Beneficiation of fluxed titaniferous slag to a marketable titania product using the modified upgraded slag process

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**ABSTRACT**
Smelting production of a limestone-fluxed titaniferous slag with low MgO content for subsequent beneficiatio using the modified Upgraded Slag (UGS) process was investigated, with the aim of producing a marketable titania product. Smelting of titanomagnetite (titanomagnetite) with a carbon reductant and limestone flux was conducted in a water-cooled copper crucible in an iron-suscepting induction furnace under argon. The resulting titaniferous slag contained high residual iron (from the susceptor and incomplete iron reduction in the titanomagnetite), which caused crystallization of an ulvospinel. The slag was beneficiated using the modified UGS process, an industrial roast–leach process used for beneficiation of low-titania slag to a feedstock suitable for production of titania pigment. The upgraded product contained 90.5 mass\% TiO\textsubscript{2} with a recovery of 83\%. Although the TiO\textsubscript{2} grade met the feedstock specification for pigment production via the chloride route, SiO\textsubscript{2}, Al\textsubscript{2}O\textsubscript{3}, CaO, and Cr\textsubscript{2}O\textsubscript{3} concentrations exceeded the specification and the particle size distribution was too fine.

**INTRODUCTION**
Titanomagnetite deposits typically offer a unique opportunity for the production of vanadium, steel, and titanium products. Titanomagnetite is the primary source of vanadium throughout the world and a significant source of steel in countries like China and Russia (Fischer 1975; Moskalyk and Alfantazi 2003; Taylor et al. 2006; Roskull 2010). Titanomagnetite is typically processed by smelting in an electric arc or blast furnace in the presence of dolomite–quartz flux and carbonaceous reductant to produce a valuable vanadium-bearing pig iron and a virtually valueless titanium-bearing slag, referred to as titaniferous slag. The pig iron is processed further to produce vanadium and steel products; the slag is generally discarded in waste dumps. Titaniferous by-product slags have been produced in many industrial operations around the world, including by New Zealand Steel (NZS) (from iron sands), in China by Panzhihua Iron and Steel Corporation (Pangang) and Chengde Iron and Steel (CHIMP), in Russia by EVRAZ Nizhny Tagil Iron and Steel Works (NTMK), and in South Africa by (now-defunct) EVRAZ Highveld Steel and Vanadium Corporation (EHSV) (Kelly 1993; Nizhny Tagil Iron and Steel Works 2003; Zhang et al. 2007; Roskull 2010; Steinberg et al. 2011). These slags are typically described by the TiO\textsubscript{2}–SiO\textsubscript{2}–Al\textsubscript{2}O\textsubscript{3}–MgO–CaO system and contain 8–40 mass\% TiO\textsubscript{2}. Table 1 summarises typical chemical compositions of titaniferous slags.

Titaniferous slag dumps have accumulated to massive stockpiles over many years of operation; for example, the slag dump at Pangang was estimated to exceed 50 Mt in 2004 and was increasing at a rate of about 3 Mt/a (Sui et al. 2004); that remaining from EHSV operations is estimated to contain 45 Mt (Mining Review Africa 2017).

The TiO\textsubscript{2} grades in titaniferous slags make them attractive for upgrading to marketable titania products. Their successful valorisation would improve the overall metallurgical process economics and maximise exploitation of valuable resources. Titania is the primary titanium product and is mainly used as pigment for various industrial applications, including in the paint, plastic, and paper industries. Titania pigment is produced via one of two processes; namely, the sulfate and chloride processes. The latter is preferred because it is relatively cheaper. In 2014, about 60\% of the 4.5 Mt of global titania pigment production was generated by the chloride process. However, feedstock requirements for the chloride process are more stringent than for the sulfate process. These include a coarser particle size range of $-850 + 106$ $\mu$m and grades of (mass\%) $> 85$ TiO\textsubscript{2}, $< 0.13$ CaO, $< 0.6$ V\textsubscript{2}O\textsubscript{5}, $< 1.5$ Al\textsubscript{2}O\textsubscript{3}, $< 0.25$ Cr\textsubscript{2}O\textsubscript{3}, and $< 2$ SiO\textsubscript{2} (Roskull 2003; Pietorius 2008; Gazquez et al. 2014). Titaniferous slags...
Table 1. Chemical compositions of selected titaniferous slags (mass%).

