1 INTRODUCTION

1.1 Background and Main Objectives of the Project.

The first recorded use of titanium dioxide as a white pigment was in 1908 when A.J. Rossi, a French metallurgist and chemist who had come to the United States in the late 1800s, mixed the material with salad oil and brushed out the mixture (Fisher, 1997). Work continued in the United State on the use of titanium dioxide as pigment and in 1916 a Titanium Pigment Company was formed in Niagara Falls, New York (Fisher, 1997). Titanium is the ninth most abundant element in the earth's crust and the fourth most abundant metallic element (Minkler and Baroch, 1981). Rutile is traditionally the feedstock of choice used in the production of white pigment and is the main or primary source of all forms of titanium concentrates in the pigment industry. Except for sulphate route pigment production, which is becoming increasingly less prevalent in the face of environmental concerns, (Minkler and Baroch, 1981) the chloride route pigment and titanium metal producers all use the same intermediate, $TiCl_4$. The titanium tetrachloride must be of high purity. Titanium sponge is also produced from $TiCl_4$ generated by the pigment producers (Minkler and Baroch, 1981).

Titania slag, a product of the reductive smelting of ilmenite ($FeO.TiO_2$), plays an increasingly important role as feedstock in the production of TiO_2 pigment by the sulphate or chloride routes. This is due to the rising price and limited resources of natural rutile (Sohn and Zhou, 1998). In the smelting of ilmenite at approximately $1650-1700^{\circ}C$, the iron content of the slag phase is decreased by a suitable carbonaceous reductant in an electric furnace to produce high titania slag as the major product. In the process, pig iron is produced as by-product (Kahn, 1983). It was found that, where high titania slag does not undergo oxidation upon tapping, there was a parallel reduction of FeO to Fe and TiO_2 to Ti_2O_3 during the ilmenite smelting process. The partial reduction of TiO_2 does not contribute to upgrading of the slag, however, the formation of Ti_2O_3 does have a beneficial effect of lowering the liquidus temperature of the slag, (Pistorius, 2002).

According to (Bessinger et al, 1997), there are four phases present in high titania slags with pseudobrookite (M_3O_5 solid solution) being the most common phase. The amount of the other phases varies from slag to slag, depending on the chemistry of the slag as well as the conditions under which each slag had been cooled. Chlorinatable high titania slag typically contains about 10%FeO, 52%TiO_2 and 33%Ti_2O_3 (with other impurities mainly SiO_2, CaO, MgO, and Al_2O_3), making up the balance (Bessinger et al, 1997).

The slag used in this work was produced by carbothermic reduction of ilmenite to form titania slag. Upon tapping, a high-pressure water jet was use to disintegrate the slag into fragments. As a result of this, the slag cooled down much faster than the block route slag. This technique of slag granulation is attractive since it avoids the long cooling time associated with slag ingots and eliminates several crushing steps. A concern is that the slag may react with water or oxygen during tapping and become oxidized. On the other hand, the block route slag used in the project (abbreviated as BSC), which was less oxidized, was produced by collecting the liquid slag in a ladle and allowing this to cool slowly. The cooled ingots were then crushed and milled to yield the size fractions required for the chlorination process. The typical size range is larger than 100μm and smaller than 850μm. The particle size range used in this work was 425-600μm.

The first purpose of this project was to identify and quantify the different phases present in the oxidized titania slag, and to investigate the microscopic nature, the amount of each phase present and the phase changes that occur during the first few minutes of chlorination of the oxidised slag as compared to that of unoxidised block route slag.

In addition to changing the phase composition, oxidation of the slag changes the energy balance during chlorination. The typical temperature used in industrial chlorination is 1223K to avoid sintering of the bed (Zhou et.al. 1996). The presence of Ti^{3+} in the slag contributes to heat evolved in the chlorinator that could cause the fluidized bed to sinter. This is because the chlorination reaction of Ti^{3+} is highly exothermic (Minkler and Baroch, 1981). Pistorius and le Roux,

(2002) also concluded that slag chlorination was exothermic due to the presence of Ti_2O_3 and therefore will produce heat in the fluidized-bed. For this reason, titania slag must have a Ti_2O_3 content of less than 25% (Minkler and Baroch, 1981).

Chlorination of FeO and other impurity oxides, like MnO, occurs within the first few minutes of the process thereby creating porosity in the slag matrix. The porosity created had a significant role on the chlorination kinetics of the slag. (Sohn and Zhou, 1998 ; Pistorius and le Roux, 2002). If the slag oxidises during or after tapping, some of the Ti^{3+} is transformed to Ti^{4+}, and upon more extensive oxidation Fe^{2+} is transformed to Fe^{3+}. In this case, the solidified slag contains both titanium and iron in the +4 and +3 oxidation states respectively hence changing the composition of the slag significantly. The resulting changes in phase composition will in turn reduce the porosity of the slag matrix (due to the slow chlorination rate of Ti and Fe in their highest oxidation states) and hence slowing down the overall rate of reaction. The behaviour of the slag during chlorination in the fluidized-bed reactor would be a good quality control test for the slag (le Roux, 2001). For these reasons, the second purpose of this project was to study the effect of slag oxidation on the chlorination kinetics of the slag.