

# **Fluidised-Bed Chlorination of Oxidised Titania Slag.**

**By**

**BUNGU PETER NDULA**

A dissertation submitted in fulfilment of the requirements for the  
degree

**MASTER OF SCIENCE ( METALLURGY)**

in the

Faculty of Engineering, the Built Environment and Information  
Technology

University of Pretoria

2004

# Fluidised-Bed Chlorination of Oxidised Titania Slag.

STUDENT : BUNGU PETER NDULA

SUPERVISOR : P.C. PISTORIUS

DEPARTMENT : MATERIAL SCIENCE AND METALLURGICAL  
ENGINEERING.

DEGREE : MASTER OF SCIENCE (METALLURGY)

## ABSTRACT

High-titanium slag (produced by carbothermic reduction of ilmenite) contains a significant percentage of trivalent titanium, which can be converted to the tetravalent form by oxidation. Oxidation can occur through contact with water vapour, for example during water granulation. This work investigated the degree of oxidation of the different size fractions of water granulated titania slag, and the resultant changes in phase composition. For this oxidised slag, the kinetics and exothermicity of the chlorination process are also reported.

### Key words

Oxidised titania slag, water granulation,  $M_3O_5$ , anatase, rutile, chlorination, block route slag.

---

## ACKNOWLEDGEMENTS

I wish to express my sincere thanks and appreciation to my supervisor, Professor P.C Pistorius for his constant advice, guidance and direction throughout this research work. I remain indebted to Kumba Resources for their support and sponsorship and the Innovation Fund awarded by the Department of Arts, Culture, Science and Technology.

My appreciation also goes to Professor T.A. Modro, the former head of Chemistry department and Zsussana Foldvari for their motivation, inspiration and support in pursuing studies in the University of Pretoria. Special thanks go to the following:

Late Mr. Johann Borman for his technical assistance, Sarah Havenga for her support, Sabine Verryn for assistance with the XRD analyses, Carl Coetzee for his assistance with the SEM work, Peter Sibiya for polishing the SEM samples, Deon Bessinger for the XRF analyses, and fellow pyrometallurgical students, Daudet T, Ulyate, Mutale and Tomi for their support and advice. The assistance of Giovanni Hearne and Antoine Mulaba (who performed the Mössbauer measurements and analyses) is also gratefully acknowledged.

I wish also to thank my Uncle Pa Lambi Umaru Kumsike for initiating my academic career and my wife Bungu Florence Kuvin for moral support and my daughter Bungu Tracey Ikeh for inspiring me to work harder. Finally, my special thanks go to the Almighty God for providing me with the wisdom, good health, and strength in successfully completing the programme.

## **DEDICATION**

The research work is dedicated to my beloved late mother, Late Ma Ikeh Agnes Ndula who supported me from birth and died on the 30<sup>th</sup> of August 1994. May her soul rest in peace.

## TABLE OF CONTENTS

ACKNOWLEDGEMENTS.....	III
DEDICATION .....	IV
<b>1 INTRODUCTION.....</b>	<b>10</b>
1.1 BACKGROUND AND MAIN OBJECTIVES OF THE PROJECT.....	10
<b>2 LITERATURE SURVEY.....</b>	<b>13</b>
2.1 PROPERTIES AND USES OF TITANIUM METAL AND ITS OXIDES.....	13
2.2. TITANIFEROUS FEEDSTOCKS.....	13
2.2.1. <i>Feedstocks for the production of titanium tetrachloride.</i> .....	13
2.2.2 <i>Characterization Of Chlorinatable Titaniferous Feedstock</i> .....	15
2.2.3 <i>Techniques for the Upgrading of Sub-Rutile feedstocks</i> .....	16
2.3 OXIDATION OF HIGH TITANIA SLAG.....	18
2.4. MINERALOGY AND PHASE CHEMISTRY OF TITANIFEROUS FEEDSTOCK .....	20
2.4.1 <i>Ti-O-Fe Phase diagram</i> .....	21
2.5 THE CHLORIDE PROCESS.....	23
2.5.1 <i>Fluidized Bed Reactor</i> .....	23
2.5.2 <i>Nature and Feedstock Requirements of the Chloride Process</i> .....	27
2.5.3 <i>Chlorination Kinetics of Titaniferous Feedstocks.</i> .....	28
2.6. LIMITATIONS OF FLUIDIZED-BED TECHNOLOGY AND POSSIBLE ALTERNATIVES.....	43
2.8. CONCLUSIONS.....	45
<b>3. MINERALOGY OF WATER - GRANULATED HIGH - TITANIA SLAG.....</b>	<b>46</b>
3.1 ANALYTICAL TECHNIQUES USED:.....	46
3.2. EXPERIMENTAL .....	48
3.3 RESULTS .....	49
3.5 CONCLUSION:.....	58
<b>4: CHLORINATION OF HIGH TITANIA SLAG .....</b>	<b>60</b>
4.1: EXPERIMENTAL .....	60
4.2 CALIBRATION OF GAS ROTAMETERS.....	61
4.2.1: <i>Nitrogen and carbon monoxide flowrates</i> .....	61
4.3: EXPERIMENTAL PROCEDURE.....	63
4.3.1: <i>Problems encountered during the chlorination process.</i> .....	64
4.3.2 <i>Optical microscopic examination of the unchlorinated slags</i> .....	65
4.4 RESULTS AND DISCUSSION.....	67
4.4.1 <i>Optical microscopic analysis of chlorinated slags.</i> .....	67

