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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

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(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 ^{o}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. $Na_{0.75}Fe_{0.75}Ti_{0.25}O_2$ was the dominant titanium-bearing phase. $NaFeTiO_4$ and$Na_2Fe_2Ti_3O_{10}$ 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 $Na_8Ti_5O_{14}$ 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 ^oC.

When anatase reactant was used to resemble an anatase ore, $Na_2Ti_6O_3$,Na_2TiO_3, $Na_8Ti_5O_{14}$ and $Na_{16}Ti_{10}O_{28}$ were identified in the products. Optimum recoveries were obtained using a 1:1 NaOH:TiO_2 mole ratio, and fusing at 800 ^oC 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 ^oC, 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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To all of you who got involved directly or indirectly in this journey

my special thanks

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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_2O_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
$FeSO_4.7H_2O$	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_2SO_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_2TiO_3	sodium titanate
$Na_8Ti_5O_{14}$	sodium orthotitanate
$NaFeO_2$	sodium ferrate
$NaFeTiO_4$	sodium and iron titanate
Na_2CO_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