

# Scoping Study of the Upgrading of Fluxed and Fluxless Titaniferous Magnetite Slags using the Upgraded Slag Process

X.C. Goso,<sup>1,2</sup> J. Petersen,<sup>2</sup> J. Nell<sup>3</sup> and K. Bisaka<sup>1</sup>

<sup>1</sup>Mintek, Randburg, South Africa

<sup>2</sup>University of Cape Town, Cape Town, South Africa

<sup>3</sup>Hatch Goba, Johannesburg, South Africa

A scoping study was undertaken to investigate the feasibility of upgrading fluxed and fluxless titaniferous magnetite (titanomagnetite) slags to saleable titania (TiO<sub>2</sub>) materials using the upgraded slag (UGS) process. The fluxed titanomagnetite slags produced by Evraz Highveld Steel and Vanadium Corporation (EHSV slag) and fluxless titanomagnetite slag produced in a pilot-scale direct-current furnace smelting campaign at Mintek (Mintek slag) were used as case studies. The basic scoping UGS conditions for processing both slags were determined. Results showed that the upgrading of these materials using the UGS process is feasible: the TiO<sub>2</sub> concentration in the EHSV slag was upgraded from about 33% to 75% and that of Mintek slag from 56% to 74%, with typical TiO<sub>2</sub> recoveries of over 80% at the various stages. Overall, the TiO<sub>2</sub> grades in the upgraded fluxed and fluxless titanomagnetite slags were significantly lower than the market grade for the preferred chloride pigment production process. The main detrimental species in both upgraded slags were magnesia and alumina that were incorporated in a chemically refractory spinel, MgAl<sub>2</sub>O<sub>4</sub>. Further optimisation on the UGS process conditions, in particular the pre-roasting stages for spinel decomposition, and scoping studies using other technically potential processes, like salt roasting, are recommended. In addition, provided that the chemical quality is met, the upgraded fluxed and fluxless titanomagnetite slags could be used in the alternative sulphate process for the production of pigment.

## INTRODUCTION

Titaniferous magnetite (titanomagnetite) contains economically appreciable reserves of vanadium and iron as well as significant contents of titanium dioxide (titania/TiO<sub>2</sub>) (Fischer, 1975). Titanomagnetite is typically smelted in an electric arc furnace to co-produce vanadium in a pig iron metal and a by-product titania-bearing slag (Geldenhuis et al, 2009; Steinberg et al., 2011). Titanomagnetite smelting may be conducted in the presence of a flux, *i.e.*, fluxed smelting (Steinberg et al., 2011), or in the absence of a flux, *i.e.*, fluxless smelting (Geldenhuis et al., 2009). The fluxed and fluxless titanomagnetite slags typically contain 20-40% TiO<sub>2</sub> (Steinberg et al., 2011) and about 60% TiO<sub>2</sub> (Geldenhuis et al., 2009), respectively. The TiO<sub>2</sub> grade in fluxless titanomagnetite slags can be increased to 80% if a clean feed concentrate and low ash reductant are used (Boyd et al., 1993); however, there are indications that the fluxless smelting process would be restricted by the formation of reduced titanium species, *i.e.*, Ti(O,C), when the TiO<sub>2</sub> content in the slag reaches 70 to 75% (Nell and McCullough, 2001).

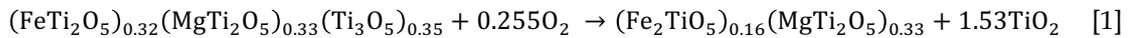
Both the fluxed and fluxless titanomagnetite slags have too low a TiO<sub>2</sub> content to qualify as marketable feedstock for chloride pigment production, which has a typical grade requirement of 85% TiO<sub>2</sub> and above (Pistorius, 2005). Low-grade titania resources, including some ilmenite slags, are effectively upgraded to chloride pigment production feed grade through technologies published in the open literature (Fouad, 2005; Van Dyk, 1999; Van Vuuren and Tshilombo, 2011). Of these, the upgraded slag (UGS) process is established for upgrading titania slags with high levels of alkaline earth impurities, such as Ca and Mg (Borowiec et al., 1998; Doan, 1996). In the UGS process, the phase composition of the slag is modified to increase the leachability of the impurities. The UGS process is used commercially in Canada for upgrading the SORESLAG™ slag generated from the Allard Lake ilmenite that contains relatively high levels of the alkaline earth impurities (Doan, 1996).

Fluxed and fluxless titanomagnetite slags typically contain high levels of alkaline earth impurities like MgO and CaO from the gangue, and from the flux in the case of fluxed smelting (Boyd et al., 1993; Geldenhuys et al., 2009; Steinberg et al., 2011). In this project, a scoping approach was adopted to investigate the upgradability of fluxed and fluxless slags using the modified UGS process by removing the alkali earth (and other) impurities. The scope involved evaluation of UGS process parameters; in particular, the leaching conditions, on the upgrading of titania in the slags.

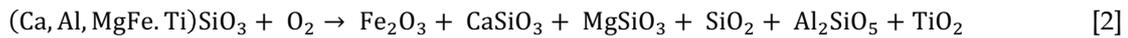
### Overview of the UGS Process

The conventional UGS process entails sizing of the titania-bearing material to a size applicable to a fluid-bed roaster, typically 106-850 μm (Borowiec et al., 1998). The sized material is then subjected to the following processing stages.

