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Fluidised-bed Chlorination of Titania Slag

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Voorgelê ter vervulling van 'n deel van die vereistes vir die graad Magister in Ingenieurswese in die Fakulteit Ingenieurswese, Bou-omgewing en Inligtingtegnologie, Universiteit van Pretoria.

February 2001

PROJECT INFORMATION

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• PROJECT DETAILS

PROJECT TITLE:	Fluidised-Bed Chlorination of Titania Slag.

Opgedra aan my Pa wat altyd daar was, maar nou die tydelike vir die ewige verruil het.

22/12/1945 - 22/4/1999

ACKNOWLEDGEMENTS

I would like to thank the following people and institutions for their contributions made to this project. This project would not have been such a success without them.

1. Prof. Chris Pistorius, my study supervisor, for his leadership and advice throughout the project.
2. Dr. Willem van Niekerk and Mr Johan Meyer, for supporting this project financially on behalf of Iscor Ltd.
3. Dr. Johan Nell, my mentor at Mintek, for his input in the project and Mintek's financial support.
4. Dr. Francoise O'Neill from Itec, for the XRF analysis.
5. Corelie Visser and Sabena Verryn, for their assistance in the XRD analysis.
6. Andre Botha, for his assistance with the SEM.
7. My fellow pyrometallurgical graduate students, Thys, Nana and Colette for their support and advice.
8. Sarah Havenga, for all her hard work and support.
9. Last, but not least, my mother for her support and love all the way.
10. I would also like to use this opportunity to thank our Heavenly Father for all His love and understanding all the way.

SUMMARY

Fluidised-bed Chlorination of Titania Slag

by

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Iscor Heavy Minerals is planning to install an ilmenite smelter at Empangeni, which will yield a TiO_2-rich slag as one of its products. The behaviour of the slag during fluidised bed chlorination would be a good quality-control test of the slag. The chlorination involves the reaction of TiO_2 slag with coke or CO and Cl_2 at approximately 1000°C to yield $TiCl_4$ as product. The aim of this project was to build a laboratory-scale chlorinator, comparing the chlorination behaviour of this slag to literature data on rutile. When the chlorinator operated as expected, the aim was to test the effect of Ti^{3+}/Ti^{4+} ratios in the slag on the subsequent chlorination behaviour. The reactor for these tests was a 5cm-diameter vertical quartz tube with a porous disk in the middle, inserted in a furnace at 1000°C whereafter the product gas was water-cooled and the $TiCl_4$ extracted with CCl_4.

Keywords: chlorination, fluidised bed, titanium dioxide, chloride process, reductant, titania slag.

SAMEVATTING

Sweefbedchlorinering van Titaandioksied Slak

deur

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"Iscor Heavy Minerals" is van plan om 'n ilmeniet smelter op te rig by Empangeni wat 'n hoë TiO_2 slak sal produseer as een van hulle produkte. Die gedrag van die slak gedurende sweefbedchlorinering sal 'n goeie aanduiding van die kwaliteit van die slak wees. Die chlorineringsreaksie kan beskryf word as die reaksie tussen die TiO_2 slak en kooks of CO en Cl_2 gas by ongeveer 1000 °C om $TiCl_4$ te produseer. Die doel van hierdie projek was om 'n laboratorium-skaal chlorineerder te bou en dan die gedrag van die slak te vergelyk met die data vir rutiel in die literatuur. Daar is ook gepoog om die invloed van die Ti^{3+}/Ti^{4+} verhouding in die slak op die chlorineringsgedrag te bepaal. Die reaktor vir die eksperimente was 'n vertikale kwartsbuis met 'n diameter van 5cm. Daar was 'n poreuse skyf in die middel van die reaktor gemonteer wat as die basis van die sweefbed gedien het. Die produkgasse is met water verkoel en die $TiCl_4$ is in CCl_4 opgelos.

Sleutelwoorde: chlorinering, gefluidiseerde bed, titaandioksied. chloried proses, reduseermiddel, titaandioksied slak.

