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Titania Recovery from Low-grade Titaniferrous Minerals

by

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Declaration

I declare that this dissertation is my own unaided work. It is being submitted for the Degree of Philosophiae Doctor at the University of Pretoria, Pretoria. It has not been submitted before for any degree or examination to any other University

.....

(Signature of Candidate)

On this day of year.....

Abstract

Titanium dioxide or titania is applied in paints, in the paper industry, fibbers, cosmetics, sunscreen products, toothpaste, foodstuffs, optical coatings, beam splitters and anti-reflection coatings. It is also used as support catalyst and its use as humidity and high-temperature oxygen sensor is under consideration. These applications are related to its high refractive index, oil absorption, tinting strength and inert chemical properties.

Commonly, titania is recovered either by leaching ilmenite with sulphuric acid and subsequently hydrolysing the resulting sulfate solution by boiling. In another process, titanium feedstock is converted into titanium tetrachloride and further oxidised to titanium dioxide. These methods are reportedly time-consuming and environmentally unfriendly. They are also unable to use all existing types of titanium minerals.

In this study, a novel process for the extraction of titanium valuables from its minerals is presented. The process entails the roasting of titanium ore with alkaline metal salt. The roasted product is hydrolysed with water and acid, and subsequently reacted with sulphuric acid. Alternatively, the hydrolysed product can be used as feedstock in the chloride process.

Roasting at 900 °C and using a 2:1 (NaOH:ilmenite) mole ratio proved to be the most efficient in releasing titanium units from its ore. Ternary phases dominate under these conditions. $\text{Na}_{0.75}\text{Fe}_{0.75}\text{Ti}_{0.25}\text{O}_2$ was the dominant titanium-bearing phase. NaFeTiO_4 and $\text{Na}_2\text{Fe}_2\text{Ti}_3\text{O}_{10}$ were also present. Whenever the Ti:Fe atom ratio was different from one, the surplus titanium was accommodated in single titanates, mainly Na_2TiO_3 , while iron was accommodated in NaFeO_2 . In many cases $\text{Na}_8\text{Ti}_5\text{O}_{14}$ was also present as a result of Na_2TiO_3 polymerisation. This is consistent with a fusion period of one hour or more. Shorter fusion periods tended to produce binary

phases. Similar results were obtained when lower fusion temperatures were employed, i.e. below 550 °C.

When anatase reactant was used to resemble an anatase ore, $\text{Na}_2\text{Ti}_6\text{O}_3$, Na_2TiO_3 , $\text{Na}_8\text{Ti}_5\text{O}_{14}$ and $\text{Na}_{16}\text{Ti}_{10}\text{O}_{28}$ were identified in the products. Optimum recoveries were obtained using a 1:1 NaOH:TiO₂ mole ratio, and fusing at 800 °C for 2 h. Close to 100% of the titanium was recovered.

A one-step leaching process was found to be effective compared with multi-step leaching. The leaching step was found to be dependent on time, solid:liquid ratio and temperature. The optimum conditions for solid:liquid ratio, time and temperature were found to be 0.20, and 15 min at 75 °C, respectively.

Acidic hydrolysis was controlled by the relative amount of iron and titanium in solution. It was found that less than 1% was dissolved between 3 and 7 in pH units. Higher pH values are recommended, since less acid will be used.

Any excess of sulphuric acid in the sulfation step proved to be unnecessary. No significant changes were observed in the amount of dissolved iron and titanium. Therefore the stoichiometric amount can be used in the sulfation process.



Dedication

To my late father

Joao Manhique

And my late mother

Marta Zandamela

To the Almighty

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Contents

Declaration.....	i
Abstract.....	ii
Dedication.....	iv
Acknowledgements.....	v
Contents.....	vii
List of Figures	xii
List of Tables	xv
List of Symbols	xvi
1 Introduction	1
1.1 Aim of the Study.....	3
1.2 Methodology.....	3
1.3 Rationale	4
1.4 References.....	5
2 Literature Review.....	8
2.1 Titanium Minerals and Ores.....	8
2.1.1 Rutile.....	9
2.2 Ilmenite	10
2.2.1 Titanium Minerals Occurrence	13
2.2.2 Mining.....	14
2.3 Synthetic Feedstock	15
2.3.1 Titanium slag.....	15

2.3.2	Synthetic rutile.....	17
2.4	Titanium Processing Technology Overview	20
2.4.1	The Sulfate Process	20
2.4.2	The Chloride Process.....	23
2.4.3	Surface Crystal Treatment	26
2.5	Other Processes.....	27
2.5.1	Direct leaching	27
2.5.2	Reduction and leaching.....	30
2.5.3	Dissolution	31
2.5.4	Oxidative roasting/fusion	35
2.5.5	Remarks on Titania Technology.....	40
2.6	Phase Diagrams	41
2.6.1	System Na ₂ O–TiO ₂	41
2.6.2	System Na ₂ O–TiO ₂ –Fe ₂ O ₃	47
2.6.3	Comments on the phase diagrams	49
2.7	The Proposed Process	52
2.7.1	The Richter Process.....	52
2.7.2	The de Wet Process	53
2.7.3	Description of the New Process.....	54
2.7.4	Benchmarks of the Proposed Process	56
2.8	References.....	57
3	Experimental.....	70
3.1	Characterisation Techniques and Materials	70
3.1.1	X-ray powder diffraction (XRD).....	70