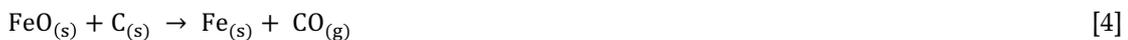
Oxidative roasting: Ti<sup>3+</sup> and Fe<sup>2+</sup> are converted to Ti<sup>4+</sup> and Fe<sup>3+</sup>, respectively, as shown in chemical reaction [1]. Rutile (TiO<sub>2</sub>) and pseudobrookite (M<sub>3</sub>O<sub>5</sub>, where M may be Fe<sup>2+</sup>, Fe<sup>3+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, V<sup>5+</sup>, Al<sup>3+</sup>, Ti<sup>3+</sup> or Ti<sup>4+</sup>) are the products of oxidation (Borowiec et al., 1998; Van Dyk, 1999):



During oxidation, the silicate structure is also decomposed, as shown in reaction [2]. In addition, the iron species migrate to the edges of the grains. This allows easy access to iron during subsequent treatment stages (Borowiec et al., 1998; Van Dyk, 1999):



Controlled reductive roasting: Fe<sup>3+</sup> is selectively reduced, without reducing Ti<sup>4+</sup>, to Fe<sup>2+</sup> or metallic Fe, which are readily leachable in HCl, as shown in reactions [3] and [4] (Borowiec et al., 1998; Van Dyk, 1999):



Leaching of detrimental species: Mg, Al, Si, Ca and Fe from the cooled titania bearing slag are leached in HCl lixiviant (Van Dyk; Borowiec et al). In some work, a caustic leaching stage is added to remove SiO<sub>2</sub> from the HCl leach residue, as shown in equation [5] (Borowiec et al., 1998; Doan, 1996):



Washing and calcining: This is carried out to remove volatiles and species adsorbed onto the TiO<sub>2</sub> particles. The waste from the UGS process generally includes soluble chloride salts of the alkali and alkali earth metals and other metals such as Fe. The other waste is a sodium silicate solution from caustic leaching. The aqueous solutions are typically subjected to waste treatment for neutralisation prior recovery of valuable by-products and disposal of non-toxic waste (Borowiec et al., 1998).

## EXPERIMENTAL

### Materials

The fluxed and fluxless slags were obtained from the slag waste dump at Evraz Highveld Steel and Vanadium Corporation (EHSV slag) and from a by-product slag of an un-optimised direct-current (DC) arc furnace titanomagnetite smelting campaign at Mintek (Mintek slag), respectively. The bulk chemical compositions of samples were determined by inductively coupled plasma optical emission spectrometry (ICP-OES) (Varian Vista-PRO CCD simultaneous instrument), whereas the morphological and phase chemical compositions were determined by scanning electron microscopy (SEM) (Zeiss MA15) equipped with a Bruker energy-dispersive spectrometer (EDS) and a Bruker D8 advanced X-ray diffractometer (XRD), respectively. All chemicals and reagents used in this study were of analytical-reagent grade.

The chemical compositions of finely ground fluxed and fluxless titanomagnetite slags are given in Table I. The microstructures and phase compositions of the fluxed and fluxless slags are illustrated in Figure 1 and Figure 2, respectively. The intensities and shapes of the crystals of pseudobrookite ( $\text{MgTi}_2\text{O}_5\text{-Al}_2\text{TiO}_5$ ) and spinel [ $(\text{Mg})(\text{Al},\text{Ti})\text{O}_4$ ] phases in the fluxed slag suggested that any of the two phases could have formed as a primary phase. The fluxless slag had pseudobrookite as the primary phase and did not show the occurrence of the spinel. In addition, it appeared that titanium species in both slags were primarily incorporated in a pseudobrookite phase.

Table I. Chemical compositions of the titanomagnetite slags (mass %)

Slag	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	CaO	*TiO <sub>2</sub>	V <sub>2</sub> O <sub>5</sub>	Cr <sub>2</sub> O <sub>3</sub>	MnO	FeO
EHSV	14.3	14.0	21.6	11.8	33.0	0.82	0.16	0.78	3.59
Mintek	15.8	7.36	8.86	1.85	56.2	1.91	0.17	0.65	7.20

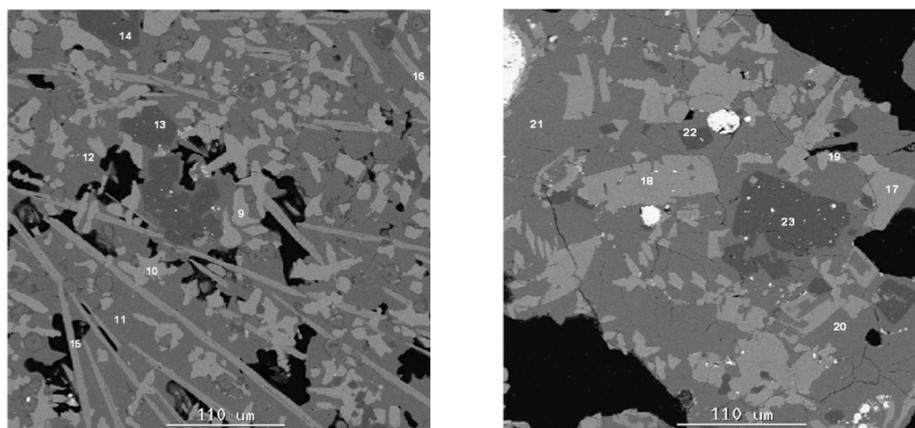
\*All titanium species (mainly Ti<sup>3+</sup> and Ti<sup>4+</sup>) are expressed as TiO<sub>2</sub>

