

1. INTRODUCTION^{1,2,3}

The minerals rutile (TiO_2) and ilmenite (FeTiO_3) are used as raw materials in the production of titanium dioxide pigments. The two main processing routes for the production of pigment are the sulphate and the chloride processes, with ilmenite being used as feed material to the sulphate process and rutile as feed material to the chloride process.

The world production of ilmenite is approximately eight times the quantity of rutile beneficiated from natural mineral deposits. Because of the decrease in rutile mineral availability as feedstock to the chloride process, rutile substitutes are used. One of the substitutes is a titanium slag (85% TiO_2), as produced by Richards Bay Minerals (Tisand PTY) in South Africa, by carbothermic reduction of ilmenite at temperatures in excess of 1600°C . A similar process is used by Namakwa Sands on the west coast of South Africa, and is to be used in Iscor's planned smelter at Empangeni, South Africa. Titanium slag is also used as feedstock in the sulphate process. This slag has a TiO_2 content ranging from 71-74% in slags produced by QIT in Canada, to 90% in slags produced in Japan.¹

In the chloride process rutile is chlorinated under reducing conditions, at $800\text{-}1000^\circ\text{C}$, in a fluidized bed to form titanium tetrachloride (TiCl_4). Coke is used as reductant and chloride gas as the reacting gas. TiO_2 pigment is subsequently formed by burning the TiCl_4 with oxygen in a specially designed burner at temperatures above 600°C . The TiO_2 produced requires the same final processing, milling etc., as used in the sulphate process. The TiCl_4 formed as intermediate product in the process can be purified by distillation to remove impurities in the form of chlorides.

In the sulphate route ilmenite (or certain other titanium-bearing phases: see below) is digested with strong sulphuric acid to render the titanium in solution as titanyl sulphate, TiOSO_4 . The ferric iron (Fe^{3+}), which is also in solution, is reduced with scrap iron to ferrous iron (Fe^{2+}), and the solution is then cooled down to crystallize the iron out as copperas ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$). The solution is adjusted with respect to pH and TiO_2 content and then boiled to precipitate the titanium dioxide in very fine colloidal form. The TiO_2 is washed to remove impurities and the TiO_2 pulp is then calcined to remove absorbed water and to establish the optimum crystal size. The TiO_2 is subsequently wet milled, hydroclassified, dried and shipped. Only natural ilmenite and titanium slag can be used as feedstock for the sulphate process because rutile is

not digested by sulphuric acid. The most suitable phase for the sulphate process is pseudobrookite because it is easily digested by sulphuric acid.

Rutile is a much better feedstock for pigment production by chlorination than ilmenite because it contains more titanium and therefore less waste is produced. The sulphate process generates 3.5 tonnes of waste per tonne of TiO_2 product and the chloride process generates only 0.2 tonnes of waste per tonne of TiO_2 product.¹ Over the last four decades the trend has been to produce more titanium dioxide pigment via the chlorination process.

Isacor's Rooiwater ilmenite deposit contains vanadium within the magnetite which is associated with ilmenite in the ore.¹³ The vanadium substitutes for the iron within the spinel structure of magnetite. Vanadium chlorides and oxychlorides formed in the chlorination process have boiling points close to the boiling point of TiCl_4 and are therefore not easily separated from TiCl_4 through a distillation process. Thus one of the quality specifications for TiO_2 -rich slag produced for chlorination processing is that the vanadium content, expressed as $\%V_2O_5$, be less than 0.6 $\%V_2O_5$ ⁴.

In the carbothermic reduction of ilmenite pig iron is produced in addition to the TiO_2 -rich slag. Because of the specification on the maximum amount of V_2O_5 allowed in the slag one would wish to transfer as much as possible vanadium from the slag into the metallic phase. However approximately 10% FeO should be maintained within the slag for fluxing purposes. Consideration of the standard free energies of formation of vanadium and iron oxides from the elements indicates that vanadium oxides are more stable than FeO. Therefore all of the FeO would first have to be reduced into the metallic phase before vanadium oxides can be carbothermically reduced. However, this is the situation when the pure components, for which the activities are equal to unity, are considered. Of importance are the activities of the metallic components within the multicomponent metallic phase, and the activities of the oxide components within the complex slag. For all practical purposes the activity of iron is equal to unity since it constitutes almost the entire metallic phase. The activity coefficient (γ_V°) of vanadium in iron, with solid vanadium as the reference phase, is 0.1 at 1600 °C and 0.11 at 1750 °C³³ so that the transfer of vanadium from the slag to the metal through reduction is enhanced. Carbon is the major solute in the iron with 2% carbon in the iron and the first order interaction coefficient (e_V^C) of carbon on vanadium in liquid iron is -0.34 ³³ so that the activity

