. (Olanipekun, 1999) For Ilmenite in HCl the activation energy was determined to range from 48.9 to 53.7 kJ/mol. (Tsuchida et al., 1982).

Using equation 10 data with the following substitution,

$$ k = 7342.9 \times \exp \left( -\frac{48770}{RT} \right) \quad \cdots (11) $$

\[ [C(t)] = \left( \left( 7342.9 \times \exp \left( -\frac{48770}{RT} \right) \times t + 1 \right) \times C(0)^{1.0464^{1-0.646}} \right)^{\frac{1}{0.646}} \quad \cdots (12) \]

The plant work was repeated five times, (Stoffels, 2005) for feed at 150 °C and five times at 140 °C while only thrice at 130°C. The statistical errors show that the 140 °C discharge from the reactor showed the greatest variation. This could be a function of weather – causing a slight deviation in discharge temperature. All together the errors are within reason and the linear fit has an $R^2 = 0.9794$ which shows little variance. Equation 12 can now be used for predicting the concentration and leach performance at different temperatures.

![Figure 9: Arrhenius equation and the determination of the equilibrium constant at different temperatures, 130 °C, 140 °C and 150 °C, the activation energy for the reaction is 48 kJ/mol.](image)

### 4.5 MODELLING LEACH PERFORMANCE

Using equation 12, reactor feed data in terms of % iron oxide can be used for the determination of temperature changes, residence time changes or acid %wt changes. The next section provides some insight as to the performance of the reactors depending on feed temperature, or initial iron concentration and residence time.
4.6 LEACH PERFORMANCE AS A FUNCTION OF TEMPERATURE

Leaching of reactants in the reactors occurs over time and at a specific temperature, according to the thermodynamics of these reactions (endothermic). There should be a step change in temperature from the feed to the discharge. This was observed during plant trials in 1999 when feed temperature increased from 130 – 140 °C showed a step change of 5 – 9 °C at the effluent from the reactors.

![Figure 10: % Iron leached as a function of temperature and residence time in reactor for temperature ranges from 120 °C to 180 °C, feed is at 1.7 % Fe₂O₃](image)

For current reactor settings the following table indicates that the maximum allowable leaching of iron for A and B, for a feed of 1.7 % Iron oxide content, is as follows,

**Table 2: Iron leached by reactors A and B; potential values and current observed leach values based on 1.7 % iron oxide in feed.**

<table>
<thead>
<tr>
<th></th>
<th>Reactor A</th>
<th>Reactor B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inlet temperature (°C)</td>
<td>160</td>
<td>160</td>
</tr>
<tr>
<td>Residence time (min)</td>
<td>28</td>
<td>43</td>
</tr>
<tr>
<td>Kinetics – Iron leached (%)</td>
<td>52</td>
<td>58</td>
</tr>
<tr>
<td>Thermodynamics – Iron leached (%)</td>
<td>60</td>
<td>60</td>
</tr>
<tr>
<td>Observed – Iron leach (%)</td>
<td>50</td>
<td>50</td>
</tr>
</tbody>
</table>

According to thermodynamics at 160 °C both reactors will have a potential to leach 60 % of the iron oxide. This is not observed; rather a smaller 50 % removal is observed. Also according to kinetics model 52 and 58 % iron removal is predicted. For the thermodynamics to work correctly the residence time need to be increased which would lead to higher leach %. Although at 160 °C leaching will never be greater than 60 % production must try and achieve this value or else the operation of this unit is inefficient.
For both reactors A and B to reach the 60% iron removal one must consider the added inefficiency due to loss of heat from the fan-blower (ID into the reactor – fan) and water evaporated during mixing of acid. In other words, if it was established that 80% iron removal is required, the equivalent increase in residence time for A is 60 minutes. The same can be done for reactor B. but increasing the residence time wouldn’t help, unless the temperature was subsequently also increased as the reaction is diffusion limited.