<table>
<thead>
<tr>
<th>Operation</th>
<th>FeO</th>
<th>MgO</th>
<th>Al₂O₃</th>
<th>SiO₂</th>
<th>CaO</th>
<th>TiO₂</th>
<th>V₂O₅</th>
</tr>
</thead>
<tbody>
<tr>
<td>NZS*</td>
<td>2.11</td>
<td>13.3</td>
<td>17.8</td>
<td>15.2</td>
<td>15.9</td>
<td>32.1</td>
<td>0.20</td>
</tr>
<tr>
<td>Pangang*</td>
<td>nr</td>
<td>7.0</td>
<td>14.0</td>
<td>22.0</td>
<td>37.0</td>
<td>22.0</td>
<td>nr</td>
</tr>
<tr>
<td>NMTK and CHMP*</td>
<td>0.6–1.0</td>
<td>11–13</td>
<td>14–16</td>
<td>28–30</td>
<td>30–32</td>
<td>8–10</td>
<td>0.18–0.30</td>
</tr>
<tr>
<td>EHSV*</td>
<td>1.0</td>
<td>14.1</td>
<td>18.0</td>
<td>16.2</td>
<td>14.1</td>
<td>35.6</td>
<td>0.90</td>
</tr>
</tbody>
</table>

* (Harrell et al. 2016), † (Sui et al. 2004), ‡ (Steinberg et al. 2011), nr – not reported.

generally exhibit complex mineral phases, such as titanaugite [(Ca)(Mg,Ti,Fe,Al)(Si,Al,Fe₂)₃O₈], perovskite (CaTiO₃), pseudobrookite [(Mg,Al,Ti,V)₂O₃], diopside [(Ca,Mg,Ti)(Si,Al,Ti)₂O₆], and spinel [Mg(Al, Ti,V)₂O₄] (Pistorius 2011; Goso, Nell et al. 2016).

These slags have not been used to date because they contain low TiO₂ and higher impurity grades than the feedstock requirements. In addition, these slags have complex phase compositions that cannot be handled by the available slag-upgrading technologies (Pistorius 2011; Van Vuuren and Tshilombo 2011). Several complex processes have been proposed for processing low-titania resources, including titaniferous slags, to marketable titania materials for direct use as pigment or as feedstock for the production of chloride pigment. Becker and Dutton (2002) patented a modified sulfite process for valorisation of EHSV titaniferous slag, which involved contacting the slag with sulfuric acid to produce titanyl sulfate, followed by hydrolysis to titanyl hydroxyde and calcination to produce titania pigment. Xiao-hua et al. (2008) investigated the leaching kinetics of TiO₂ from Pangang titaniferous slag using H₂SO₄ as lixiviant. Hassell et al. (2016) patented a similar sulfate process for beneficiation of titanium-bearing materials.

Van Vuuren and Tshilombo (2011) proposed an alternative process for beneficiation of materials such as EHSV titaniferous slag, in which the slag is subjected to treatment at high temperatures and excessive reducing conditions in nitrogen atmosphere for selective nitridding of titanium to form titanium nitride, followed by relatively low-temperature chlorination of titanium nitride to produce liquid titanium tetrachloride. This is beneficiated further using conventional processes to produce titania pigment. Zhang et al. (2007) aerated molten Pangang titaniferous slag to grow the perovskite phase, which was then recovered from the slag by flotation (Wang et al. 2006; Zhang et al. 2006). Wang et al. (2010) showed that TiO₂ can be recovered from a perovskite concentrate by alkaline roasting followed by leaching removal of Ca and other impurities.