3.1.2	X-ray fluorescence (XRF)	70
3.1.3	FT-IR absorption.....	71
3.1.4	Thermogravimetric analysis.....	71
3.1.5	Particle size distribution.....	71
3.1.6	Scanning electron microscopy	72
3.1.7	Materials	72
3.2	Fusion Temperature	72
3.3	Fusion Samples.....	73
3.4	Optimisation of Fusion Stage	73
3.5	Leaching.....	74
3.6	Leaching Solution	76
3.7	Hydrolysis	77
3.8	Sulfation Process	77
4.	Results and Discussions	81
4.1	Material Composition.....	81
4.2	Thermogravimetric Analysis.....	82
4.3	Fusion Results.....	84
4.3.1	Fusions at lower temperatures and extended periods	84
4.3.2	Effect of fusion temperature	85
4.3.3	Effect of mole ratio and time.....	89
4.3.4	Fusions under NaOH starved conditions	91
4.4	FT-IR Analysis.....	92
4.5	Scanning Electron Microscopy	96
4.6	Ilmenite Alkali Fusion Reaction	99

4.7	Kinetics of the Ilmenite Alkali Fusion Reaction	102
4.7.1	Theoretical Background	102
4.7.2	Kinetic Analysis of Alkali Fusion Reaction	105
4.8	Optimisation of the Fusion Process	110
4.8.1	Effect of particle size	110
4.8.2	Effect of mole ratio	112
4.8.3	Effect of time	113
4.8.4	Effect of temperature	114
4.9	Reagent Consumption	115
4.10	Optimisation of the Leaching Process	116
4.10.1	Effect of solid:liquid ratio	116
4.10.2	Effect of time and temperature	117
4.10.3	Batch leaching	118
4.10.4	Kinetics of the leaching process	119
4.11	Optimal Hydrolysis pH	121
4.12	Sulfation Process	122
4.13	Trials with Anatase	123
4.14	Summary of the Discussions	127
4.15	References	129
5	Conclusions	134
5.1	Fusion Step	135
5.2	Leaching Step	136
5.3	Other Steps	136
5.4	Recommendations	137

Appendix A: X-ray diffraction diagrams 138

Appendix B: Particle size analysis 173

List of Figures

Figure 1: Crystal structure of rutile (a), anatase (b) and brookite (c).....	10
Figure 2: Crystal structure of ilmenite.....	11
Figure 3: The sulfate process	22
Figure 4: The chloride process	24
Figure 5: Surface treatment.....	28
Figure 6: Na ₂ O – TiO ₂ phase diagrams (Bouaziz and Mayer, 1971; Gicquel <i>et al.</i> , 1972).....	42
Figure 7: Na ₂ O – Fe ₂ O ₃ – TiO ₂ phase diagram (Li <i>et al.</i> , 1971).....	47
Figure 8: Block diagram of the proposed process of titania recovery using ilmenite ore.....	52
Figure 9: TG curves of the reaction of ilmenite ore and FeTiO ₃ reactant (analytical grade) with two moles of NaOH (10 °C/min in oxygen).....	83
Figure 10: Effect of fusion temperature on the product spectra of the ilmenite alkali fusion reaction. Samples prepared with two mole NaOH per mole of ilmenite.....	86
Figure 11: XRD diffractograms of alkali fusion decomposed ilmenite. Samples of ilmenite:NaOH (2:1 mole ratio) were fused for 1 h at the indicated temperatures	87
Figure 12: Phase correlation in the alkali fusion products, from the XRD semiquantitative weight percent. Samples were obtained by fusing the ore with NaOH (2:1 mole ratio) for 1 h.....	89
Figure 13: FT-IR spectra of alkali fusion decomposed ilmenite. Samples were obtained by fusing NaOH:FeTiO ₃ mixtures (2:1 mole ratio) for 1 h at the indicated temperatures.....	93
Figure 14: FT-IR spectra of the fusion-processed NaOH:FeTiO ₄ mixtures (2:1 mole ratio), mid infra-red range. Samples were fused for 1 h at the indicated temperatures.....	95
Figure 15: Microphotography of ilmenite ore material used in this study. (a) Lower magnification; (b) higher magnification.....	97

Figure 16: Microstructure evolution induced by the ilmenite alkali fusion reaction. (a) Ilmenite raw material; (b) NaOH:FeTiO₃ fused at 700 °C for 1 h; (c) NaOH:FeTiO₃ fused at 750 °C for 1 h; (d) NaOH:FeTiO₃ fused at 850 °C for 1 h 98