LIST OF SYMBOLS

Symbol	Description	Units
a	Reaction order w.r.t. particle size	-
b	Constant to be determined by experiments	-
B	Constant to be determined by experiments	-
c	Constant to be determined by experiments	-
A_B	Cross-sectional area of bed	cm^2
d_p	Particle diameter	cm, μm
$d_{p'}$	Minimum particle diameter	cm
d_H	Diameter of the denser (heavier) particle	μm
d_L	Diameter of the less dense (lighter) particle	μm
d_{ER}	Shape corrected diameter ratio, $\phi_H d_H/\phi_L d_L$	-
d_i	Inside diameter of reactor tube	cm
D	Bed diameter	mm
E_{app}	Apparent Activation Energy	J/mol
g	Acceleration due to gravity	cm/s^2
ΔH_R	Heat of reaction	kJ/mol
H	Bed height	mm
H^*	Reduced aspect ratio, 1-exp(-H/D)	-
k_1	A temporary constant used to determine experimental data	-
k_0	Constant to be determined from experimental data	$min^{-1}.\mu m^{-a}.kPa^{-(m+n)}$
k_{app}	Apparent rate constant	min^{-1}
L	Depth of fluidised bed	cm
L_{mf}	Depth of bed at point of minimum fluidisation	cm
m	Reaction order with ref. to CO partial pressure	-
M	Mixing index	-
n	Reaction order with ref. to Cl_2 partial pressure	-
N	Molar ratio of Ti^{3+}/Ti^{4+} in the slag	-
p_{Cl_2}	Partial Cl_2 pressure	kPa, atm

p_{CO}	Partial CO pressure	kPa, atm
ΔP	Pressure drop across depth L	Pa
Q_{Cl_2}	Volumetric Cl_2 flow	ℓ/min
Q_{CO}	Volumetric CO flow	ℓ/min
Q_{mf}	Minimum fluidising velocity	cm^3/s or ℓ/min
Q_{N_2}	Volumetric N_2 flow	ℓ/min
Q_o	Volumetric flow at operating temperature	ℓ/min
Q_r	Volumetric flow at room temperature	ℓ/min
Q_t	Elutriation velocity	cm^3/s or ℓ/min
R	Ideal gas constant	J/mol.K
$Re_{dp'}$	Reynolds Number for elutriation velocity	-
S	Constant to be determined by experiments	-
t	Time	min
t_0	Initiation period	min
T	Temperature	K, ºC
T_f	Final temperature	K, ºC
T_o	Operating temperature	K, ºC
T_p	Peak temperature	K, ºC
T_r	Room temperature	K, ºC
u_{mf}	Minimum fluidising velocity	cm/s
u_{mf}^f	The u_{mf} of the component with the lower u_{mf}	m/s
u_{mf}^p	The u_{mf} of the component with the higher u_{mf}	m/s
u_0	Superficial gas velocity or Operating gas velocity (volumetric flow/bed cross-sectional area)	cm/s
u_{TO}	The velocity above which mixing takes over	m/s
u_t	Elutriation velocity	cm/s
$W_{o(TiO_2)}$	Initial sample mass	g
$W_{t(TiO_2)}$	Sample mass at time t	g
x	Mass fraction of jetsam in the upper uniform part of the bed	-
$\bar{x}$	Average mass fraction of jetsam in the bed	-
X	Conversion of a compound	fraction or %
X_{TiO_2}	Conversion of TiO_2	fraction or %

$X_{TiO_2}^{initial}$, X_{init}	Initial conversion of TiO_2	fraction or %
X_T	Total conversion of a TiO_2	fraction or %
Z	Constant to be determined by u_0, u_{mf}^f and u_{TO}	-

Greek Symbols

Symbol	Description	Units
ε	Porosity of the bed	-
ε_{mf}	Bed voidage at point of minimum fluidisation	-
ϕ_H	Shape factor, sphericity of the heavier particle	-
ϕ_L	Shape factor, sphericity of the lighter particle	-
ϕ_s	Particle shape factor	-
ρ_g	Gas density	g/cm^3
ρ_H	Density of the heavier particle	kg/m^3
ρ_L	Density of the lighter particle	kg/m^3
ρ_R	Density ratio, ρ_H/ρ_L	-
ρ_s	Density of solid particles	g/cm^3
μ	Gas viscosity	g/cm.s

Abbreviations

EDS, EDX	Energy-Dispersive X-ray Spectroscopy
WDS	Wave-Dispersive X-ray Spectroscopy
EPMA	Electron Probe Micro Analysis
MM	Molecular Mass
RBM	Richardsbay Minerals
QIT	Quebec Iron and Titanium
SEM	Scanning Electron Microscope
XRD	X-Ray Powder Diffraction
XRF	X-Ray Fluorescence Spectroscopy

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