Goso, Petersen et al. (2016) proposed use of the established Upgraded Slag (UGS) process (Borowiec et al. 1998) for beneficiation of titaniferous materials that contain high concentrations of alkaline-earth impurities. In the conventional UGS process, the particle size of the slag is reduced to a range suitable for effective fluidisation, typically 106–850 µm. This slag is roasted in a fluidized-bed furnace under oxidising conditions to convert titanium species to the sparingly soluble Ti⁴⁺ species. Metallic and ferrous iron species are adversely oxidised to the sparingly soluble Fe⁴⁺ species; hence, roasting is strictly controlled under reducing conditions to selectively reduce Fe³⁺ species to HCl-soluble metallic and ferrous iron species. The roast product is subjected to leaching in HCl for removal of impurities such as Mg, Al, Ca, and Fe, followed by a caustic leach to remove SiO₂ from the HCl leach residue. The caustic leach residue is then subjected to calcination to produce a high-purity titania product, typically containing above 90 mass% TiO₂. The UGS process is used commercially at Rio Tinto Fer et Titane (RTFT) in Canada for upgrading the SORELSLAG* generated from Allard Lake ilmenite, which contains relatively high levels of alkaline-earth impurities (Doan 1996; Borowiec et al. 1998). Goso, Petersen et al. (2016) showed that the modified UGS process could increase the TiO₂ concentrations of 33 and 58 mass% in respective fluxed and fluxless titaniferous slags to 75%. In both UGS products, the major impurities were Mg and Al that were contained in a chemically inert magnesia alumina spinel (MgAl₂O₄).

The modified UGS process is one of the promising processes for the beneficiation of titaniferous slags. It is relatively simple and is already in commercial operation (Doan 1996; Borowiec et al. 1998); however, to produce a marketable titania product from titaniferous slag using the modified UGS process, the fluxing strategy during the primary smelting process needs to avoid solidification of the chemically inert spinel.

This study aimed to improve the fluxing strategy during smelting to produce a titaniferous slag with little or no spinel, followed by beneficiation using the modified UGS process. Jochens (1967) and Goso, Nell et al. (2016) showed that smelting of a South African titanomagnetite to produce a by-product slag containing a high CaO/MgO ratio would crystallize perovskite as the primary phase, followed by rutile and diopside. Moreover, Goso, Nell et al. (2016) showed that the phase assemblage of reviewed slag compositions with more than 5% MgO included spinel. The concentration of spinel in the slag is directly proportional to the concentration of MgO present. The current approach thus involved smelting of titanomagnetite in a magnesium-deficient system to avoid or minimise crystallization of the chemically inert spinel. Magnesium dissolved in the slag
Table 2. Bulk compositions of titanomagnetite materials, reductant, and fluxes (mass%).

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Titanomagnetite ore</th>
<th>Titanomagnetite concentrate</th>
<th>Sascarb</th>
<th>MgO</th>
<th>Al₂O₃</th>
<th>SiO₂</th>
<th>CaO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe₂O₃*</td>
<td>77.7</td>
<td>77.9</td>
<td>0.01</td>
<td>0.004</td>
<td>0.09</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MgO</td>
<td>1.64</td>
<td>1.34</td>
<td>99</td>
<td>0.09</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>3.97</td>
<td>4.17</td>
<td>98</td>
<td>0.8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiO₂</td>
<td>1.34</td>
<td>1.25</td>
<td>0.02</td>
<td>96.8</td>
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<td></td>
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</tr>
<tr>
<td>CaO</td>
<td>0.07</td>
<td>&lt;0.05</td>
<td>0.09</td>
<td>96</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TiO₂</td>
<td>13.3</td>
<td>13.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>V₂O₅</td>
<td>1.67</td>
<td>1.86</td>
<td></td>
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<td></td>
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<td></td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>0.20</td>
<td>&lt;0.05</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MnO</td>
<td>0.24</td>
<td>0.30</td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Alkalis</td>
<td></td>
<td>0.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>98.7</td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Ash</td>
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<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>LOI**</td>
<td>0.97</td>
<td></td>
<td>0.5</td>
<td>3.5</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Total Fe expressed as Fe₂O₃; < 0.05 mass% indicates that concentration was below the limit of detection; ² titanium species (Ti⁷⁺ and Ti⁴⁺) expressed as TiO₂. ** loss on ignition.

originates mainly from the dolomite flux and, to a lesser extent, from the titanomagnetite feed and furnace refractory; hence, this study investigated the use of limestone as an alternative flux. Limestone-fluxed titaniferous slag was subjected to the modified UGS process for upgrading of the titania content to a marketable grade.