### 4.7 LEACH PERFORMANCE AT 160 °C VS. % IRON IN FEED

In order to determine the adjustments and the justification for an online feed sample to the reactors it is imperative that a relationship between the % iron in the feed be correlated to the % iron in the discharge. With this information instrumentation will be highly successful. The aim of this section is to provide such information and establish the range of % iron in feed to reactors. For this portion of the study 3 % Fe₂O₃ is taken as the maximum iron content, though it has been higher than this at NS before. From the graph data the following table can be constructed,

**Table 3: % Iron in discharge as a function of iron in feed at 160 °C**

<table>
<thead>
<tr>
<th>Feed content</th>
<th>Reactor A (28 min)</th>
<th>Reactor B (45 min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 % Fe₂O₃</td>
<td>1.7</td>
<td>1.1</td>
</tr>
<tr>
<td>2.5 % Fe₂O₃</td>
<td>1.5</td>
<td>0.9</td>
</tr>
<tr>
<td>2 % Fe₂O₃</td>
<td>1.2</td>
<td>0.8</td>
</tr>
<tr>
<td>1.5 % Fe₂O₃</td>
<td>0.9</td>
<td>0.6</td>
</tr>
</tbody>
</table>

It is clear that with a throughput of 12 t/hr to reactor A and 27 t/hr to reactor B the resulting total iron concentration of the discharge will be for a given feed concentration of 2 % Fe₂O₃ to both reactors,

\[
\frac{1.2 \times 100 + 0.8 \times 27}{12 + 27} \times 100\% = 0.92\%
\]

Under current acid, temperature and feed settings 0.92 % iron oxide is being predicted. According to plant data the average is just below 1 (Figure 2), which indicates that the above rate holds true. Figure 11 has the exact details in terms of iron remaining vs. iron fed. The relationship established adequately explains the observed iron concentration at 1 %.
5 CONCLUSIONS

Based on the above data and discussions the following conclusions can be drawn,

1. Current residence times on reactor A and B, 28 minutes for A and 40 minutes for B, are inadequate and cause iron removal inefficiencies, equating to max removal of iron from 1.7 – 0.9 % Fe₂O₃

2. Reactors function close to adiabatically since the temperature drops across the reactors, from 150 °C to 70 °C, This closely matches the prediction by thermodynamics with a 15 % heat loss across the reactor. Industrial practice is at 10%.

3. Leaching of iron is selective and reduction of Ilmenite will occur before iron oxide, based on thermodynamics

4. Moisture content in discharge is a function of feed moisture and feed temperature, also day, night atmospheric temperature changes

5. Based on kinetics a mechanism derived for the dissolution process suggests that the reaction occurs via Fe(OH)²⁻ as an intermediate step. This conforms to the reaction thermodynamics.

6. At 60 °C observable ferric and ferrous ions appear in the dissolution process suggesting that at 60 °C the activation energy is sufficient

7. The activation energy for the dissolution reaction is 48 kJ/mol while the empirical order of reaction is 0.646
6 RECOMMENDATIONS

Based on the above conclusions the following recommendations are made,

1. Perform post-graduate studies on the quantifying of the leaching of iron from zircon and investigate the acid dosing and concentration together with the optimal solid liquid ratio required for optimal leaching of iron.

2. Continue with current post-graduate studies to investigate the diffusion limitations in further detail and provide a solution to current acid/solids mixing.

3. Change the inlet feed temperature from 160 °C to 180 °C. This will result in an iron oxide dissolution of above 90% for B and 90% for A and result in an iron concentration of less than 0.44% Fe₂O₃.

4. Increase the temperature of the feed and decrease the residence time to 90 minutes for reactor B and 60 minutes for reactor A.

5. Investigate the use of reactors in series this will achieve a higher iron dissolution

6. Investigate possible segregation within the reactor system, where fine particles occupy longer residence times compared to large particles

7 REFERENCES


The Authors

Jonathan Patrick Ledgerwood, Graduate chemical engineer, Exxaro Namakwa Sands

Graduate from the University of Cape Town Cum Laude and started in process development at Namakwa Sands where his primary responsibility is to provide process support and unit optimisation. Part-time he has continued with his studies pursuing a MSc. at UCT in chemical engineering.

Pieter van Aarde van der Westhuizen, Process Development Manager, Exxaro Namakwa Sands

He started his career in the diamond mining industry (15 years), working in South Africa and Botswana, where he was involved in production and technical services (plant designs). After 2 years as the Lead Process Engineer, designing a Uranium Plant, he joined Namakwa Sands as the Process Development Manager, responsible for process designs and optimisation of unit processes.