**Technical considerations and viability of higher titania slag feedstock for the chloride process**

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Increasing pressure is being experienced by chloride slag producers to produce slag with more than 90% TiO$_2$. An increase in TiO$_2$ content will significantly decrease the waste generated during the chlorination process and also reduce operational costs. To produce a high grade slag requires increased electrical energy as well as increased reductant in the smelting furnace. The yield of metal from smelting increases considerably, but less slag is produced. The change in certain operational costs, such as refractory wear, is, however, difficult to predict. In the chlorinator the utilization of a high grade slag reduces the amount of waste generated and the disposal costs. Value-in-use calculations show that the production cost of high grade slag is more than the savings realized at the pigment plant, based on certain cost and plant assumptions.

**Introduction**

There is an increasing demand from TiO$_2$ pigment producers who utilize the chlorination process, to obtain high TiO$_2$ (>90% TiO$_2$) slag as feedstock. Increased environmental pressure to minimize waste from the chlorination process is one of the main drivers for this. The chloride pigment process produces between 2 to 5 tons of waste per ton of pigment product (Fischer, 1997). A secondary driver for utilization of high grade slag is to lower chlorine and petroleum coke costs.

The feed to a chlorinator is usually a blend of a number of titania feedstocks, which could include the following:

- Synthetic rutile (SR)
- Natural rutile
- Upgraded titania slag (UGS)
- High grade QIT slag (with ilmenite from QMM, Madagascar, not produced yet)
- Chloride slag
- Ilmenite (used only by DuPont).

It is estimated that about thirteen kilograms less waste is generated for every percentage point increase in TiO$_2$ content (Exxaro, 2008). For example, a ton of 85% TiO$_2$ slag will generate sixty-five kilograms more waste when compared with a 90% TiO$_2$ slag.

Producing a higher (>90%) TiO$_2$ feedstock presents a challenge to the chloride slag producer (to upgrade the feedstock and remain cost competitive), given the increases in energy costs and reductant availability and quality. The various technical and commercial challenges facing the feedstock supplier are discussed in this article, mainly from a slag producer perspective. Through the application of value-in-use models for smelting and chlorination, a large part of the value chain will be analysed to determine the challenges and opportunities in producing a high grade slag. For the purpose of this article when reference is made to high grade slag, it will mean a 90% TiO$_2$ equivalent slag.

The conference theme of ‘What next’ certainly applies to a changing feedstock market in the next five years. This will bring significant technical challenges for both feedstock suppliers and pigment producers.

**The future of slag as a TiO$_2$ feedstock**

In the chlorination feedstock market, chloride slag competes with synthetic rutile, natural rutile and upgraded titania slag. Feedstocks can be classified into two distinct categories based on the resource origin. Chloride slag is generally produced from ilmenite sources containing <60% TiO$_2$. However, SR, high grade QIT slag and natural rutile requires a mineral resource containing secondary ilmenite (>60% TiO$_2$). The pie graph in Figure 1 gives an indication of the relative amounts of high TiO$_2$ feedstocks for 2008 to the chloride process (TZMI, 2009).

High grade mineral resources are being depleted, specifically the mineral resources containing large quantities of secondary ilmenite. The impact of this over the next few years can be seen in Table I, which gives the predicted change in feedstock supply between 2007 figures and estimated figures for 2015 (TZMI, 2008).

The anticipated change in supply is mainly triggered by historically low level of capital investment in new resource development—a direct result of the low profitability of the titanium feedstock industry.
The challenge that pigment producers face is that they will have to be more flexible to adapt their mix of feedstocks. The demand for higher TiO$_2$ chloride slag will also increase as the synthetic rutile supply decreases. Slag suppliers will have to position themselves to handle the changing supply and demand. To better understand the issues with high grade slag production and use, fundamentals and predicted behaviour of the slag will be discussed, both for the smelting and chlorination process.