Experimental procedures

Materials

A titanomagnetite ore mined from the main magnetite layer of South Africa's Bushveld Complex was supplied by EHSV. The ore was subjected to elementary concentration by low-intensity magnetic separation to minimise MgO in the feed to smelting and thereby minimise the MgO content in the subsequent titaniferous slag. Fe metal flakes (99%) were supplied by Sigma Aldrich and used as induction susceptor. A low-ash and low-sulfur carbonaceous material (sascarb) (LS SASCARB, Sasol, South Africa) was used as the reductant. Chemical-grade MgO, Al₂O₃, SiO₂, and CaO were supplied by Associated Chemical Enterprises (South Africa) and used as synthetic fluxes during smelting of the concentrate. The bulk chemical compositions of the materials used in the study are presented in Table 2. Reagent grade HCl (37%) and NaOH pellets (99%) were used to prepare the respective lixivants. De-ionised water was used for making up the lixivants and washing the solids.

Equipment

Smelting of the titanomagnetite concentrate to produce a spinel-free titaniferous slag for beneficiation studies was conducted in a water-cooled copper crucible in a high-frequency 75 kVA induction furnace. A

Figure 1. Schematic representation of crucible setup in cold copper crucible induction furnace.
schematic representation of the crucible setup in the induction furnace is shown in Figure 1.

Bulk chemical analyses of testwork samples were conducted using a Varian Vista-PRO CCD simultaneous inductively coupled plasma optical emission spectrometer (ICP-OES) and CS744 LECO instrument. Mineralogical characterisation was conducted using a Bruker D8 advanced X-ray diffractometer (XRD) and Zeiss EVO* MA15 scanning electron microscope (SEM) coupled with a Bruker energy-dispersive spectrometer (EDS), operated using Bruker Esprit software.

**Production of titaniferous slag**

The titanomagnetite concentrate was smelted in the cold copper crucible in the presence of sascarburant and synthetic flux. Reductant addition was calculated using Equations [1] and [2]. Based on previous testwork (Maphutha et al. 2017), the stoichiometric reductant addition in the smelting mixture was maintained at 110%.

\[
\begin{align*}
\text{Fe}_3\text{O}_4 + 4\text{C} & \rightarrow 3\text{Fe} + 4\text{CO} \\
\text{V}_2\text{O}_5 + 5\text{C} & \rightarrow 2\text{V} + 5\text{CO}
\end{align*}
\]

The adopted fluxing strategy aimed to achieve a slag with minimum or no crystallization of the spinel. To relate results to the phase diagram for synthetic titaniferous slags (Jochens 1967; Goso, Nell et al. 2016), the amounts of SiO₂ and Al₂O₃ in the smelting mixture and the overall flux amount (for TiO₂ control) were adjusted such that the resulting slag would have an approximate chemical composition of 20 mass% SiO₂, 13 mass% Al₂O₃, and 37 mass% TiO₂. CaO was added to act as synthetic calcined limestone flux. When smelting was conducted in the presence of a MgO-free flux while maintaining a constant flux amount, it was anticipated that a slag with a MgO: CaO mass ratio of 4:26 would be produced, i.e. MgO would only originate from the concentrate.

Smelting tests were conducted in triplicate at 300 g scale. The normalised mass composition of the smelting feed was 27.3 g titanomagnetite concentrate, 13.8 g sascarburant, 7.7 g CaO, 0.5 g Al₂O₃, and 4.5 g SiO₂. The respective components of the smelting feed were weighed and blended using a ring mill to produce a homogeneous feed. In each test, the smelt mixture was transferred into a copper crucible that was coated with boron nitride to avoid leaking of the finely ground feed or molten charge and to facilitate removal of charge from the crucible after the test. A mass of 20 g of Fe metal flakes was placed on top of the feed inside the cold crucible to act as a susceptor. Smelting was conducted under Ar atmosphere. Smelting was undertaken by increasing the furnace power to 80% capacity and allowing the test to continue for 10 min. Reactions within the crucible were vigorous in the first 5 min and then slowed down until there was no further activity after 8 min. The reactor was left for an additional 2 min to ascertain that no further reaction took place. During smelting, the Fe metal susceptor melted and descended to the bottom of the crucible while heating and melting the charge below. The mixture melted and produced a titaniferous slag and pig iron, which was diluted by the presence of the Fe metal susceptor. There was no available option for measurement of the melt temperature during tests; however, visual inspection of the melt within the copper crucible was deemed satisfactory for the purpose of producing titaniferous slag for subsequent beneficiation testwork. The furnace power was shut off and the water circuits continued to run to allow the products to cool down. The resulting alloy and slag samples were prepared and analysed by ICP-OES and LECO. The slag samples were subjected to mineralogical characterisation by XRD and SEM-EDS.

