



# Fluidised-bed Chlorination of Titania Slag

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

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## SUMMARY

### Fluidised-bed Chlorination of Titania Slag

by

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Isacor Heavy Minerals is planning to install an ilmenite smelter at Empangeni, which will yield a  $\text{TiO}_2$ -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  $\text{TiO}_2$  slag with coke or CO and  $\text{Cl}_2$  at approximately  $1000^\circ\text{C}$  to yield  $\text{TiCl}_4$  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  $\text{Ti}^{3+}/\text{Ti}^{4+}$  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  $1000^\circ\text{C}$  whereafter the product gas was water-cooled and the  $\text{TiCl}_4$  extracted with  $\text{CCl}_4$ .

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

## SAMEVATTING

### Swefbedchlorinering van Titaandioksied Slak

deur

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“Isacor Heavy Minerals” is van plan om ‘n ilmeniet smelter op te rig by Empangeni wat ‘n hoë  $\text{TiO}_2$  slak sal produseer as een van hulle produkte. Die gedrag van die slak gedurende swefbedchlorinering sal ‘n goeie aanduiding van die kwaliteit van die slak wees. Die chlorineringsreaksie kan beskryf word as die reaksie tussen die  $\text{TiO}_2$  slak en kooks of CO en  $\text{Cl}_2$  gas by ongeveer 1000 °C om  $\text{TiCl}_4$  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  $\text{Ti}^{3+}/\text{Ti}^{4+}$  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 swefbed gedien het. Die produkgame is met water verkoel en die  $\text{TiCl}_4$  is in  $\text{CCl}_4$  opgelos.

**Slutelwoorde:** chlorinering, gefluidiseerde bed, titaandioksied, chloried proses, reduseermiddel, titaandioksied slak.

## LIST OF SYMBOLS

<u>Symbol</u>	<u>Description</u>	<u>Units</u>
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	$\text{cm}^2$
$d_p$	Particle diameter	cm, $\mu\text{m}$
$d_p'$	Minimum particle diameter	cm
$d_H$	Diameter of the denser (heavier) particle	$\mu\text{m}$
$d_L$	Diameter of the less dense (lighter) particle	$\mu\text{m}$
$d_{ER}$	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	$\text{cm/s}^2$
$\Delta H_R$	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	$\text{min}^{-1} \cdot \mu\text{m}^{-a} \cdot \text{kPa}^{-(m+n)}$
$k_{app}$	Apparent rate constant	$\text{min}^{-1}$
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 $\text{Cl}_2$ partial pressure	-
N	Molar ratio of $\text{Ti}^{3+}/\text{Ti}^{4+}$ in the slag	-
$p_{\text{Cl}_2}$	Partial $\text{Cl}_2$ pressure	kPa, atm

$p_{CO}$	Partial CO pressure	kPa, atm
$\Delta P$	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 <sup>3</sup> /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 <sup>3</sup> /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, °C
$T_f$	Final temperature	K, °C
$T_o$	Operating temperature	K, °C
$T_p$	Peak temperature	K, °C
$T_r$	Room temperature	K, °C
$u_{mf}$	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
$u_{T0}$	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 %



$X_{\text{TiO}_2}^{\text{initial}}, X_{\text{init}}$	Initial conversion of $\text{TiO}_2$	fraction or %
$X_{\text{T}}$	Total conversion of a $\text{TiO}_2$	fraction or %
$Z$	Constant to be determined by $u_0, u_{\text{mf}}^f$ and $u_{\text{TO}}$	-

## Greek Symbols

<u>Symbol</u>	<u>Description</u>	<u>Units</u>
$\varepsilon$	Porosity of the bed	-
$\varepsilon_{\text{mf}}$	Bed voidage at point of minimum fluidisation	-
$\phi_{\text{H}}$	Shape factor, sphericity of the heavier particle	-
$\phi_{\text{L}}$	Shape factor, sphericity of the lighter particle	-
$\phi_{\text{s}}$	Particle shape factor	-
$\rho_{\text{g}}$	Gas density	$\text{g/cm}^3$
$\rho_{\text{H}}$	Density of the heavier particle	$\text{kg/m}^3$
$\rho_{\text{L}}$	Density of the lighter particle	$\text{kg/m}^3$
$\rho_{\text{R}}$	Density ratio, $\rho_{\text{H}}/\rho_{\text{L}}$	-
$\rho_{\text{s}}$	Density of solid particles	$\text{g/cm}^3$
$\mu$	Gas viscosity	$\text{g/cm.s}$

## 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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