



1 Introduction

1.1 TiO₂ pigment feedstock

Titanium dioxide (TiO₂) is used as pigment in amongst others paints, coatings, plastics, paper, inks, foods, toothpaste and cosmetics due to its brightness, high refractive index, whiteness, opacity and resistance to discolouration under ultraviolet light¹.

The value chain of the titanium dioxide (TiO₂) pigment industry starts with the mining of a group of minerals collectively referred to as heavy minerals. This group of minerals includes ilmenite (FeTiO₃), zircon (ZrSiO₄), rutile (TiO₂), leucoxene (a weathered form of ilmenite) and monazite ((Ce, La, Pr, Nd, Th, Y)PO₄). When of sufficiently high grade, ilmenite can be used directly as feedstock in the TiO₂ pigment manufacturing processes. Alternatively, it can be upgraded to feedstock quality through reduction in rotary kilns to manufacture synthetic rutile, or reductive smelting in electric arc furnaces to produce TiO₂ slag.

The required feedstock quality (TiO₂ content and impurity level of individual oxides) depends on the pigment manufacturing process: chloride process or sulphate process. With the chloride process the feedstock is converted from TiO₂ to TiCl₄ in a fluidised bed after which the TiCl₄ is oxidised back into a pure TiO₂ crystal which is further surface treated to yield a pigment with the desired properties². During the sulphate process, the feedstock is dissolved in sulphuric acid before controlled crystallisation of the titanium units to yield TiO₂ pigment². Due to the different processing routes, the chemical specifications differ for the two products.

The two pigment manufacturing processes furthermore impose a specification on the particle size distribution of the feedstock. The fluidised bed technology used in the chloride process necessitates an upper and lower limit on the particle size distribution (in some instances also a d₅₀ constraint). This is the origin of the very specific particle size range specification of -850 µm +106 µm for feedstock intended for the chloride route. The sulphate process requires a large surface area and feedstock is milled to very fine particle sizes. The -106 µm fraction is therefore sold as feedstock in the sulphate process market.

At Exxaro KZN Sands, TiO₂ slag produced via reductive smelting of ilmenite is crushed and milled to -850 µm. The milled slag is classified into the coarser -850 µm +106 µm fraction intended as feedstock in the chloride pigment manufacturing processes and referred to as “chloride slag”. The finer -106 µm fraction is sold as feedstock for the sulphate pigment manufacturing route, and is referred to as “sulphate slag” or “fine slag”. However, since chloride slag has a higher market value than fine slag, a primary key performance indicator of plant production is the ratio of chloride to fine slag; a high ratio indicates that size reduction of the slag to below -850 µm is achieved, while avoiding formation of -106 µm material.

1.2 The origin of Exxaro KZN Sands

During the mid 1990's Iscor (then a steel producer and mining company) identified the opportunity to invest in the heavy minerals industry. The Iscor Heavy Minerals project (IHM Heavy Minerals) commenced with a feasibility study flowing into an engineering and design phase. These started in 1996 and concluded in 2000 with Board approval of phase 1 of the project – Hillendale Mine and the Mineral Beneficiation Plant. Construction of the two Smelters and Slag Processing Plant – phase 2 – was subsequently announced in August 2001. Commissioning of the Smelters commenced during the last quarter of 2003 followed by that of the Slag Processing Plant in March 2004.

Between 1995 and 2001 Exxaro KZN Sands (then IHM Heavy Minerals) conducted 12 ilmenite smelting campaigns on the 3MVA DC pilot furnace at Exxaro's Research and Development facilities. These campaigns varied in length from one week to six weeks, with the majority running for two weeks. Technical objectives for these campaigns included testing of different ilmenite and reductant sources, production of TiO₂ slag market samples and formulating operating philosophies for the smelting process³.

During these smelting campaigns it became clear that the TiO₂ slag as tapped from the furnace showed characteristics different from typical slags encountered in other metallurgical operations, e.g. iron and steelmaking⁴. One pronounced difference was the tendency of these slags to decrepitate from a solid block into a powder with particle sizes finer than 100 µm. This phenomenon was intensively investigated in the subsequent years^{5, 6, 7}.