**Considerations on the production of high titania slags**

**Fundamental considerations**

Various chemical reactions play a role in the ilmenite smelting process. The various reduction reactions in ilmenite smelting are as follows:

- $\text{FeO} + C = \text{Fe} + \text{CO}$ \hspace{1cm} [A]
- $2\text{Fe}_2\text{O}_3 + 3\text{C} = 2\text{Fe} + 3\text{CO}$ \hspace{1cm} [B]
- $2\text{TiO}_2 + C = \text{Ti}_2\text{O}_3 + \text{CO}$ \hspace{1cm} [C]
- $\text{MO}_x + x\text{C} = M + x\text{CO} (M = \text{Cr, Si, Mn, V})$ \hspace{1cm} [D]

Reactions A to C are the most important reactions and dictate to a large extent the final composition of the slag. Geldenhuis and Pistorius (1999) showed that equilibrium conditions are never attained in the ilmenite smelting process. In the production of 90% TiO$_2$ slags it is clear that more carbon (together with the associated increase in energy) will be required for reduction. This results in a decrease in the FeO content of the slags, as well as an increase in the Ti$_2$O$_3$ content of the slags. Excessive reduction of TiO$_2$ to Ti$_2$O$_3$ at high reductant ratios could, however, result in the formation of titanium oxycarbides, which is in a solid phase at smelting temperatures. This, however, is only expected as the FeO content of the slag approaches zero. With increased reduction, the liquidus temperatures of the slag increases. The reason for this is the decrease in the FeO content of the slag, which acts as a fluxing agent.

With an increase in reduction to produce higher quality slags, more of the trace elements (Mn, Cr, V, etc.) will also be reduced (see reaction D), resulting in a lower grade of pig iron being produced.

Pistorius (1999) used a mass and energy balance for ilmenite smelting to calculate the combinations of energy and reductant input which are required to produce a slag product of a given composition. Pure carbon and ilmenite were used or these calculations, thereby providing information only on the trends. These results are shown in Figure 2. Also shown in Figure 2 are actual slag compositions from QIT, RBM and Namakwa Sands, as well as pilot test work at the then Iscor 1.5 MW furnace. The slag composition data points at the lower right of Figure 2 are for slags with a total equivalent TiO$_2$ content of 80%, compared to 92% at the upper left. These calculations show that the slag composition can be manipulated by changing both the energy and reductant inputs.

Over most of the map of slag compositions, the reductant and energy isopleths run parallel. This implies that only a single energy input rate can be used with a specific reductant addition. If the energy input rate is changed by 50 kWh/t ilmenite, the carbon addition must be increased by 10 kg/t ilmenite. If this ratio is not maintained the system will depart from the steady state condition at the slag liquidus temperature. An increase in slag temperature could result in decreasing the size of the freeze lining protecting the sidewall refractories, while a lowering in slag temperature could result in solids being present in the slag with a resultant increase in slag viscosity.

<table>
<thead>
<tr>
<th>Chloride feedstocks</th>
<th>2015 Supply ('000 t)</th>
<th>% Change from 2007</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloride ilmenite</td>
<td>613</td>
<td>10%</td>
<td>Limited new availability</td>
</tr>
<tr>
<td>Leucoxene</td>
<td>56</td>
<td>-57%</td>
<td>Declining production from Tiwest, Iluka and DuPont</td>
</tr>
<tr>
<td>Rutile</td>
<td>772</td>
<td>28%</td>
<td>Supply from new projects</td>
</tr>
<tr>
<td>Upgraded slag</td>
<td>380</td>
<td>11%</td>
<td>Could possibly be expanded</td>
</tr>
<tr>
<td>Chloride slag</td>
<td>1601</td>
<td>46%</td>
<td>RTIT expansion</td>
</tr>
<tr>
<td>Synthetic rutile</td>
<td>373</td>
<td>-53%</td>
<td>Declining Iluka production</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>8%</td>
<td></td>
</tr>
</tbody>
</table>

**Table I**

Summary of predicted feedstock supply changes to 2015 (TZMI, 2008)