Generic material balance methodologies described by Maphutha et al. (2017) were adopted to determine partitioning of the respective elements between product streams.

**Beneficiation of titaniferous slag by modified upgraded slag process**

Three batches of titaniferous slag were blended to provide sufficient sample for the subsequent upGU slag testwork. The best upGU conditions determined by Goso, Petersen et al. (2016) for processing the EHHSV titaniferous slag were adopted as the baseline. The slag was sized to 150–600 μm particle size distribution (PSD). A 300 g mass of slag was roasted in a fluidized-bed furnace in an oxidizing atmosphere of air at 875°C for 2 h, followed by reduction in a CO atmosphere at 875°C for 0.5 h. In this study, the effects of HCl and NaOH leaching times on the titania grade of the products were evaluated at 20 g mass scale of roasted feed slag. The HCl leaching time was varied at 4, 24, and 48 h, while the NaOH leaching time was varied at 1, 3, and 24 h.

A 100 g mass of roasted slag was then subjected to a single-pass treatment using the best HCl and NaOH leaching conditions. The roasted slag was leached with 20% HCl under reflux at 110°C for 24 h at a solid:liquid (S:L; mass:volume) ratio of 1:4. This leach residue was then leached in 8.6% NaOH at 100°C for 3 h at a S:L ratio of 1:4. After each leaching stage, the solids were washed with copious amounts of de-ionised water until a filtrate with pH 6–7.5 was achieved. The resultant solid was calcined at 900°C for 3 h. Bulk chemical and mineralogical analyses using ICP-OES, XRD, and SEM-EDS, as well as PSD examination, were
Table 3. Average chemical compositions of pig iron and slag (mass%).

<table>
<thead>
<tr>
<th></th>
<th>Mg</th>
<th>Al</th>
<th>Si</th>
<th>Ca</th>
<th>Ti</th>
<th>V</th>
<th>Cr</th>
<th>Mn</th>
<th>Fe</th>
<th>C</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>EHSV</td>
<td>-</td>
<td>-</td>
<td>0.20</td>
<td>-</td>
<td>0.20</td>
<td>1.29</td>
<td>0.34</td>
<td>-</td>
<td>94.50</td>
<td>3.20</td>
<td>99.70</td>
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<tr>
<td>Current</td>
<td>0.02</td>
<td>0.03</td>
<td>&lt;0.025</td>
<td>0.04</td>
<td>0.07</td>
<td>0.66</td>
<td>0.08</td>
<td>0.08</td>
<td>98.04</td>
<td>1.51</td>
<td>99.94</td>
</tr>
<tr>
<td></td>
<td>MgO</td>
<td>Al₂O₃</td>
<td>SiO₂</td>
<td>CaO</td>
<td>TiO₂</td>
<td>V₂O₅</td>
<td>Cr₂O₃</td>
<td>MnO</td>
<td>*FeO</td>
<td>Total</td>
<td></td>
</tr>
<tr>
<td>EHSV</td>
<td>4.00</td>
<td>13.12</td>
<td>19.69</td>
<td>26.00</td>
<td>37.19</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>100.0</td>
<td>101.0</td>
<td></td>
</tr>
<tr>
<td>Current</td>
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<td>7.97</td>
<td>12.40</td>
<td>17.30</td>
<td>22.00</td>
<td>2.91</td>
<td>0.57</td>
<td>0.43</td>
<td>34.30</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Notes: < 0.025%: analyse concentration below the detection limit; *total Ti species (Ti⁴⁺ and Ti⁷⁺) expressed as TiO₂; *total Fe species (Fe⁶⁺ and Fe⁷⁺) expressed as FeO.

Table 4. Chemical compositions of HCl leach solids as a function of leach time (mass%).