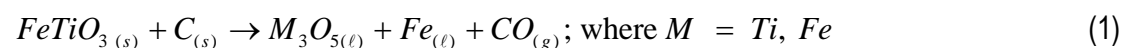
In addition to these studies which focused primarily on the decrepitation of TiO₂ slag, experimental work was initiated during the 9th 3MVA ilmenite smelting campaign to investigate the effect of various cooling conditions on the decrepitation behaviour of the slag, as well as the possible effect of such cooling conditions on the particle size distribution of the final products (and hence on the ratio of chloride to fine slag). This testwork and the results thereof are discussed in Part 1 of this thesis. Part 2 of this document presents the results of subsequent plant trials. Part 3 describes a cooling model, based on finite element principles, to calculate the internal and surface temperatures of TiO₂ slag blocks as functions of time.

While Campaign 9 was performed during June 2001, the plant trials were only conducted during January 2005. The four-year lapse between the experimental work of Parts 1 and 2 was mainly due to the industrial-scale plant only being commissioned during the first quarter of 2003. This time lapse created the opportunity for lessons learned during the pilot plant campaigns to be implemented already during the design and construction phases of the Slag Processing Plant.

1.3 Ilmenite smelting and slag processing

To enable the context of this work be seen in perspective, a brief process description of the ilmenite smelting and slag processing processes is required⁸.

During the smelting process as applied in a DC electric arc furnace, ilmenite is continuously fed together with anthracite in a tightly controlled ratio through a hollow electrode into the operating furnace. The primary reduction reaction can be simplified and written as in equation (1) (equation not balanced):



The primary product - titanium oxide slag, written as M₃O₅ - contains an average of 85% TiO₂*. In addition the slag also contains approximately 10% FeO. Also present are impurities such as SiO₂, Al₂O₃, MgO, MnO, CaO, Cr₂O₃, V₂O₃ and ZrO₂. The slag contains titanium in both the +3 and +4 oxidation states. Substitution of the Ti³⁺ ions by Cr³⁺, V³⁺ and Al³⁺, and that of Fe²⁺ by Mg²⁺ and Mn²⁺ also occur. The oxides SiO₂, CaO and in part Al₂O₃ separate into silicate phases (including a glass phase).

* Total Ti expressed as TiO₂ (Ti in slag is present in both the +3 and +4 oxidation states).

Due to the reducing conditions in ilmenite smelting titanium units and some of the impurities are partially reduced to report to the metal phase. The maximum limits of impurities in both the slag and iron are fixed in supplier-customer contractual agreements.

The smelting and reduction processes are conducted within a crucible of a solidified, high titanium content slag (known as the freeze lining), contained within the furnace refractory walls. This freeze lining protects the magnesia refractory from chemical attack by the slag (chemical attack will not only reduce the refractory life, but will also contaminate the slag).

The slag has a lower density than the iron and separation of the two liquid products occurs within the furnace. Slag and iron are tapped periodically from separate sets of tapholes located around the circumference of the furnace – the slag tapholes are at a higher elevation than those of the iron. Slag is tapped into 20 t steel pots and cooled for several hours within these pots before being tipped out. These blocks are subsequently transported to the block yard where they are cooled under water sprays for a number of days. They are then crushed, milled and classified according to particle size into the chloride and fine slag products. A block flow diagram of the Slag Processing Plant is given in Figure 1 .

The tapped pig iron is re-carburised and desulphurised and cast into 7 kg pigs for use in among others, the automotive industry.