*Chloride 2015 Supply % Change Comments feedstocks ('000 t) from 2007*

- Chloride ilmenite: 613, 10% Limited new availability
- Leucoxene: 56, -57% Declining production from Tiwest, Iluka and DuPont
- Rutile: 772, 28% Supply from new projects
- Upgraded slag: 380, 11% Could possibly be expanded
- Chloride slag: 1601, 46% RTIT expansion
- Synthetic rutile: 373, -53% Declining Iluka production
- Total: 8%

Figure 2. Calculated maps of reductant and energy inputs required to obtain given slag compositions. In 2(a) the reductant requirements (broken lines) are in kg C/t ilmenite and energy requirements (solid lines) in MWh/t ilmenite. In 2(b) the energy requirements (solid lines) are shown with the estimated liquidus temperatures (broken lines) in °C (From Pistorius, 1999)
Experimental data on the production of high titania slag
Smelting test work carried out on the 500 kW and 1.5 MW pilot furnaces at Exxaro R&D over the last decade or so has demonstrated that 92 % TiO₂ slags can be produced. These slag compositions have, however, only been produced for relatively short periods, as the focus previously has been on the production of 86 % TiO₂ slags.

Figure 3 shows the relationship between the total equivalent TiO₂ and FeO content of titania slags (Bessinger, 2000) from data obtained from the 1.5 MW pilot furnace test work.

Figure 4 shows the relationship between FeO and Ti₂O₃ content of slags (Bessinger, 2000). For 86% TiO₂ slags the Ti₂O₃ content is in the order of 25–30%. This increases to 35–40% Ti₂O₃ for 92% TiO₂ slags. Chlorinators that use slag as feedstock usually have an upper limit on the Ti₂O₃ content of the slag, usually 35%.

Figure 5 shows the relationship between tapping temperature and the FeO content of the slags (Bessinger, 2000). Typical 86% TiO₂ slags can have an FeO content of approximately 11%, with tapping temperatures in the order of 1675°C. Tapping temperatures of approximately 1725°C is expected for 92% TiO₂ slags (FeO content in the order of 5%).

Operational issues
The theory does not always describe the operational issues that are experienced by the plant operators with a change in operational philosophy. An influence diagram (Figure 6) is used to describe the possible impact of changes in the furnace operations. The diagram should be read from the top where reducing conditions are a function of ilmenite feed, electricity and reductant feed. The possible operational issues that will be observed and might have a monetary impact are shown at the bottom of the diagram.

The operational issues are, however, difficult to quantify, but are shown to indicate the full impact of producing high grade slag.

Considerations for the chlorination of high grade slags
The impact of chlorinating a high grade slag must be understood to fully address the value-in-use of the proposed feedstock. Chlorination technologies as well as operating philosophies between producers differ, which may have an impact. There are, for example, at least three different plant configurations utilized for the condensation systems to handle waste oxides as discussed by Fischer (1997). There

Figure 3. Relationship between FeO and the total equivalent TiO₂ content of titania slags

Figure 4. Relationship between the FeO and Ti₂O₃ content of titania slags

Figure 5. Tap temperatures of titania slag as a function of the FeO content of the slag

Figure 6. Influence diagram describing the impact of increasing electric energy and reductant
are also differences between the behaviour of the different feedstocks in the chlorinator. Rutile, chloride slag and synthetic rutile differ in physical properties, mineralogy and morphology, even though the TiO₂ content might be similar. This section will highlight some of the differences between feedstocks with particular emphasis on how high grade slag will react.

**Fluidization properties**
Fluidization characteristics of a feedstock are determined by its physical properties such as shape, density and particle size distribution. It is not expected that these physical properties will change significantly with an increase in TiO₂ content of the slag. A higher TiO₂ content of the slag particle will slightly increase the density, but it is not considered significant enough to quantify at this stage. It can be assumed that higher TiO₂ levels in slag will not affect its fluidization properties.

**Reaction mechanisms and rates for different feedstocks**
The different feedstock materials react slightly differently during chlorination, but in general they all follow the same reaction mechanism:

- All products are in the gaseous phase (no diffusion control through the product layer).
- The rate of chlorination is proportional to the exposed surface of the particle and this controls the rate of reaction.

