Upgrading of titania slag: a mineralogical perspective

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(1985-2007)
The TiO2 feedstock balance

- Rock Ilmenite
  - 1200 t

- Beach Sand Ilmenite
  - 2910 t

- Rutile + Leucoxene
  - 390 t

- Sulphate Slag
  - 250
  - 640

- Chloride Slag
  - 130
  - 860

- Synthetic Rutile
  - 470

- UGS
  - 170

- SULPHATE PIGMENT
  - 1800 x 0.88* = 1585

- CHLORIDE PIGMENT
  - Ti METAL
  - 2700 x 0.95* = 2565

- 000 t contained TiO2
Forecast demand for all feedstock

000 TiO₂ Units


Ref: 960
The case for upgrading sulphate slag to chloride slag: forecast slag demand

![Graph showing forecast slag demand from 2000 to 2016. The x-axis represents years from 2000 to 2016, and the y-axis represents '000 TiO₂ units. The graph compares sulfate slag and chloride slag demand. Sulfate slag demand remains relatively constant, while chloride slag demand shows a significant increase over the years.]
Typical feedstock compositions

<table>
<thead>
<tr>
<th>Element</th>
<th>RIT slag</th>
<th>Tinfos slag</th>
<th>RBM slag</th>
<th>Namakwa slag</th>
<th>Iluka SR</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂</td>
<td>79.0</td>
<td>77.0</td>
<td>85.5</td>
<td>86.0</td>
<td>92.5</td>
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<tr>
<td>FeO</td>
<td>9.0</td>
<td>10.0</td>
<td>10.5</td>
<td>10.0</td>
<td>2.7*</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>0.18</td>
<td>0.09</td>
<td>0.17</td>
<td>0.08</td>
<td>0.15</td>
</tr>
<tr>
<td>V₂O₅</td>
<td>0.57</td>
<td>0.4</td>
<td>0.45</td>
<td>0.42</td>
<td>0.30</td>
</tr>
<tr>
<td>MgO</td>
<td>5.1</td>
<td>5.0</td>
<td>1.05</td>
<td>0.8</td>
<td>0.30</td>
</tr>
<tr>
<td>CaO</td>
<td>0.6</td>
<td>0.5</td>
<td>0.17</td>
<td>0.16</td>
<td>0.03</td>
</tr>
<tr>
<td>MnO</td>
<td>0.24</td>
<td>0.7</td>
<td>1.6</td>
<td>1.6</td>
<td>0.8</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>Tr.</td>
<td>Tr</td>
<td>0.25</td>
<td>0.25</td>
<td>0.1</td>
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<tr>
<td>SiO₂</td>
<td>2.5</td>
<td>5.3</td>
<td>2.1</td>
<td>1.8</td>
<td>1.0</td>
</tr>
<tr>
<td>Nb₂O₅</td>
<td>0.03</td>
<td>0.09</td>
<td>0.15</td>
<td>0.12</td>
<td>0.20</td>
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<tr>
<td>Al₂O₃</td>
<td>3.1</td>
<td>1.2</td>
<td>1.6</td>
<td>1.5</td>
<td>1.1</td>
</tr>
<tr>
<td>U + Th ppm</td>
<td>&lt;2</td>
<td>&lt;2</td>
<td>25</td>
<td>20</td>
<td>80</td>
</tr>
</tbody>
</table>
Upgrading options

• Roast-leach
  – Sulphate- to chloride-grade slag
  – commercial: UGS

• Conditioning during smelting then leach
  – Removal of U and Th
  – Pilot testing

• Slag ‘stripping’
  – Sulphate- to chloride-grade slag
  – Waste slag to chloride-grade slag
  – Conceptual: Inferred smelting conditions from atypical plant samples
    (selective chlorination)
    (sulphidation)
Roast-leach (UGS)

Key success factor: Manipulation of the oxidation states of iron and titanium

After roasting: Rutile & ilmenite

Slag as tapped
Initial oxidizing roast

- Convert Ti$^{3+}$ to Ti$^{4+}$ (rutile, anatase)
- Inevitably, Fe$^{2+}$ oxidizes to Fe$^{3+}$ (hematite)
- Select roasting conditions to induce migration of iron to grain boundaries
Reductive roast