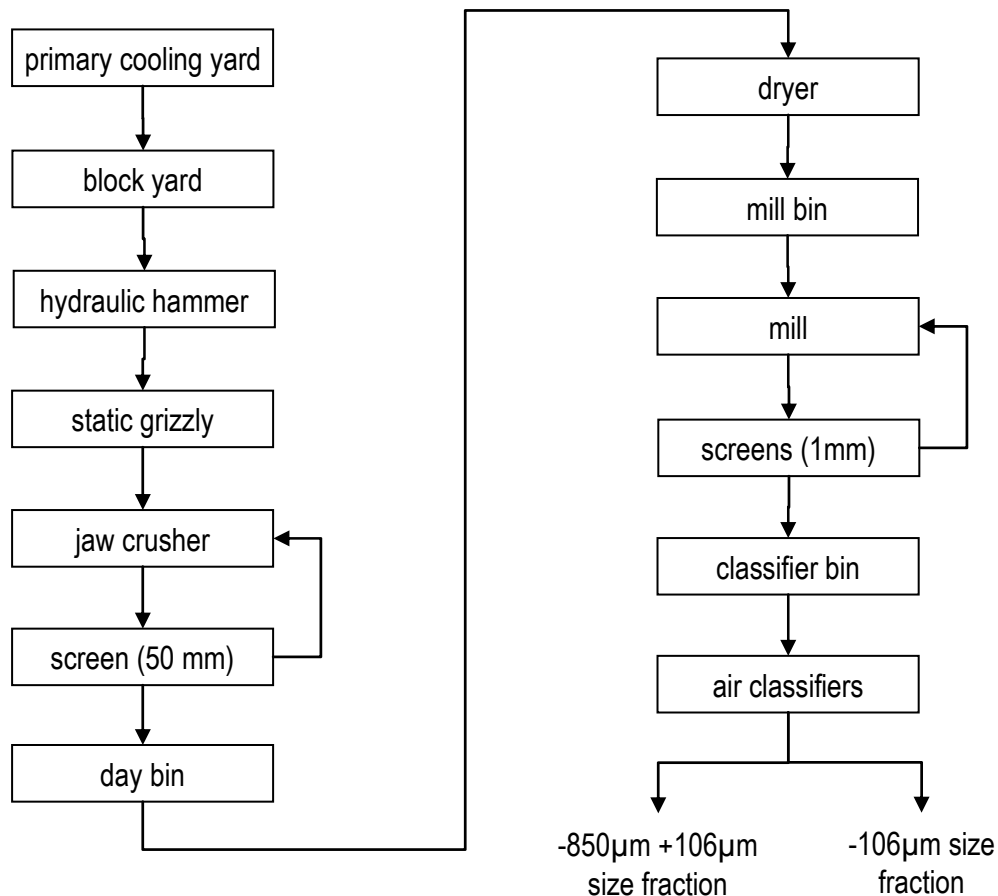


Figure 1 Block diagram depicting the process flow of the Exxaro KZN Sands Slag Processing Plant.

The layout of the Exxaro KZN Sands furnace and metal treatment buildings, slag block yard and slag processing plant is shown in Figure 2.