### Experiments

The fluxed and fluxless slags were crushed and milled, using conventional equipment, to a particle size range of 150 to 600  $\mu\text{m}$ , which was compatible for use in the fluid-bed reactor. Batch masses of 400 g of each slag were separately weighed and transferred into a laboratory-scale fluid-bed furnace setup which was equipped with a quartz reactor with an internal diameter of 110 mm. Each sample was fluidized with a flow of 10 normal litres per minute of Ar gas and heated up at 10°C/min to 875°C. After the temperature had reached 875°C, the argon (Ar) gas was replaced with air to oxidise the sample for 2 h before changing back to Ar and cooling to room temperature by switching off the fluid-bed furnace elements. A sample of oxidised material was collected and subjected to XRD and SEM-EDS analyses. For reduction, the oxidised slag was processed as per the above heating cycle, except that the air operation was replaced by carbon monoxide (CO) which ran for 0.5 h. The reduced slags were collected and subjected to XRD and SEM-EDS analyses.

### HCl leaching

The HCl leaching testwork entailed the investigation of the basic combination of leaching parameters for the removal of detrimental species from the roasted fluxed and fluxless slags. The main parameters in the testwork were pulp density studied at solid-to-liquid (S:L) ratios of 1:2 (50 weight-volume percentage or w/v%) and 1:4 (25 w/v%), leaching test duration (8 and 24 h) and HCl lixiviant concentration (studied at 20%, 25% and 30%).



	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	CaO	TiO <sub>2</sub>	V <sub>2</sub> O <sub>5</sub>	FeO	Total	Phases
9	0.2	0.4	0.0	39.7	55.3	0.3	0.0	95.9	Perovskite
10	0.1	0.2	0.1	39.6	55.8	0.1	0.0	95.9	Perovskite
11	18.0	11.3	30.5	18.5	15.3	0.3	0.3	94.2	Non-crystalline
12	13.9	8.2	38.7	22.1	12.6	0.1	0.2	95.8	Non-crystalline
13	28.9	60.6	0.1	0.0	11.3	1.7	0.3	102.9	Spinel
14	28.9	63.0	0.2	0.1	8.0	2.3	0.2	102.7	Spinel
15	9.4	2.0	0.7	1.0	81.6	0.3	0.6	95.6	Pseudobrookite
16	8.9	2.1	0.3	0.7	82.3	1.1	0.2	95.6	Pseudobrookite
17	5.8	2.7	0.1	0.2	90.3	0.2	0.1	99.4	Pseudobrookite
18	9.3	1.8	0.3	0.3	86.6	1.9	0.0	100.2	Pseudobrookite
19	0.2	0.3	0.1	39.5	56.1	0.0	0.1	96.3	Perovskite
20	10.5	9.7	34.8	23.4	16.7	0.1	0.2	95.4	Non-crystalline
21	9.6	10.1	34.3	23.9	18.6	0.4	0.2	97.1	Non-crystalline
22	28.1	65.2	0.3	0.1	7.9	0.7	0.4	102.7	Spinel
23	27.6	62.5	0.5	0.2	9.2	1.4	0.4	101.8	Spinel

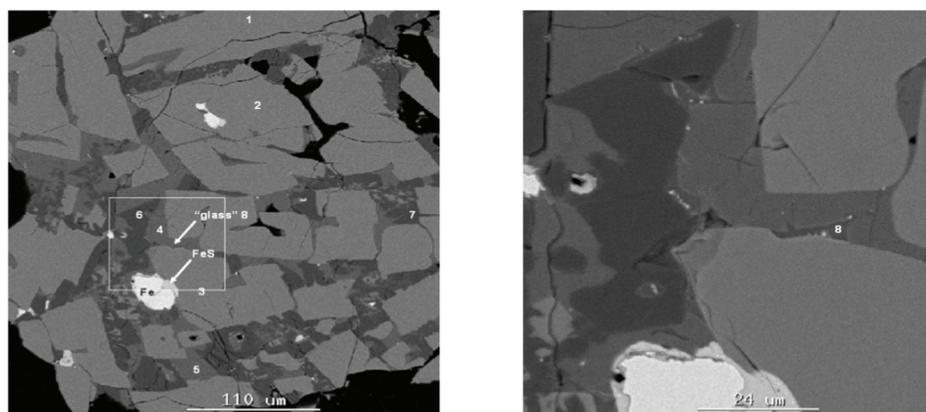
Figure 1. Microstructure, EDS (mass %) and XRD results of the EHSV slag.