Figure 17: Colour evolution in ilmenite:NaOH mixtures (2:1 mole ratio) after fusion for 1 h at the indicated temperatures 99

Figure 18: TGA, DTG and DTA curves of the ilmenite alkali fusion reaction at three different heating rates, 2, 5 and 10 °C/min 106

Figure 19: Section of the DTG and DTA signal displaying the new maximum..... 107

Figure 20: Conversion (α) as function of temperature in the alkali fusion reaction of ilmenite 108

Figure 21: Kissinger plot for the dominant alkali fusion reaction..... 110

Figure 22: Effect of particle size. (a) Residue; (b) iron; (c) titanium 111

Figure 23: Effect of mole ratio on fusions conducted at 850 °C for 1 h 112

Figure 24: Effect of fusion time on the ilmenite alkali reaction (2:1 NaOH:FeTiO₃ mole ratio, 750 °C)..... 113

Figure 25: Effect of fusion temperature on titania recovery..... 114

Figure 26: Efficiency of the fusion process 115

Figure 27: Effect of solid:liquid ratio on the leaching process at room temperature. Samples of AFDI were prepared by fusing two moles of NaOH with one mole of FeTiO₃ for 1 h at 750 °C 116

Figure 28: Effect of time and temperature on the leaching process. Samples of AFDI were prepared by fusing two moles of NaOH with one mole of FeTiO₃ for 1 h at 750°C 117

Figure 29: Effect of repeated leaching at indicated leaching times (batch leaching) 118

Figure 30: Plot of leaching kinetics 121

Figure 31: Determination of the optimal hydrolysis pH 122

Figure 33: Optimisation of the sulfation process 123

Figure 34: TGA and DTA curves of the alkali fusion reaction 124

Figure 35: XRD patterns of alkali fused anatase (2:1 NaOH:TiO₂ mole ratio) 125

Figure 36: Effect of time on the recovery of titania from anatase ores using the proposed
process 126

Figure 37: Effect of temperature on the titania recovery from anatase ores using the proposed
process 126

List of Tables

Table 1: Non-commercial natural occurring titanium minerals	8
Table 2: Minor titanium bearing naturally occurring minerals	9
Table 3: Minerals associated with HMS and their typical impurities	12
Table 4:Composition of ilmenite raw material (major elements)	81
Table 5: Composition of ilmenite raw material (minor elements)	82
Table 6:Phase composition of the ilmenite raw material.....	82
Table 7: Identified phases in XRD patterns (Appendix A2–A6) of AFDI obtained after fusing for 336 h.....	84
Table 8: Identified phases by XRD in the AFDI diagrams obtained after roasting a mixture of ilmenite with sodium hydroxide for 1 h.....	90
Table 9: Fusions of NaOH:Ilmenite ore under starving conditions for 1 h	91
Table 10: Assignments of FT-IR bands in ilmenite and fused products.....	96
Table 11: Characteristics of TGA and DTA results of the ilmenite alkali fusion reaction	106
Table 12: Selected mathematical functions of the reaction mechanismstested with produced data	109

List of Symbols

AFDI	Alkali Fusion Decomposed Ilmenite
Fe ²⁺	Iron (II), ferrous ion
Fe ³⁺	iron (III), ferric ion
FeTiO ₃	Ilmenite, iron titanate
Fe ₂ O ₃	iron oxide, iron (III) oxide, iron trioxide, hematite
FeOOH	goethite
FeO	iron oxide, iron (II) oxide, iron dioxide
FeSO ₄	iron sulfate, iron (II) sulfate, ferrous sulfate
FeSO ₄ ·7H ₂ O	iron sulfate heptahydrate, copperas
Fe ₂ (SO ₄) ₃	iron sulfate, iron (III) sulfate, ferric sulfate
FT-IR	Fourier transform infra-red spectrometry
g	grams
H ₂ SO ₄	sulphuric acid
HCl	hydrochloric acid, hydrogen chloride
ICP-MS	Inductively coupled plasma mass spectroscopy
K	Kelvin
L	liquid
l	litre
M	concentration, mol/l
mL	millilitres
NaTiO ₂	sodium metatitanate
Na ₂ TiO ₃	sodium titanate
Na ₈ Ti ₅ O ₁₄	sodium orthotitanate
NaFeO ₂	sodium ferrate
NaFeTiO ₄	sodium and iron titanate
Na ₂ CO ₃	sodium carbonate
NaOH	sodium hydroxide
REE	rare earth elements
S	solid
SEM	scanning electron microscopy
TiO ₂	titania, titanium dioxide, rutile, anatase
Ti(SO ₄) ₂	titanium sulfate
TiO ₂ ²⁺	titanyl ion
TiOSO ₄	titanyl sulfate
XRD	X-ray diffraction