4.4.2	<i>XRD Analytical Results</i> .....	69
4.4.3:	<i>SEM Analytical Result</i> .....	69
4.5	VARIATION OF BED TEMPERATURE DURING CHLORINATION .....	73
4.6	INITIAL RATE OF CHLORINATION .....	76
4.6.1	<i>Chlorination rate of FeOx and MnO</i> .....	76
4.6.2:	<i>Chlorination of MgO</i> .....	78
4.6.3:	<i>Chlorination of TiO<sub>2</sub></i> .....	80
4.8	CONCLUSIONS.....	82
<b>5.</b>	<b>REFERENCES</b> .....	<b>83</b>
	APPENDIX.....	86

## LIST OF FIGURES

Figure 2.2.3:	Possible Ilmenite to Rutile Routes (Kahn, 1983) .....	16
Figure 2.4.1:	Binary Section $FeTi_2O_5$ - $Ti_3O_5$ through The Fe-Ti-O Phase Diagram (Eriksson et al. 1996).....	22
Fig 2.5.1:	a.) Fixed bed, b.) Fixed bed of maximum voidage, c.) Fluidized bed (Szekely and Themelis, 1971). .....	24
Fig 2.5.3a:	Schematic Diagram of Laboratory Chlorinator (le Roux, 2001).....	38
Figure 2.5.3b:	Bed Temperature during Initial Chlorination of Slag A and B (Pistorius and le Roux, 2002).....	40
Fig 2.5.3c:	Increase in degree of chlorination of titanium from two slags at $950^{\circ}C$ (Pistorius and le Roux, 2002) .....	41
Fig 2.5.3e:	Scanning electron micrograph (using back scattered electron imaging) of block route slag chlorinated for 30 seconds (Pistorius and le Roux, 2002). .....	43
Figure 3.3.1:	%Mass distribution of the particle sizes of granulated titania slag sample C. 50	
Figure 3.3.2:	XRD spectrum showing four different phases present in oxidized titania slag of size range $2360 - 3350\mu m$ .....	52
Figure 3.3.3:	Variation in the amount of rutile, anatase and iron titanium oxide phase relative to $M_3O_5$ for the granulated slag. ....	53
Fig 3.3.4;	Granulated slag of size in the range $106-425\mu m$ showing random distribution of both lower-Z (iron-poor) and higher-Z (less iron-poor) phases throughout the particle. Back-scattered electron image. ....	56
Fig. 3.3.5a;	Edge of granulated slag of size range $> 4750\mu m$ .....	57
Fig. 3.3.5 b;	Centre of granulated slag of size range $> 4750\mu m$ .....	57
Fig. 3.3.6:	SEM micrograph of block route slag of the campaign(BSC).....	58
Figure 4.2.1:	Schematic diagram of the apparatus used to determine the flowrate of CO and $N_2$ . .....	61
Figure 4.2.2:	Schematic diagram of the apparatus used to determine the flowrate of chlorine. 62	
Figure 4.3 a:	Optical micrograph of unchlorinated block route slag of the campaign (BSC). 65	
Figure 4.3 b:	Optical micrograph of granulated slag of size range $1700\mu m-2360\mu m$ after crushing to the size range $425-600\mu m$ , and before chlorination. ....	66
Figure 4.3 c:	Optical micrograph of granulated slag of size range $425\mu m-600\mu m$ . ....	66
Figure 4.4.1a:	Optical micrograph of block route slag of the campaign (BSC) chlorinated for 15 minutes.....	67
Figure 4.4.1b:	Optical micrograph of granulated slag of size range $1700-2360\mu m$ , chlorinated for 15 minutes.....	68
Figure 4.4.1c:	Optical micrograph of granulated slag of size range $425\mu m-600\mu m$ , chlorinated for 15 minutes.....	68
Figure 4.4.3a:	SEM micrograph of a black particle of slag of size range $425-600\mu m$ chlorinated for 15 minutes .....	69
Figure 4.4.3b:	SEM micrograph of the light particle of slag of size range $425-600\mu m$ chlorinated for 15 minutes.....	70
Figure 4.4.3c:	SEM micrograph of chlorinated slag of size range $1700\mu m-2360\mu m$ chlorinated for 15 minutes.....	71
Figure 4.4.3d:	SEM micrograph of chlorinated block route slag of the Campaign(BSC) chlorinated for 5 minutes.....	72