The general leaching procedure involved the measurement of the HCl lixiviant volume (100 mL or 200 mL) into a batch leach reactor (round-bottomed flask) followed by addition of a 50 g mass of the roasted titanomagnetite slag into the same reactor to achieve the targeted S:L ratio. A magnetic stirrer bar was also inserted into the reactor. The reactor was immersed into an oil bath placed on a magnetic hotplate. The slurry in the reactor was heated at 110°C under constant agitation at a speed of 250 rpm for the targeted test duration before cooling down to room temperature. The slurry was then filtered through Whatman 542 hardened ashless filter paper using a Buchner funnel. The residue was re-slurried in 200 mL of warm de-ionised water at 60°C and re-filtered. The filter cake was washed with 50 mL of de-ionised water. A subsample of the residual sample was dried overnight at 105°C. The dried sample was subjected to bulk chemical analysis by ICP-OES to track the TiO<sub>2</sub> grades. The indicative TiO<sub>2</sub> recoveries were calculated based on the TiO<sub>2</sub> recovery to the residue, as shown in equation [6]:

$$\% \text{TiO}_2 \text{ recovery to residue} = \frac{\% \text{TiO}_2_{\text{residue}} \times \text{Mass}_{\text{residue}}}{\% \text{TiO}_2_{\text{feed}} \times \text{Mass}_{\text{feed}}} \times 100 \quad [6]$$

### Caustic leaching

The aim of this testwork was to evaluate the feasibility of caustic leaching on the removal of SiO<sub>2</sub> from the HCl leach residue material. Here, the basic test parameter was pulp density, which was studied at 100 w/v%, 50 w/v% and 25 w/v%.



	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	CaO	TiO <sub>2</sub>	V <sub>2</sub> O <sub>5</sub>	FeO	Total	Phases
1	12.0	2.5	0.2	0.1	79.6	2.9	2.9	100.9	Pseudobrookite
2	10.5	2.6	0.2	0.0	79.4	4.0	1.8	98.9	Pseudobrookite
3	12.1	2.9	0.1	0.1	78.6	3.1	1.9	99.1	Pseudobrookite
4	9.5	12.0	36.0	21.9	12.1	0.2	2.1	95.7	Non-crystalline
5	9.9	11.1	37.9	22.0	11.4	0.2	2.2	96.6	Non-crystalline
6	53.1	0.4	42.2	0.3	1.1	0.0	3.3	101.4	Forsterite
7	53.8	0.6	41.3	0.2	1.4	0.1	3.1	101.6	Forsterite
8	2.1	19.1	47.0	5.9	4.4	0.0	3.1	88.5	Non-crystalline

Figure 2. Microstructure, EDS (mass %) and XRD results of the Mintek slag.

The general caustic leaching procedure entailed the measurement of 2.15 M NaOH solution (20 mL, 40 mL, or 80 mL) into a caustic resistant Teflon reactor (beaker) followed by the addition of a 20 g mass of the wet HCl leaching residual filter cake into the same reactor. A magnetic stirrer bar was inserted into the reactor. The reactor was closed and placed on a hot magnetic hotplate. The slurry was agitated at 250 rpm while being heated at 100°C for 3 h. At the end of the test, the slurry was removed from the hotplate and allowed to cool down to room temperature. The slurry was filtered through a Whatman 542 hardened ashless filter paper using a Buchner system. The filter cake was re-slurried in 80 mL of warm de-ionised water (60°C) and re-filtered. The filter cake was washed with 20 mL of de-ionised water.

### Calcination

The calcination of the wet NaOH leach residue was conducted to remove volatile matter, crystalline water and other species that might be adsorbed onto the TiO<sub>2</sub> particles. The calcination was conducted in a muffle furnace at 900°C for 3 h. The calcines were subjected to bulk chemical analysis by ICP-OES; calcines from the best conditions were further analysed by XRD and SEM-EDS.

## RESULTS AND DISCUSSION

The results of the XRD and SEM-EDS analyses of the roasted EHSV and Mintek slags are shown in Figure 3 and Figure 4, respectively. The results show that, after oxidation, the EHSV slag did not undergo a significant phase transformation; however, after reductive roasting, metallization of iron was observed. The results further show that, after oxidation, the Mintek slag also did not undergo a significant phase transformation except for the identification of a spinel that was not observed in the starting material. After reduction, the spinel was not observed. A dedicated assignment may be required to track the spinel development in the untreated, oxidised and reduced Mintek slags. Moreover, rutile and alumina silicate phases were observed in the reduced Mintek slag. In the reduced sample, the metallization of iron and titanium was also observed.