<table>
<thead>
<tr>
<th>Leaching time (h)</th>
<th>MgO</th>
<th>Al₂O₃</th>
<th>SiO₂</th>
<th>CaO</th>
<th>TiO₂</th>
<th>V₂O₅</th>
<th>Cr₂O₃</th>
<th>MnO</th>
<th>FeO</th>
</tr>
</thead>
<tbody>
<tr>
<td>*Feed</td>
<td>2.80</td>
<td>7.22</td>
<td>11.80</td>
<td>15.20</td>
<td>20.20</td>
<td>2.85</td>
<td>0.64</td>
<td>0.43</td>
<td>38.10</td>
</tr>
<tr>
<td>4</td>
<td>2.75</td>
<td>7.27</td>
<td>18.11</td>
<td>13.58</td>
<td>22.85</td>
<td>1.46</td>
<td>0.77</td>
<td>0.36</td>
<td>32.85</td>
</tr>
<tr>
<td>24</td>
<td>2.37</td>
<td>6.99</td>
<td>17.97</td>
<td>13.74</td>
<td>36.46</td>
<td>2.18</td>
<td>0.73</td>
<td>0.22</td>
<td>20.24</td>
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<td>48</td>
<td>0.50</td>
<td>1.45</td>
<td>32.93</td>
<td>0.29</td>
<td>63.18</td>
<td>0.21</td>
<td>0.20</td>
<td>&lt;0.05</td>
<td>1.23</td>
</tr>
</tbody>
</table>

*Oxidised—reduced—roasted titaniferous slag.

Table 5. Effect of NaOH leaching time on chemical composition of UGS product (mass%).

<table>
<thead>
<tr>
<th>Leach time (h)</th>
<th>MgO</th>
<th>Al₂O₃</th>
<th>SiO₂</th>
<th>CaO</th>
<th>TiO₂</th>
<th>V₂O₅</th>
<th>Cr₂O₃</th>
<th>MnO</th>
<th>FeO</th>
</tr>
</thead>
<tbody>
<tr>
<td>*Feed</td>
<td>0.50</td>
<td>1.45</td>
<td>32.93</td>
<td>0.29</td>
<td>63.18</td>
<td>0.21</td>
<td>0.20</td>
<td>&lt;0.05</td>
<td>1.23</td>
</tr>
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<td>1</td>
<td>0.80</td>
<td>1.71</td>
<td>3.77</td>
<td>0.62</td>
<td>90.45</td>
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<td>0.29</td>
<td>0.07</td>
<td>1.98</td>
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<td>3</td>
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<td>3.31</td>
<td>0.72</td>
<td>91.00</td>
<td>0.29</td>
<td>0.28</td>
<td>0.07</td>
<td>1.70</td>
</tr>
<tr>
<td>24</td>
<td>0.84</td>
<td>2.04</td>
<td>3.32</td>
<td>0.58</td>
<td>90.87</td>
<td>0.29</td>
<td>0.29</td>
<td>0.07</td>
<td>1.69</td>
</tr>
</tbody>
</table>

*Residue from HCl leach for 48 h.

conduct  at different stages during UGS processing of the slag.

Recoveries of TiO₂ to the solid streams after the HCl and NaOH leaching steps are based on solid analyses; recoveries to the leachate were determined by difference.

Results and discussion

Masses of smelting products

During smelting, not all charge within the crucible reacted to form pig iron and the target titaniferous slag; some of the feed material formed a freeze lining inside the crucible as a consequence of continuous cooling on its surface. The smelting tests therefore produced four products: (1) an off-gas primarily composed of CO, produced as a consequence of the reduction reactions; (2) the freeze lining; (3) pig iron, which comprised the Fe metal added for induction purposes and Fe and V produced according to Equations [1] and [2]; (4) titaniferous slag.

Average mass proportions of the smelting products were 29.1% mass loss, 12.9% freeze lining, 35.9% Fe–V alloy, and 22.1% slag. The mass loss is primarily attributed to the emission of CO as per the chemical reactions shown in Equations [1] and [2]. The alloy mass suggested that there was about 80% metallisation of Fe present in the titanomagnetite, assuming that Fe from the susceptor was quantitatively recovered to the alloy phase. Based on this estimation, the reported freeze lining mass was lower than the anticipated mass of about 20%. This additional mass loss is attributed to ejection of unreacted sample from the crucible because of the violent nature of the reduction reactions. Mass losses due to CO emissions were determined by difference and were consequently overestimated.