• Convert Fe$^{3+}$ to Fe$^{2+}$ (FeTiO$_3$)
• Limited formation of Fe$^0$

Ilmenite (FeTiO$_3$)

Fe$^0$ in iron-depleted zones
Leaching

- Leaching in HCl to dissolve Fe$^{2+}$ (in ilmenite, leaving behind a porous residue of TiO$_2$ (rutile))
Ineffective roasting

- Complete reaction, but:
  - No iron migration
  - Impervious rim of rutile
  - Poor upgrading

Mineralogy guides the selection of roasting conditions

Impervious rutile rim
Slag conditioning: Objective

- Remove Th and U from the slag.
  - Where does the uranium and thorium reside?

<table>
<thead>
<tr>
<th></th>
<th>A1</th>
<th>A6</th>
<th>A12</th>
<th>B4</th>
<th>BB1</th>
<th>BBB1</th>
<th>E2</th>
<th>F3</th>
<th>G3</th>
<th>H4</th>
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</thead>
<tbody>
<tr>
<td>TiO₂</td>
<td>84.6</td>
<td>80.5</td>
<td>76.8</td>
<td>82.9</td>
<td>81.1</td>
<td>80.3</td>
<td>80.0</td>
<td>82.2</td>
<td>82.2</td>
<td>82.15</td>
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<tr>
<td>FeO</td>
<td>7.35</td>
<td>11.9</td>
<td>15.3</td>
<td>9.24</td>
<td>6.79</td>
<td>6.88</td>
<td>11.8</td>
<td>11.2</td>
<td>11.7</td>
<td>10.7</td>
</tr>
<tr>
<td>MgO</td>
<td>1.65</td>
<td>1.33</td>
<td>1.43</td>
<td>1.37</td>
<td>1.90</td>
<td>1.90</td>
<td>1.28</td>
<td>0.77</td>
<td>1.26</td>
<td>1.41</td>
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<tr>
<td>MnO</td>
<td>1.82</td>
<td>1.67</td>
<td>1.65</td>
<td>1.64</td>
<td>1.87</td>
<td>1.86</td>
<td>1.69</td>
<td>1.78</td>
<td>1.70</td>
<td>1.91</td>
</tr>
<tr>
<td>SiO₂</td>
<td>2.12</td>
<td>1.76</td>
<td>1.82</td>
<td>2.19</td>
<td>3.30</td>
<td>3.30</td>
<td>1.86</td>
<td>1.75</td>
<td>1.37</td>
<td>1.81</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>2.59</td>
<td>2.09</td>
<td>2.31</td>
<td>2.03</td>
<td>3.88</td>
<td>3.83</td>
<td>2.09</td>
<td>1.86</td>
<td>1.45</td>
<td>1.89</td>
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<tr>
<td>Th</td>
<td>139</td>
<td>182</td>
<td>161</td>
<td>177</td>
<td>203</td>
<td>173</td>
<td>336</td>
<td>220</td>
<td>177</td>
<td>50</td>
</tr>
<tr>
<td>U</td>
<td>11</td>
<td>20</td>
<td>12</td>
<td>19</td>
<td>17</td>
<td>16</td>
<td>14</td>
<td>0</td>
<td>20</td>
<td>8</td>
</tr>
</tbody>
</table>
PIXE element maps: Ti, Mn, Fe

$M_3O_5$ (M = Fe, Ti, Mg, Al)

Silicate
PIXE element maps: Th, U
PIXE element maps: La, Ce, Y
Slag conditioning: strategies

Strategies to remove silicates:

- Flux roast (B-bearing flux) / HCl leach
  - SREP concept: form acid-soluble boro-silicates
- ‘Condition slag’ before solidification
  - Boric acid addition; acid leach
  - Novel concept, potential advantages
The case for slag conditioning

- Do not create fines (roast / leach ↓)
- Retain ratio of Ti$^{3+}$/Ti$^{4+}$ (roast / leach ↓)
- Minimize ‘locked’ silicates (slag conditioning ↑)
- Do not contaminate (slag conditioning ↓)
Slag conditioning – the outcome

- Boron additions decrease liquidus temperature of the slag and facilitates the collection of low-melting silicates in the core of the button