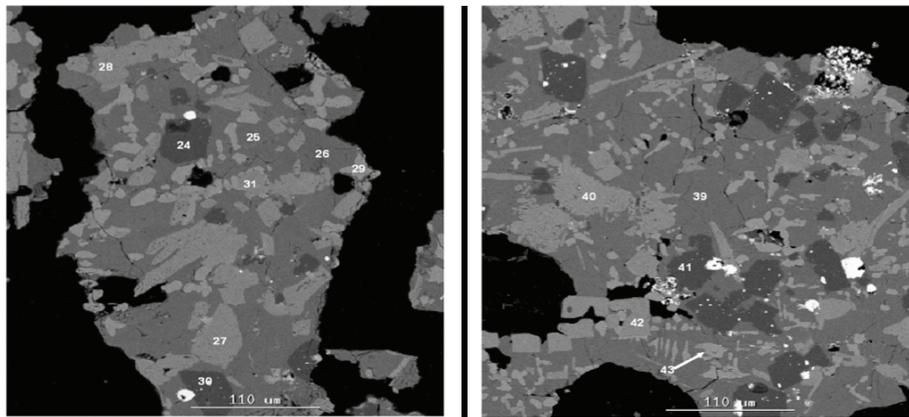
## HCl Leaching

### Effect of pulp density

Because the impurity compositions of the EHSV and Mintek slags were similar, the effect of pulp density is reported for only one slag, *i.e.*, the Mintek slag, which had a higher TiO<sub>2</sub> content. The pulp density scoping study was investigated at 50 w/v% and 25 w/v%, in which case the lixiviant concentration and leaching time were kept constant at 20% HCl and 24 h, respectively. The TiO<sub>2</sub> grades and recoveries to residues are given in Table II. Although the points are too few to establish the equilibrium pulp density, the available results show that the TiO<sub>2</sub> grade and recovery increased with decreasing pulp density. The lower pulp density of 25 w/v% (S:L = 1:4), which resulted in the highest TiO<sub>2</sub> grade and recovery of 67.1% and 96.6%, respectively, was adopted to study the other parameters.

Table II. Effect of pulp density on TiO<sub>2</sub> grade and recovery

Pulp density (w/v%)	TiO <sub>2</sub> grade (%)	TiO <sub>2</sub> recovery to residue (%)
50	64.80	92.72
25	67.10	96.56

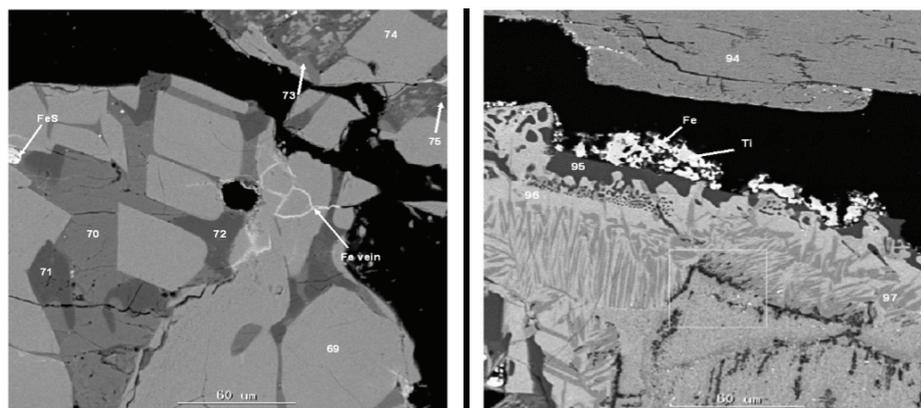


	Phase		Phase
24	Spinel	39	Non-crystalline
25	Non-crystalline	40	Pseudobrookite
26	Non-crystalline	41	Spinel
27	Pseudobrookite	42	Pseudobrookite
28	Pseudobrookite		Perovskite
29	Perovskite		Fe
30	Spinel		
31	Pseudobrookite		
<b>Oxidised EHSV slag</b>		<b>Reduced EHSV slag</b>	

Figure 3. Microstructure, EDS and XRD results for the roasted EHSV slag.

### Effect of acid leaching time

The effect of acid leaching time was investigated only for the Mintek slag. In this scoping study, the upgrading of titania content was investigated only at two points, namely, 8 and 24 h. Investigations were conducted at one HCl lixiviant concentration and pulp density of 20% and 25 w/v%, respectively. The results of the effect of leaching time on titania upgrading are summarized in Table III. The results show that the TiO<sub>2</sub> grade and recovery increased with increasing leaching time. The equilibrium leaching time was not established. The leaching time of 24 h, which resulted in the highest TiO<sub>2</sub> grade and recoveries of 67.8% and 97.0%, respectively, was adopted to study other parameters.



	Phase		Phase
69	Pseudobrookite	94	Pseudobrookite
70	Non-crystalline	95	Non-crystalline
71	Forsterite	96	Pseudobrookite
72	Spinel	97	Rutile
73	Non-crystalline		Alumina silicate
74	Pseudobrookite		Forsterite
75	Forsterite		
<b>Oxidised Mintek slag</b>		<b>Reduced Mintek slag</b>	

Figure 4. Microstructure, EDS and XRD results for the roasted Mintek slag.

Table III. Effect of leaching time on  $TiO_2$  grade and recovery

Leaching time (h)	$TiO_2$ grade (%)	$TiO_2$ recovery to residue (%)
8	63.30	91.48
24	*67.80	97.04

\*Repeat of second pulp density test

#### Effect of HCl lixiviant concentration

The effect of HCl lixiviant concentration on the upgrading of  $TiO_2$  was conducted on both the EHSV and Mintek slags. The pulp density and reaction time were kept constant at 25 w/v% and 24 h, respectively. The HCl lixiviant concentration was investigated at 20%, 25% and 30%. The results of the effect of HCl lixiviant concentration on the upgrading of  $TiO_2$  in the EHSV and Mintek slags are given in Figure 5(a) and (b), respectively. These show that the variation of the HCl concentration between 20% and 30% resulted in small upgrades of only 3.2% and 1.8%  $TiO_2$  in the leach residues of the EHSV and Mintek slags, respectively; however, the  $TiO_2$  recoveries to the residues were in the vicinity of 90% and above.

Table IV and V give the results of the bulk chemical analysis of the HCl leach residues of the EHSV and Mintek slags, respectively. In both slags, the HCl leaching exercise effectively leached out iron and calcium species; however, only limited leaching of Mg, Al and Si species was observed. This implies that these species are in the phases that are refractory in the HCl lixiviant.