The morphology of the particles has an impact on the reaction rate. At the onset of chlorination, slag is denser than rutile or SR, but through the rapid chlorination of FeO in the first 10 minutes of the reaction, the slag becomes more porous. This particle then has a greater surface area on which the chlorination reaction can occur. This is in contrast to rutile where the particle shrinks as the reaction takes place only on the outside surface. This effect of FeO in slag can be seen in Figure 7 where slag (83% TiO₂) chlorinates faster than rutile (Den Hoed and Nell, 2003).

Increasing the TiO₂ content of slag will decrease the extent of FeO chlorination thereby decreasing the area available for subsequent TiO₂ chlorination. The rate of chlorination of high grade slag should approach that of rutile. This however needs to be confirmed.

**Impact of higher Ti₂O₃**
Slag has significant amounts of Ti₂O₃ (20–30%) due to the reducing condition it has been subjected to (Reaction C). As mentioned the upper limit is usually specified as 35% Ti₂O₃ for the chlorination process and the motivation behind this is due to management of the energy balance in the chlorinators. During the chlorination process Ti³⁺ is oxidized to Ti⁴⁺, which is a highly exothermic reaction. In extreme cases, high levels of Ti₂O₃ could lead to sintering of the bed material. From Figure 4, it seems that the 35% Ti₂O₃ limit is reached at slags of > 91–92% TiO₂.

**Impact on waste generation**
Decreasing the waste generated during chlorination is one of the main reasons in the quest for high grade slag. For feedstocks with TiO₂ contents of 10–15%, a cyclone separator (after chlorination) is used to remove condensed low vapour pressure metal chlorides and entrained coke and ore before condensation (Fischer, 1997). Waste treatment is mostly dependant on the FeO content of the feedstocks. The amount of entrainment of the feedstocks however differs and slag is more likely to be entrained due to its relative finer fraction.

**Methodology for value-in-use modelling of the production of high grade slags**
In order to determine the impact of changes on the furnace and how the resulting slag will affect the chlorinators, value-in-use (ViU) models were developed for each of the two processes. In the model a comparative product value (CPV) is determined for an alternative feedstock, which can be compared with a reference or base feedstock.

This concept has been successfully used by Exxaro Resources since the mid 1990s (then as Iscor) specifically for the use of iron ore in the blast furnace. Value-in-use models combine technical know-how as well as financial information to provide a decision-making tool for product development and customer interaction. The ViU models were applied in this study to evaluate the production of high grade slag.

**Smelter value in use model**
The Smelter ViU model was used to calculate the required furnace operating parameters for the production of 85% and 90% TiO₂ slags. The model uses thermodynamic data for
the calculation of the energy balance, while the mass balance is calculated based on experimental data obtained from the production smelters.

The following assumptions were made in the model:

- All feed materials are assumed to exist at 25ºC
- Ilmenite feed analysis from Hillendale Mine
- Reductant analysis from ZAC (Zululand Anthracite Collieries)
- Recovery factors, dust loss rates, dust analyses and carbon contribution are derived from operating experience
- Carbon content of tapped iron is 2%
- Carbon efficiency factor of 94.5%

The results from the smelting model are summarized in Table II. These results were used as the basis for the cost comparative studies.

Chlorination value-in-use model

Development of the value-in-use model provided an understanding of the process as well cost drivers for feedstock selection. Refining and validating the model is an ongoing process. The following assumptions were made in the model:

- The model includes only processing up to raw pigment and does not include finishing
- All feed materials enter the reactor at 25ºC
- Chemical equilibrium is assumed within the chlorinator
- Blow-over is determined by the elutriation constant, which was determined experimentally for different size fractions and different feedstocks
- 100% slag was used as slag feed. Feed to the reactors is generally a mix of feedstocks
- Waste treatment includes neutralization of the waste with lime
- Chlorinator operating temperature is 1050ºC
- The exit gas stream from the chlorinator is cooled to 200ºC by liquid TiCl₄ sprays (below the sublimation point of ferric chloride).
- The molar ratio of CO/CO₂ in the gas product from the chlorination reactor is 1.