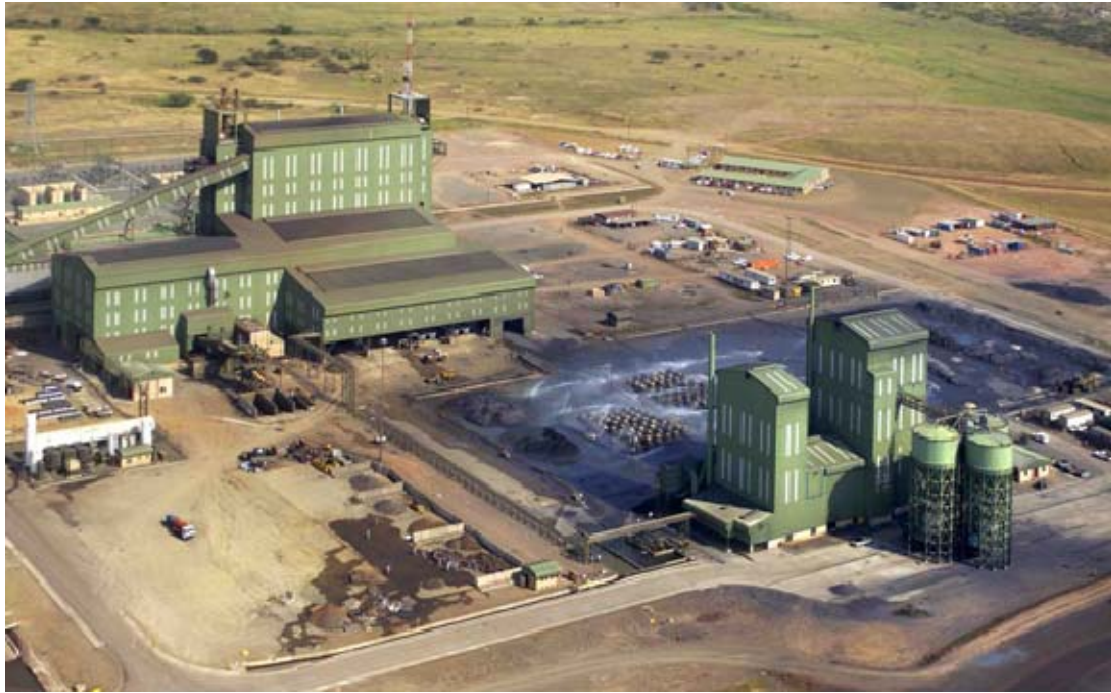


Figure 2 Aerial photograph of the furnace and metal treatment building (upper left hand corner) and slag processing building (lower right hand corner). The block yard is located between these two buildings.

1.4 Problem statement

The relatively young process of titania slag production and the closed nature of the industry led the present situation where little information regarding the characteristics of titania slags is available in the open literature. Although useful information was published from research work conducted by the Canadian QIT research laboratories during the 1970s, these slags contained approximately 70% TiO_2 whereas titania slags produced by South-African producers typically contain around 85% TiO_2 . From the available information, this difference in composition was expected to have a considerable influence on the slag properties and behaviour. Only fairly recently was more information published regarding the properties of these relatively higher grade titania slags. These publications focused on mineralogy of the solid phases, decrepitation behaviour and in some instances even included smelting behaviour, and are summarised later in this section.

During the ilmenite smelting campaigns conducted by IHM Heavy Minerals (as the forerunner of Exxaro KZN Sands was known at the time), it became evident that the final particle size of the slag is a strong function of the cooling environment. This initiated various studies into decrepitation behaviour (discussed below). It soon became evident, however, that the final slag product size distribution was the consequence of parameters other than just decrepitation.

This study therefore focused on testing the hypothesis that various aspects of the cooling environment influence the particle size distribution of the final product. This was in contrast with the general concept of the time (prevalent within IHM Heavy Minerals) that crushing and milling are the primary factors determining the particle size distribution.

General mineralogy of titania slags

The ilmenite smelting process^{9,10} and slag structure^{4,11,12} have been reviewed recently, and hence only a brief summary is given here (based on these references), focusing on the factors which can affect the phases which are present in the slag (since these phases are expected to influence the crushing behaviour of the solidified slag).

The most striking feature of the solidified slag is that it largely consists of a single phase, which is a solid solution which follows M_3O_5 stoichiometry.⁴ This phase can be viewed as a solid solution of the end members $FeTi_2O_5$, Ti_3O_5 , $MnTi_2O_5$, $MgTi_2O_5$, Cr_2TiO_5 , Al_2TiO_5 and V_2TiO_5 , and incorporates all or nearly all of the iron, titanium, manganese, magnesium, aluminium and vanadium which are present in the product. The major elements which are not incorporated in the M_3O_5 ("pseudobrookite" or "karrooite") solid solution are silicon and calcium; these report as separate silicate phases (both crystalline and glassy), which also contain aluminium, and some titanium (all of these in the form of oxides). The silicate phases are present between the M_3O_5 grains, and appear to form during the latest stages of solidification. Some rutile (TiO_2) is generally present in the solidified slag, also at the positions of final solidification. This is in agreement with the predicted solidification behaviour of the slag, as reviewed below.

The tendency of SiO_2 and CaO to form separate silicate phases between the M_3O_5 grains may well contribute to the crushing behaviour of the slag; this possibility was studied in this project.