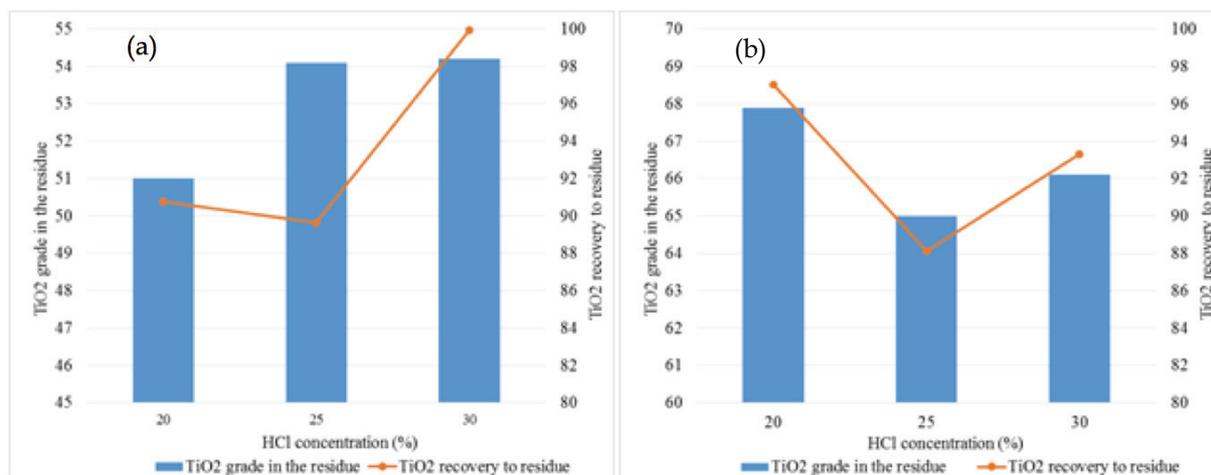


Figure 5. Effect of HCl lixiviant concentration on the TiO<sub>2</sub> upgrading and recovery to (a) EHSV and (b) Mintek slag residues.

Table IV. Chemical compositions of EHSV slag leach residues at different HCl concentrations

	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	CaO	TiO <sub>2</sub>	V <sub>2</sub> O <sub>5</sub>	Cr <sub>2</sub> O <sub>3</sub>	MnO	FeO
Feed	14.3	14.0	21.6	11.8	33.0	0.82	0.16	0.78	3.59
20% HCl lixiviant	7.29	9.75	27.5	3.20	51.0	<0.05	0.19	0.26	0.87
25% HCl lixiviant	6.98	10.1	27.3	0.11	54.1	0.90	0.16	0.38	<0.05
30% HCl lixiviant	7.59	11.0	25.7	0.10	54.2	0.92	0.18	0.40	<0.05

Table V. Chemical compositions of Mintek slag leach residues at different HCl concentrations

	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	CaO	TiO <sub>2</sub>	V <sub>2</sub> O <sub>5</sub>	Cr <sub>2</sub> O <sub>3</sub>	MnO	FeO
Feed	15.8	7.36	8.86	1.85	56.2	1.91	0.17	0.65	7.20
20% HCl lixiviant	11.9	7.00	8.79	<0.05	67.9	0.95	0.18	0.39	2.83
25% HCl lixiviant	11.3	8.08	9.68	0.06	65.0	2.54	0.19	0.36	2.80
30% HCl lixiviant	11.4	7.34	9.25	<0.05	66.1	2.52	0.19	0.36	2.83

### Caustic Leaching

The leaching of SiO<sub>2</sub> can be achieved through a caustic leach (Borowiec et al., 1998; Doan, 1996). The caustic leaching study was conducted only on the 20% HCl leach residue of the EHSV slag, which had a higher SiO<sub>2</sub> content compared with the Mintek slag. The effect of caustic leaching on the upgrading of TiO<sub>2</sub> in the EHSV slag was studied at pulp densities of 25 w/v%, 50 w/v% and 100 w/v%. The NaOH lixiviant concentration and leaching time were kept constant at 2.15 M and 3 h, respectively. The results of the TiO<sub>2</sub> grades as a consequence of SiO<sub>2</sub> removal in the caustic leach residues at varying pulp densities are given in Figure 6. The results show that the upgrading of TiO<sub>2</sub> increased with decreasing pulp density. There was only slight TiO<sub>2</sub> upgrading from 72.3% to 74.6% (2.3% upgrading) when the pulp density was lowered from 50 w/v% to 25 w/v%. The TiO<sub>2</sub> recovery generally increased with increasing pulp density. This implies that the highest TiO<sub>2</sub> grade was achieved with the lowest recovery of 83.3%. Further optimization is required.

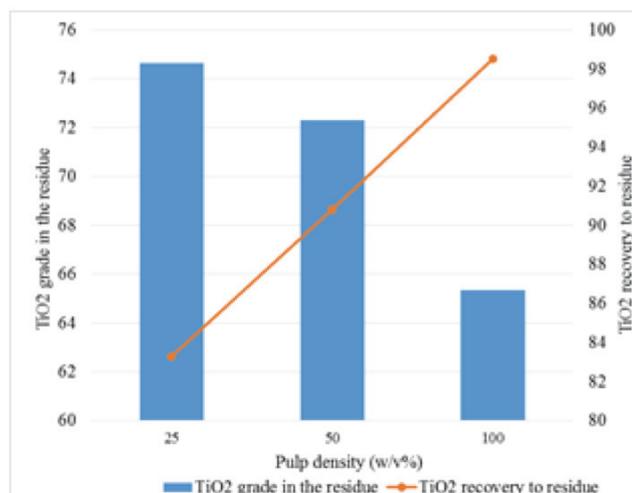


Figure 6. Effect of caustic leaching pulp density on the TiO<sub>2</sub> upgrading and recovery to EHSV slag leach residues.