coefficient of vanadium in the liquid iron will be further reduced. The activity coefficient of vanadium within the metallic phase will not be substantially lowered further without the addition of large quantities of alloying elements to the metallic iron phase. The study of activity-composition relations of iron oxides and vanadium oxides in TiO_2 -rich slags are therefore of importance. The activity behaviour of the vanadium and iron oxides in the TiO_2 -rich slag may render the carbothermic reduction of vanadium from the slag possible, whilst still maintaining FeO as flux.

Furthermore the activities of the iron and vanadium oxides in the liquid phase of the TiO_2 -rich slag are of great significance, because reduction of the oxides predominantly occurs from the liquid portion of the slag due to kinetic considerations. Determination of phase relations is necessary groundwork that has to be done before activity-composition relations within the oxide system can be measured. Furthermore, from crystal chemical considerations the phase relation data indicates the activity behaviour to be expected in the oxide mixtures e.g. the ionic radii of vanadium and iron cations indicates that solid solution formation between Fe^{2+} , Fe^{3+} and V^{3+} is possible because the ionic radii of the cations differ by less than 15%.²⁵ The ionic radii of titanium and vanadium cations indicates that V^{5+} , V^{4+} and V^{3+} may substitute for Ti^{4+} , and V^{3+} and V^{2+} may substitute for Ti^{3+} to form vanadium containing titanium-rich solid solutions. Consequently, it is imperative that phase constitution of slags within the TiO_2 - FeO_y - VO_z pseudo-ternary oxide system be known so that the liquid phase areas can be fully defined. Neither this phase diagram, nor the two pseudo-binary phase diagrams, VO_x - FeO_y and VO_z - TiO_2 , are known. This study therefore focused on the determination of phase relations within these binary oxide systems at 1400°C, 1500°C and 1600°C and $P_{\text{CO}}/P_{\text{CO}_2} = 3$. This gas mixture represents oxygen partial pressures of 3.02×10^{-10} atm, 2.99×10^{-9} atm and 2.31×10^{-8} atm at 1400°C, 1500°C and 1600°C respectively. All of these partial oxygen pressures were chosen to be slightly above the Fe/FeO equilibrium oxygen partial pressure as is summarised in Table 1.1. The reason for using these partial oxygen pressures is that the phase constitution of the respective oxide systems, in the presence of FeO, is of interest.

Table 1.1: Fe/FeO Equilibrium Oxygen Partial Pressures at 1400, 1500 and 1600 °C³²

Temperature (°C)	Equilibrium Partial Oxygen Pressure (atm.)	Experimental Partial Oxygen Pressure (atm.)
1400	4.84×10^{-11}	3.02×10^{-10}
1500	3.45×10^{-10}	2.99×10^{-9}
1600	2.12×10^{-9}	2.31×10^{-8}

The equilibrium partial oxygen pressures for the VO/V₂O₃ and V₂O₃/VO₂ equilibria are indicated in Table 1.2. Comparison of the partial oxygen pressures for the vanadium oxides in Table 1.2 with the experimental partial oxygen pressures in Table 1.1 indicates V₂O₃ to be the stable vanadium oxide under experimental conditions used in this work.

Table 1.2: Equilibrium Oxygen Partial Pressures for Vanadium Oxides at 1400, 1500 and 1600 °C³⁴

Reaction	Reaction Temperature (°C)		
	1400	1500	1600
$2VO + 1/2O_2 \leftrightarrow V_2O_3$	1.50×10^{-14} atm	2.65×10^{-13} atm	3.45×10^{-12} atm
$V_2O_3 + 1/2O_2 \leftrightarrow 2VO_2$	1.42×10^{-6} atm	2.88×10^{-6} atm	5.29×10^{-6} atm

The information determined in this study will be the basis for the complete determination of phase relations within the TiO₂-FeO_y-VO_z pseudo-ternary oxide system, as required for activity measurements. Such activity data will provide clarity on the criteria for the optimum transfer of vanadium from the slag into the metallic phase under the constraints outlined above. This project therefore makes a first but essential contribution towards an answer to this problem.