The reason why the slag composition remains close to M_3O_5 stoichiometry is not clear; suggested reasons include chemical equilibrium¹³ (of the reaction $FeO + Ti_2O_3 = Fe + 2TiO_2$), and phase equilibrium¹⁰ (involving transient solidification and remelting, driven by the temperature difference between the slag and the metal). The main reason for this uncertainty is that the calculated activities in the liquid slag and solid phases are based on extrapolations from the binary systems¹⁴ (mainly $FeO-TiO_2$ and $Ti_2O_3-TiO_2$), measurements of sub-solidus equilibria,¹⁵ and a few measurements involving melts in the $FeO-TiO_2-Ti_2O_3$ system.¹⁶ The available data as evaluated in references 14 and 15 have been incorporated in the FactSage database.¹⁷ Given the limited and uncertain experimental data, it is not surprising that predicted phase equilibria differ. For example, the "Multi-Phase Equilibrium" (MPE) package of the CSIRO¹⁸ appears to predict a much wider liquidus-solidus gap than FactSage predicts; a cell model predicts a smaller liquidus region at temperatures of 1500°C, 1600°C and 1700°C (hence higher melting points overall) than does FactSage.¹⁹

While it is realised that there are uncertainties in the reaction and phase equilibria as predicted by FactSage, this package was used to provide much of fundamental thermodynamic data which were used in this work, since the package was the most comprehensive and convenient data source available to the author.

Reactions during solidification

Figure 3 gives a calculated pseudo-binary section through the $FeO-Ti_2O_3-TiO_2$ system, at a constant mole fraction of FeO ; the section was calculated using FactSage, suppressing the Magnéli phases.²⁰ As mentioned before, the slag compositions are close to M_3O_5 , but solidified slags contain a small but significant fraction of rutile.⁴ The presence of rutile indicates that the slag contains more TiO_2 (and hence less Ti_2O_3) than M_3O_5 stoichiometry would require; that is, the slag composition lies between M_3O_5 stoichiometry and point A on the diagram (there is no evidence that the slag composition lies beyond point A, which would imply rutile forming as primary phase upon solidification, and the presence of a large fraction of rutile in the solidified

slag.) The implication of the presence of rutile in the solidified slag is hence that the titanium in the slag is less strongly reduced (containing more TiO_2 and less Ti_2O_3) than M_3O_5 stoichiometry would require. One way in which this can arise, is for the slag to conform to M_3O_5 stoichiometry within the furnace (whether for reasons of chemical equilibrium or phase equilibrium, as discussed above), but that some of the Ti_2O_3 can be oxidised to TiO_2 during tapping, when the slag stream is exposed to air. This is certainly thermodynamically possible, since the calculated partial pressure of oxygen for equilibrium between TiO_2 and Ti_2O_3 in the slag is approximately 10^{-9} atm,²¹ much lower than the partial pressure of oxygen in air.

The possibility that oxidation of slag during tapping can change the crushing behaviour of the slag (by changing the solidified microstructure, mainly by increasing the volume fraction of rutile in the structure) is one which was investigated in this work.