### Final Upgraded Slag Products

Final upgraded EHSV and Mintek slags were produced under the conditions of fluid-bed roasting oxidation at 875°C for 120 min in air and reduction at 875°C for 30 min in CO, leaching with 20% HCl lixiviant under refluxing at 110°C for 24 h in a pulp density of 25 w/v% (S:L = 1:4), caustic leaching with 2.15 M NaOH at 100°C for 3 h at a pulp density of 25 w/v%, and calcination at 900°C for 3 h. The chemical compositions of the final upgraded slags are shown in Table VI. The results show that, in both slags, the concentrations of the detrimental species were lowered significantly, except for MgO and Al<sub>2</sub>O<sub>3</sub>.

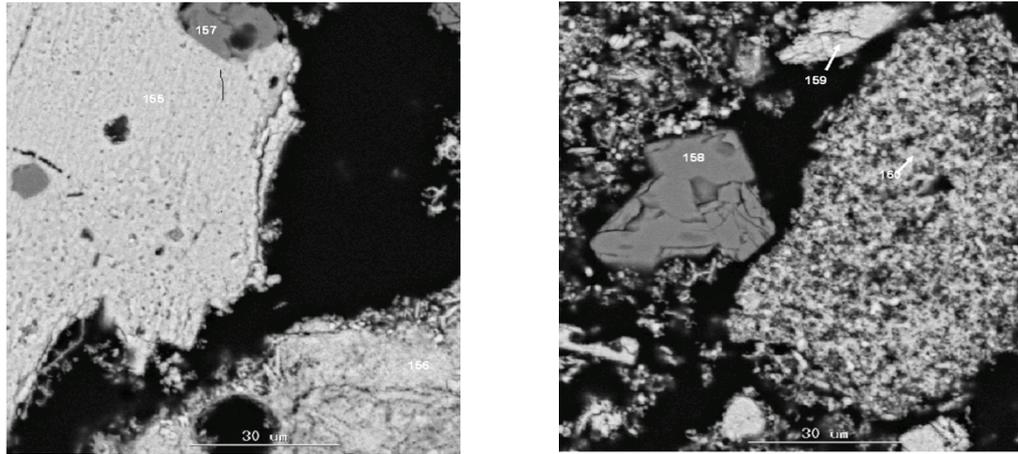
Table VI. Chemical compositions of the upgraded titanomagnetite slags (mass %)

Slag	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	CaO	TiO <sub>2</sub>	V <sub>2</sub> O <sub>5</sub>	Cr <sub>2</sub> O <sub>3</sub>	MnO	FeO
EHSV	8.05	13.0	1.10	0.95	74.6	0.97	0.21	0.24	0.86
Mintek	12.9	7.46	0.99	<0.05	74.0	0.94	0.20	0.44	3.15

Phase chemical analysis results for the upgraded EHSV and Mintek slags, as determined by SEM-EDS and XRD, to investigate the phases of existence of MgO and Al<sub>2</sub>O<sub>3</sub> are shown in Figure 7 and 8. The results show that, in both slags, MgO and Al<sub>2</sub>O<sub>3</sub> are incorporated in a spinel phase [Mg(Al,Ti,V)<sub>2</sub>O<sub>4</sub>] and pseudobrookite solid solution (MgTi<sub>2</sub>O<sub>5</sub>-FeTi<sub>2</sub>O<sub>5</sub>-Al<sub>2</sub>TiO<sub>5</sub>). It should be noted that the spinel phase was not observed in the reduced Mintek slag. The recurrence of the spinel in the final product motivates for a dedicated assignment to track the spinel department in the untreated, oxidised, reduced and upgraded Mintek slag.