Silicates be mostly found here
Slag stripping

2-stage smelting process

- 1\textsuperscript{st} stage: high-purity pig iron and 86\% TiO\textsubscript{2} slag (when applied to ilmenite smelting)
- Hot slag transfer to stripping furnace
- 2\textsuperscript{nd} stage: high-grade slag (>90\% TiO\textsubscript{2}) and impure metal
TiO$_2$-Fe$_2$O$_3$-FeO phase diagram

Increase in liquidus temperature
Lessons from samples representing very reduced furnace conditions

26 - $\text{Ti}_2\text{O}_3$

25 - alloy phase containing about 3 wt% C,

27 and 28 - $(\text{Ti}, \text{Nb})(\text{O},\text{C})$

$\text{Ti}_2\text{O}_3$: 1.1% Mg, 1.8% Mn, 63% Ti
Phases in over-reduced slag

1 and 2 - Ti$_3$O$_5$,
3 and 4 - Ti$_2$O$_3$,
5 and 6 - Ti(O,C)
7 - silicate phase.

Ti(O,C) appears to be the primary liquidus phase of the slag.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Fe</th>
<th>Mg</th>
<th>Mn</th>
<th>Ti</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti$_3$O$_5$</td>
<td>0.1%</td>
<td>0.7%</td>
<td>0.2%</td>
<td>63%</td>
</tr>
<tr>
<td>Ti$_2$O$_3$</td>
<td>0.1%</td>
<td>1.2%</td>
<td>1.7%</td>
<td>66%</td>
</tr>
</tbody>
</table>
Phases in over-reduced slag

35 and 39 - alloy contain about 3 wt% Si,

36 and 37 - alloy with high carbon (4 – 7 wt%) and high Si (about 3 wt%),

40 - MnS,

41 - Ti$_3$O$_5$

42 and 43 – Nb-Ti-V carbides

Ti$_3$O$_5$: 0.8% Fe, 0.9% Mg, 1.2% Mn, 62.5% Ti
The Ti-O phase diagram
Slag stripping conditions

An indication of expected furnace conditions based on the phases that were observed

\[
\frac{4}{5} \text{Nb} + \text{O}_2 = \frac{2}{5} \text{Nb}_2\text{O}_5
\]

\[
\frac{4}{3} \text{V} + \text{O}_2 = \frac{2}{3} \text{V}_2\text{O}_3
\]

\[
2\text{Fe} + \text{O}_2 = 2\text{FeO}
\]

\[
2\text{Ti}_2\text{O}_3 + \text{O}_2 = 4\text{TiO}_2
\]

\[
2\text{Ti} + \text{O}_2 = 2\text{TiO}
\]
Slag from titaniferous magnetite

- Typical composition of Main Magnetite Layer:
  \[17\% \text{FeO}, 60\% \text{Fe}_2\text{O}_3, 12.5\% \text{TiO}_2, 1.5\% \text{SiO}_2, 4\% \text{Al}_2\text{O}_3, 1.5\% \text{MgO}, 1.7\% \text{V}_2\text{O}_5\]

- Calculate (FACTSage):
  - slag composition
  - slag / metal ratio
  - liquidus temperature
  - vanadium recovery
Expected slag composition

![Graph showing the expected slag composition with concentrations of FeO, Al₂O₃, MgO, and TiO₂ as a function of FeO in slag.](image-url)
Slag mineralogy

\[ \text{M}_3\text{O}_5: 6.6\% \text{ MgO}, 5.4\% \text{ Al}_2\text{O}_3, 75.8\% \text{ TiO}_2, 1\% \text{ V}_2\text{O}_5, 14.2\% \text{ FeO} \]

Spinel: 6.4\% \text{ MgO}, 10\% \text{ Al}_2\text{O}_3, 34.3\% \text{ TiO}_2, 1.7\% \text{ MnO}, 47\% \text{ FeO}
After further reduction..

M₃O₅: 11% MgO, 4% Al₂O₃, 80% TiO₂, 7% FeO

Alloy with 4% Ti
In summary

Metallurgy is guided by mineralogy: learn from the mineralogy and use the observations to optimise the metallurgy