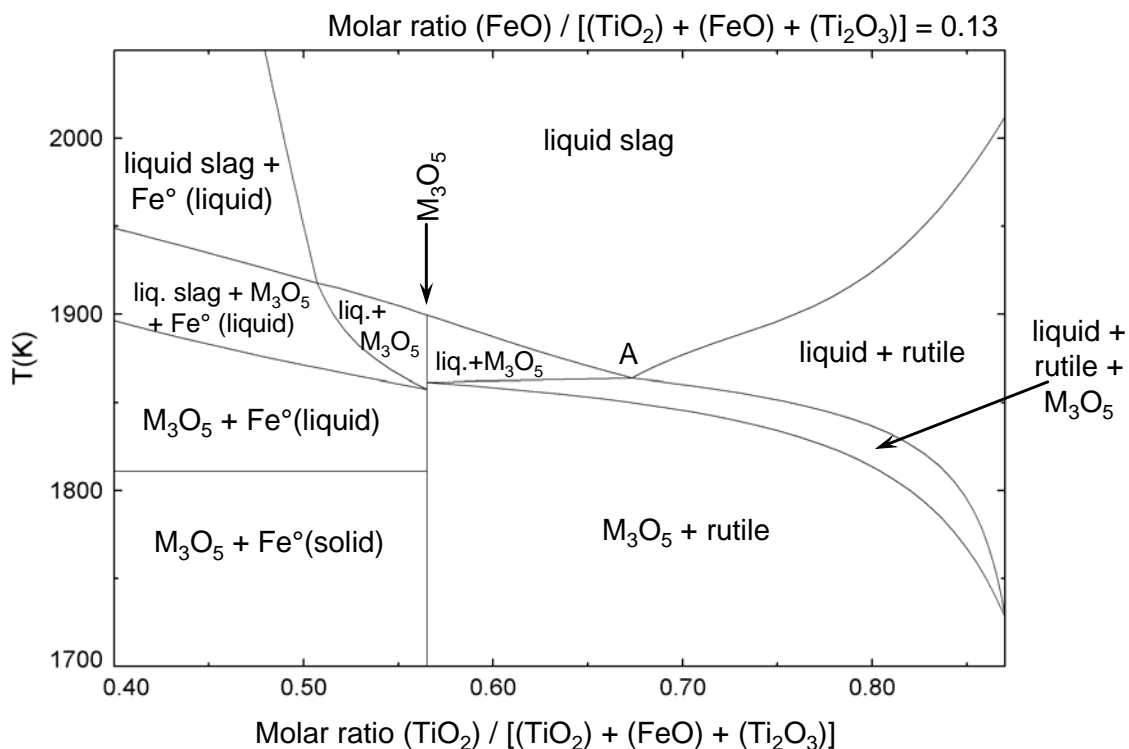


Figure 3 Calculated partial pseudobinary section through the $\text{FeO-Ti}_2\text{O}_3\text{-TiO}_2$ system, at an FeO mole fraction of 0.13.²⁰

Reactions after solidification

Changes in microstructure can occur through phase transformations below the solidus temperature. One possible reaction is the decomposition of M_3O_5 into rutile and metallic iron; M_3O_5 tends to undergo this reaction below approximately 1100°C (depending on composition).¹⁵ However, this reaction is generally not observed in solidified slags during practical cooling, and the M_3O_5 structure persists (metastably) down to room temperature. A small degree of oxidation of slag can trigger this transformation of M_3O_5 to rutile (or anatase) and metallic iron, though.²² If such a transformation does occur, it could influence crushing, but there is no evidence from any of the microstructural studies on these slags that this decomposition reaction normally occurs to any significant extent.

What is expected to play a significant role is the formation of the " M_6O_{11} " phase by low-temperature oxidation (that is, at 400°C or below).^{7,23} As indicated by its stoichiometry, formation of M_6O_{11} involves only a small degree of oxidation of M_3O_5 , yet it has been shown to cause severe decrepitation of the material: the solidified slag breaks up into small flakelike particles.^{5,6} Suppression of this low-temperature oxidation reaction is one of the main reasons why water cooling is applied to the surfaces of the slag blocks in the "block yard" of the plant. Possible effects of low-temperature oxidation were hence also studied in this project.

Higher-temperature oxidation reactions lead to different reaction products, and can also give substantial changes in the microstructure.⁶ However, such reaction products are not evident in the slag microstructures. Such higher-temperature oxidation of the slag (typically in the temperature range $900\text{-}1100^\circ\text{C}$) was hence not expected to be relevant to this project; such oxidation reactions play a central role in processes which upgrade solidified slags to higher- TiO_2 products, though.^{12,24}

1.5 Research approach

Based on the background information (as summarised above), the investigation into the influence of the cooling environment on the final particle size distribution was conducted in three parts:

Part 1 was conducted on pilot scale; given the flexibility of a pilot plant this afforded the opportunity to investigate the effects of several cooling methods. Although this work touched on the decrepitation behaviour of titania slags, the primary objective of this part was to determine whether a correlation exists between the cooling environment and cooling history, and the particle size distribution of the slag blocks which remain intact after cooling – in other words that portion of the block which appears to be untouched by decrepitation.

Part 2 built on the information obtained in Part 1. Part 2 sought to test the influence of those parameters (as identified in Part 1 as factors determining the crushing behaviour of the slag) which can be manipulated at the industrial scale plant of Exxaro KZN Sands.

Part 3 was a logical follow-up on the preceding parts, in predicting cooling. Since temperature is a predominant driver in the processes and factors influencing the slag particle size distribution, knowledge of the temperature profiles along the slag block surface and within the slag block over time is essential to understanding the problem, and to enabling the formulation of potential improvements in titania slag processing. Part 3 therefore describes the construction and results obtained from a finite element model of a cooling slag block. The predictions by this model provide insight into the temperature-time profiles of a slag block.