Chemical composition of smelting products

Bulk chemical compositions of the pig iron produced in the smelting tests are given in Table 3. For comparison, the chemical composition of a typical pig iron produced by EHSV is also included. At EHSV, successful furnace control produced pig iron with C, V, and Ti concentrations of 3.5, 1.5, and 0.18 mass%, respectively. When the desired chemical composition of the alloy was achieved, the process was said to be ‘chemistry satisfactory’ (Steinberg 2008). Chemical analysis of the pig iron produced in the cold crucible reported lower C and V concentrations than this ‘chemistry satisfactory’ composition. These results suggest that the smelting conditions were not adequately reducing and/or the reduction reactions were far from equilibrium. The presence of substantial freeze lining material and low degree of Fe metallisation (80%) support the view that the conditions were not at equilibrium. The smelting process stopped as soon as the Fe metal susceptor settled to the bottom of the crucible. The suspended slag and freeze lining material were not effective in susceptor energy from the induction coils. Hence, the smelting testwork was inevitably stopped far from completion of the reactions.
Figure 2. Backscattered electron microstructures of (a) starting titaniferous slag, (b) titaniferous slag after oxidative roasting, (c) titaniferous slag after (oxidative and then) reductive roasting, (d) solids from 48 h HCl leach of roasted titaniferous slag, and (e) solids from 1 h NaOH leach of solids from 48 h HCl leach of roasted titaniferous slag, (UGS product).

Average chemical composition of the titaniferous slag is compared with the target composition in Table 3. The FeO content of the slag was higher than the target. The high FeO concentration supports the assumption that the smelting tests did not achieve complete reduction. Concentrations of other
components of the slags were significantly diluted by the high iron concentration. Moreover, the chemical compositions, particularly the FeO and V₂O₅ contents, were not comparable with those of typical titaniferous slags. Recoveries of vanadium and titanium to the slag exceeded 95%.
Upgraded slag processing of titaniferous slag

A composite titaniferous slag was used as feed to the modified UGS process. The baseline UGS oxidative and reductive roasting conditions were adopted from previous studies (Goso, Petersen et al. 2016), as summarised under experimental procedures. The effects of HCl and NaOH leaching times on the upgrading of TiO₂ are reported.

Effect of HCl leaching time on titania upgrading

Results showing the effect of HCl leaching time on the upgrading of TiO₂ in the oxidised-reduced-roasted titaniferous slag are presented in Table 4. The TiO₂ grade of the solids increased with leaching time and did not reach a steady value after a reaction time of 48 h. The slow leaching kinetics of the impurities are attributed to the coarse particle size of the feed, which is a consequence of the particle size required for effective fluidisation during roasting. TiO₂ recovery to the solids was very high, at more than 90%, suggesting that the concentration of the HCl-soluble Ti⁵⁺ species in the roast feed was low.

Mg, Al, Ca, V, Cr, Mn, and Fe were effectively removed during HCl leaching. The crucial removal of Mg and Al to very low or insignificant (in the case of Mg) concentrations in the solids confirmed that the chemically inert magnesium alumina spinel did not crystallize in the feed slag.

Effect of NaOH leaching time on titania upgrading in solids produced after 48 h of HCl leaching

The residue produced after 48 h of HCl leaching was subjected to a NaOH leach. The effect of leach time on the upgrading of TiO₂ in the solids is presented in Table 5. A maximum TiO₂ grade of about 91 mass% was achieved within 1 h; however, recovery of TiO₂ decreased with increasing leaching time. Hence, NaOH leaching times exceeding 1 h are not recommended.

The NaOH leach was effective in exclusively leaching silicon species from the HCl leach solids; however, a residual concentration of > 3 mass% SiO₂ remained in the UGS product, even at an extended caustic leaching time of 24 h.
Chemical compositions
The bulk chemical compositions of the untreated, intermediate, and final products from UGS processing of the titaniferous slag (presented in Tables 3–5, respectively) demonstrate that 48 h HCl leach effectively removed Al, Ca, Cr, Fe, Mg, Mn, and V from the solids produced after oxidative and then reductive roasting of the titaniferous slag; Si-containing species were removed in the 1 h NaOH leach. Titanium losses of 8% and 4% occurred during the respective HCl and NaOH leach steps, which were attributed to some dissolution of Ti³⁺ species. The cumulative recovery of TiO₂ to the UGS product was 83%.