Price assumptions for the model are on a very high level and loosely based on figures obtained from a TZMI publication (TZMI, 2007).

The costs used in the study are generic costs for a typical chlorination plant based in the United States. The costs are highly dependent on location and also dependent on the waste treatment method. For this study relative high waste treatment costs were assumed, which compares well with European costs.

In Table III the change in selected consumption figures on a chlorination plant is shown for different TiO₂ contents.

The changed are due to the following reasons:
- **Coke consumption**—higher TiO₂ in feedstock requires more energy.
- **Chlorine consumption**—more chlorine is recycled (not lost in the waste as FeCl₃), decreasing the need for make-up chlorine.
- **Lime usage**—Less FeCl₃ in the waste requires less neutralization.

### Value-in-use results

#### Smelting of ilmenite

The results of the value-in-use calculation for smelting are shown in Figure 9 as a waterfall graph. The price of 85% TiO₂ is given in the figure as 100%. The cost of a high grade slag containing 90% TiO₂ was determined using an 85% TiO₂ slag as the reference. The calculation shows that high grade slag should cost 13.5% more per ton of 85% TiO₂ slag, taking into account the results from the technical modelling.

The costs elements shown in Figure 9 contributing to the high grade slag price can be described as follows:

- **Reductant and electrical energy input**: more reductant and energy is required to increase reducing conditions in the furnace. It is expected that energy costs in South Africa would significantly increase in the next three years, which would further increase this cost element. (This element was included under Operational costs in Figure 9)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>% change from 85% TiO₂ slag</th>
</tr>
</thead>
<tbody>
<tr>
<td>Petroleum coke consumption</td>
<td>+ 2.5%</td>
</tr>
<tr>
<td>Make-up chlorine gas</td>
<td>- 7.4%</td>
</tr>
<tr>
<td>Lime added for neutralization</td>
<td>-23.6%</td>
</tr>
<tr>
<td>Waste generated</td>
<td>-24.2%</td>
</tr>
</tbody>
</table>

#### Table III

Summary of the major results from the chlorination ViU model

<table>
<thead>
<tr>
<th>Parameter</th>
<th>% change from 85% TiO₂ slag</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slag yield (per ton ilmenite)</td>
<td>- 5.5%</td>
</tr>
<tr>
<td>Metal yield (per ton ilmenite)</td>
<td>+ 7.2%</td>
</tr>
<tr>
<td>Electrode consumption</td>
<td>+ 3.1%</td>
</tr>
<tr>
<td>Energy consumption</td>
<td>+ 3.8%</td>
</tr>
<tr>
<td>Reductant usage</td>
<td>+ 7.1%</td>
</tr>
</tbody>
</table>

**Figure 9**. Breakdown of smelting costs and income to produce high grade slags

*This cost element was included under operational costs in Figure 9*
• Electrode consumption\(^1\) — due to the higher energy input, the electrode consumption increases.
• Refractory wear\(^1\) — the impact of the higher slag temperature on refractory wear is unknown and the figure might be over- or understated. A 10% reduction in campaign life was assumed, mainly attributed to decreased tap hole life.

**Pig iron revenue** — The cost element is very sensitive to changes in the pig iron price assumptions. The pig iron quality and subsequent price is determined by the impurities (such as Mn, Cr, V, P) in the metal. With the increased reducing condition in the furnace, more metal is produced (7.2%), but also more impurities are transferred to the metal, decreasing the price.

Although value-in-use modelling provides a quantitative tool to access the changes in products, the risk associated with production remains high. The risk of operating at elevated temperatures for extended periods of time cannot be quantified. It has been attempted through the refractory cost element quantification, but it needs to be verified.

**Chlorination of slag**

Figure 10 shows the cost elements that will change on a generic chlorination plant for a high grade slag. The impact is significant on the waste treatment cost. As mentioned earlier, this cost element is highly site specific and the cost assumptions made probably implies the worst case scenario.