Figure 4.5a	Temperature profile during initial chlorination of slag of size range 1700 - 2360 $\mu$ m, (results from three repeat runs shown).....	74
Figure 4.5b:	Variation of the temperature change obtained for the initial chlorination of the three slag samples.....	75
Figure 4.5c:	Temperature profile showing the effect of sample mass on reaction exothermicity of the block route slag of the campaign (BSC). ....	76
Figure 4.6.1a:	Chlorination trend of iron oxides (FeOx). ....	77
Figure 4.6.1b:	Chlorination trend of manganese oxides (MnO). ....	78
Figure 4.6.2:	Chlorination trend of magnesium oxides.....	78
Figure 4.6.3:	%Chlorination trend of Titanium dioxides.....	81



## LIST OF TABLES

<b>Table 2.2:</b>	Typical Composition Of Rutile, Ilmenite and High Titania Slag (Kahn, 1983; Minkler and Baroch, 1981).....	15
<b>Table 2.4:</b>	Chemical Composition of Various Upgraded Titaniferous Feedstocks (van Dyk et al. 1999). .....	20
<b>Table 2.5.2:</b>	Melting and Boiling Points of Chlorides of Calcium, Magnesium, Iron and Titanium (www.webelements.com).....	28
<b>Table 2.5.3a:</b>	List of activation energies for the chlorination of titanium.....	30
	feedstock in different gas mixtures.....	30
<b>Table 2.5.3b:</b>	Effect of reaction time on the degree of chlorination of titania slag at 1393K <sup>a</sup> . .....	35
<b>Table 2.5.3b:</b>	Composition slags before chlorination (Pistorius and le Roux, 2002).....	39
<b>Table 3.1:</b>	The values of 2 $\theta$ used to identify various phases. ....	46
<b>Table 3.2:</b>	% chemical composition of the two sets of samples used during the chlorination experiments as determined by XRF analysis. ....	50
<b>Table 3.4</b>	Composition of chlorinated black particles of size range 425-600 $\mu\text{m}$ (in wt %). Fe, Mn, O, Ti by WDS.....	54
<b>Table 4.3:</b>	Gas mixture used during the runs. ....	63
<b>Table 4.6:</b>	Summary of % chlorination of main oxides in titania slag after 5minutes. ....	80
<b>Appendix A:</b>	Data for EDS analysis of different regions on the oxidized granulated slag sample of size range 106-425 $\mu\text{m}$ , in figure 3.3.4. ....	86
<b>Appendix B:</b>	Data for EDS analysis of different regions on the oxidized granulated slag sample of size range 1700-2360 $\mu\text{m}$ .....	86
<b>Appendix C:</b>	Data for EDS analysis of different regions on the oxidized granulated slag sample of size range > 4750 $\mu\text{m}$ , in figure 3.3.5. ....	87
<b>Appendix D:</b>	EDS analysis of unoxidized block route slag, as in figure 3.3.6. ....	87
<b>Appendix E1:</b>	EDS analysis of black particles of granulated slag of size range 425-600 $\mu\text{m}$ chlorinated for 15 minutes, as seen in figure 4.4.3a .....	88
<b>Appendix E2:</b>	EDS analysis of light particles of granulated slag of size range 425-600 $\mu\text{m}$ chlorinated for 15 minutes, as seen in figure 4.4.3c.....	88
<b>Appendix E3:</b>	EDS Analysis of granulated slag of size range 1700-2360 $\mu\text{m}$ chlorinated for 15 minutes, as seen in figure 4.4.3d.....	88
<b>Appendix E4:</b>	EDS analysis of block route slag chlorinated for 5 minutes, as seen in figure 4.4.3e.....	89
<b>Appendix H:</b>	Hyperfine interaction parameters of the different size ranges of granulated slag ( Mössbauer analysis).....	92
<b>Appendix I:</b>	Chlorination parameters and results obtained. ....	93
<b>Appendix K:</b>	XRF analysis of both the chlorinated and unchlorinated slag.....	103
<b>APPENDIX M:</b>	Composition of various phases in titania slags (in wt%). Fe, Mn, O, Ti, and V by WDS, other elements by EDS;.....	104