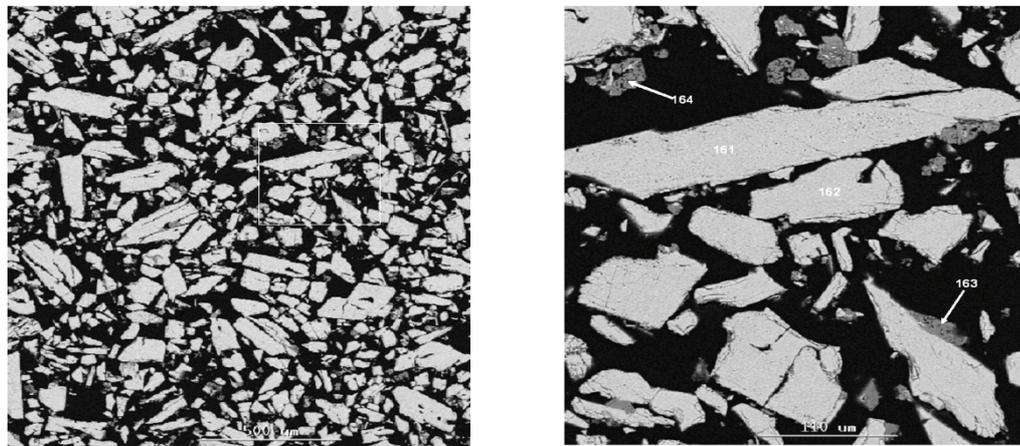
### CONCLUSIONS

From a chemical point of view, the chemical compositions of the final upgraded EHSV and Mintek slags showed that the upgrading of the fluxed and fluxless titanomagnetite slags to marketable titania materials using the UGS process is fairly feasible. Through the un-optimised UGS process, the TiO<sub>2</sub> concentration in the EHSV slag was upgraded from about 33% to 75% and that of Mintek slag from 56% to 74%. The TiO<sub>2</sub> recoveries in the respective UGS process stages were above 80%; however, the scoping study results show that the TiO<sub>2</sub> grades in the upgraded EHSV and Mintek slags were still lower than the feed grade for the chloride pigment production, *i.e.*, above 85% TiO<sub>2</sub>. The main detrimental species in both upgraded slags were MgO and Al<sub>2</sub>O<sub>3</sub>, which were primarily incorporated in a spinel.



	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	CaO	TiO <sub>2</sub>	V <sub>2</sub> O <sub>5</sub>	FeO	Phase
155	6.9	2.0	0.2	0.1	85.4	0.1	0.8	Pseudobrookite
156	0.2	1.1	2.5	0.1	87.9	0.0	0.2	Rutile
157	26.6	64.7	0.0	0.0	9.4	0.7	0.1	Spinel
158	25.0	65.4	0.1	0.0	6.0	4.4	1.4	Spinel
159	7.2	1.3	0.6	0.1	83.6	1.0	1.3	Pseudobrookite
160	0.9	0.3	10.3	0.5	69.8	1.9	0.7	Na-Si-Ti-O

Figure 7. Microstructure, EDS and XRD results for the final upgraded EHSV slag.



	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	CaO	TiO <sub>2</sub>	V <sub>2</sub> O <sub>5</sub>	FeO	Phases
161	11.5	3.6	0.0	0.2	77.5	2.7	1.8	Pseudobrookite
162	8.5	2.4	0.1	0.2	81.3	3.8	1.1	Pseudobrookite
163	26.2	68.5	0.0	0.0	3.9	1.5	0.8	Spinel
164	23.8	63.6	0.1	0.0	6.0	1.6	4.0	Spinel Rutile

Figure 8. Microstructure, EDS and XRD results of the final upgraded Mintek slag.

It is recommended that further investigations be conducted to establish the optimum UGS process conditions, in particular the pre-treatment roasting stages for spinel decomposition and the tracking of the particle size distribution throughout the UGS process stages to assess the suitability of final upgraded slag for use in the fluid-bed of the chloride pigment production process. Further scoping studies using other technically potential processes, like salt roasting, are recommended. In addition,

provided that the chemical quality is met, the upgraded fluxed and fluxless titanomagnetite slags could be used in the alternative sulphate process for the production of pigment.

## ACKNOWLEDGEMENTS

The authors wish to thank Mintek for financial support.

## REFERENCES

- Borowiec, K., Grau, A.E., Gueguin, M. and Turgeon, J.-F. (1998). Method to upgrade titania slag and resulting product. *US Patent*. No 5,830,420.
- Boyd, M.D., Schoukens, A.F.S. and Denton, G.M. (1993). The recovery of titanium from titanomagnetite. *South African Patent*. No. P11756 MVS/mdg.
- Doan, P.H. (1996). Upgraded slag (UGS): implications for TiO<sub>2</sub> feedstock supply. *Proceedings of the 12th Industrial Minerals International Congress*. Industrial Minerals Information Division, Worcester Park. pp. 71-76.
- Fischer, R.P. (1975). Vanadium resources of titaniferous magnetite deposits. *Geological Survey Professional Paper*, 926-B. United States Government Printing Office, Washington. pp. B1-B10.
- Fouad, O.A. (2005). Upgrading of a low-grade titanium slag by sulphation roasting technique to produce synthetic rutile. *Acta Metallurgical Slovaca*, 11 (1), 14-24.
- Geldenhuys, I., Xakalashé, B. and Ligege, T. (2009). DC arc smelting of titaniferous magnetite for Tivani (Pty) Ltd. *Confidential Report*, No. 5303, Mintek, Randburg.
- Nell, J. and McCullough, S. (2001). Upgrading of titania proxy slag derived from titaniferous magnetite. *Confidential Report*, No. C3269M, Mintek, Randburg.
- Pistorius, P.C. (2011). Titania slag smelting and calcination of crude zinc oxide: examples of processing under thermodynamic and kinetic constraints. *Proceedings of the 2<sup>nd</sup> International Slag Valorization Symposium*. Leuven, Belgium. pp. 263-270.
- Steinberg, W.S., Geyser, W. and Nell, J. (2011). The history and development of the pyrometallurgical processes at Evraz Highveld Steel and Vanadium. *Journal of the Southern African Institute of Mining and Metallurgy*, 111, 63-76.
- Van Dyk, J.P. (1999). Process development for the production of beneficiated titania slag. PhD thesis, University of Pretoria. <http://repository.up.ac.za/dspace/handle/2263/28654?show=full> [accessed on 19 Feb 2016].