The comparative product value for high grade slag in a chlorinator is 10.1% per ton higher compared with the 85% TiO\(_2\) slag.

The changes in operating parameters changed due to the following:

• Coke consumption — higher TiO\(_2\) in feedstock requires more energy.
• Chlorine consumption — more chlorine is recycled and not lost in the waste to FeCl\(_3\), decreasing the need for make-up chlorine.
• Lime usage — less FeCl\(_3\) in the waste requires less neutralization.

Not taken into account in the calculations was the increase in pigment production from the increase in TiO\(_2\) units per ton feedstock. This could make a significant contribution and could increase the slag price by as much as 18%, compared with the 85% TiO\(_2\) slag. This should, however, only be included in the calculation if the capacity constraint on the pigment plant is the chlorinator. It seems that the capacity constraint is in most cases downstream, i.e. the oxidizing plant or grinding and finishing.

**Discussion**

The CPV in percentage for smelting is 13.5% and for chlorination it is 10.1%, which means that the additional cost of producing high grade slag is more than the savings on the chlorinator. It does not make economic sense to produce high grade slag with the current assumptions. It should, however, be noted that these costs assumptions are very sensitive to changes in the slag and pig iron prices, as well as the waste treatment costs on the chlorination side. The pig iron prices are relatively volatile, following the steel market trends. The waste treatment and disposal costs assumed were very high, which means that for most pigment producers the CPV would actually be lower. In this respect geographical location of the pigment plant has a large effect on the chlorination CPV as waste disposal costs differ from region to region, with Europe having the highest average disposal cost.

Upgrading through smelting is not the only technical option. There are other processing routes to decrease the cost of producing high grade slags:

• Combination of smelting ilmenite and then leaching the impurities from the resulting slag (similar to the UGS process route)
• Pre-reduction of the ilmenite, followed by smelting which would reduce the electrical energy and reductant required
• Pre-heating of the ilmenite followed by smelting which would reduce the electrical energy and reductant required, but not to the same extent as pre-reduction
• Partial chlorination of the ilmenite of slag to remove only the FeO
• Utilizing a higher TiO\(_2\) ilmenite (>60%) as a feed to the smelting furnace which is the approach QIT is following.

All these technical options address the need that a significant amount of energy needs to be introduced and also that the FeO needs to be either reduced (smelting or direct reduction) or chemically removed (leaching or chlorination). The capital outlay for these processes to basically upgrade the slag remains in disproportion to the benefit received for the incremental increase in TiO\(_2\) units. The direct smelting of ilmenite to produce a high grade slag as discussed in this article seems to be the most viable option, although not economical given current price and cost assumptions. It remains something that should be investigated and addressed in the medium term.

**Conclusions**

Although the calculations show that the smelting of a 90% slag is not viable, based on the assumptions used, there are specific cases where it will be viable. It also shows that a decision on high grade slag production is very sensitive to changes in prices of specific elements. The value-in-use principles are best applied for a specific plant and conditions.
The value-in-use principles are a good tool for quantifying and evaluating changes to products in complex processes. It is especially valuable in understanding customer requirements. The process technology that is being modelled, must, however, be well understood.

It is clear that slag as a feedstock will play a bigger role in the industry. Synthetic rutile as a high TiO₂ feedstock will become less available and slag will have to fill some of the void, which will increase the pressure to produce high grade slags. Pigment producers might be prepared to pay higher prices for slag based on savings on the waste material, but it is not enough to compensate the feedstock producers. Ilmenite smelters will, however, have to do development work to address the high cost elements to produce high grade slags.

References

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Hennie is a metallurgical engineer which started working in the iron- and steelmaking industry, then Iscor as a production engineer and later also as a process engineer. After working on various projects and feasibility studies he joined the Kumba Resources R&D department as Manager Pyrometallurgy. He was appointed in 2005 as Technology Manager Mineral Sands in Exxaro.