Phase chemistry
Backscattered electron microstructures, EDS, and XRD results of the starting titaniferous slag, intermediate, and final products of the UGS process are presented in Figure 2 and Table 6. The phases in the slag included perovskite, pseudobrookite, olivine, wüstitie, and iron-rich ulvospinel (Fe₂TiO₄). The spinel content was approximated by the MgO concentration in the slag; however, the slag contained the iron-rich and less refractory ulvospinel.

Backscattered electron images, EDS, and XRD results of the (oxidised and then) reduced titaniferous slag showed that wüstitie observed in the cast titaniferous slag was oxidised to hematite (Fe₂O₃) after oxidative roasting, and subsequently reduced back to wüstitie in the reductive roasting stage. Phase composition of the reduced slag did not show evidence of over-reduction, which would likely have been demonstrated by the adverse reduction of Ti⁴⁺ to Ti³⁺. Ti³⁺ is relatively soluble in HCl, so if substantial titanium in the slag is in the form of Ti³⁺, there can be substantial titanium losses to the leachate (Doan 1996; Borowiec et al. 1998).

Backscattered electron image, EDS, and XRD results identified phases in the solids from the 48 h HCl leach as pseudobrookite, rutile, titanate, and quartz. These phases primarily comprised Ti and/or Si species that were not removed in the HCl leach. It is important to note that these solids did not contain any spinel, indicating that the ulvospinel observed in the cast and roasted slags was not as inert as the MgAl₂O₄ spinel typically observed in titaniferous slags (Goso, Petersen et al. 2016).

Analogous analyses of the NaOH leach solids (final UGS product) (Figure 2 and Table 6) showed that this was primarily composed of rutile and, to a lesser extent, perovskite and pseudobrookite. The EDS and XRD results showed that residual Si occurred in a titanate (CaO·TiO₂·SiO₃), a minor phase in the UGS product. The decomposition and consequent removal of Si-containing species was not sensitive to an increase in NaOH leach time above 1 h. Further testwork is required to investigate the effect of other parameters (such as NaOH concentration, pulp density, leaching temperature, and leaching pressure) on the decomposition of the titanate phase to enable effective removal of silica.
Particle size distribution

PSD analyses of the solids produced in the different stages of the modified UGS process are shown in Figure 3. The particle size was significantly reduced after the two leaching stages: the final UGS product exhibited 70% of particles passing 150 μm, compared with just 2.5% of particles in the feed. The PSD requirement for chloride pigment feedstock is $-850 + 106$ μm, so this product was too fine to meet the specification.

Conclusions

The smelting production of a limestone-fluxed titaniferous slag with a suitably low MgO content for subsequent beneficiation using the modified UGS process was investigated, with the aim of producing a marketable titania material. Slag produced in a cold copper crucible had high residual iron, originating from the iron susceptor and incomplete iron reduction of the titanomagnetite. The high iron concentration in the slag caused crystallization of an ulvospinel.

The feasibility of beneficiating this slag using the UGS process was investigated. The optimised UGS product contained 90.5% TiO₂. Although the TiO₂ grade of this product was adequate, the SiO₂, Al₂O₃, CaO, and Cr₂O₃ concentrations were higher and the particle size was finer than the feedstock specification for chloride pigment production. The UGS product mainly comprised rutile, so that was also not suitable for use as feed to the sulfate pigment production process because rutile is sparingly soluble in sulfuric acid.

Acknowledgements

The paper is published with the permission of Mintek. The authors thank Mintek for financial and test equipment support. Appreciation is also extended to the Norwegian University of Science and Technology (NTNU) for availing their cold copper crucible induction furnace for completion of some of the experiments under the INTPART metal production project. English editing of this manuscript was carried out by Prof. K. C. Sole.

Funding

This work was supported by Mintek: [grant number: TM01].

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