Mineral to Metal: Processing of Titaniferous Ore to Synthetic Rutile (TiO₂) and Ti metal
Objective

To produce ultra pure high grade synthetic rutile (TiO$_2$) from ilmenite ore and Ti metal from anatase or rutile
Outline

1. Introduction
2. Why titaniferous minerals?
3. Processing Methods for synthetic rutile (TiO$_2$)
   (i) Alkali Roasting
   (ii) Reduction followed by leaching
5. Results and discussion
6. Commercialisation
7. Conclusion
8. Bradford Metallurgy on Ti metal powder production
9. Future Plans
Introduction

• Titanium always exist as bonded to other elements in nature.
• It is the ninth-most abundant element in the Earth.
• It is widely distributed and occurs primarily in the minerals such as anatase, brookite, ilmenite, perovskite, rutile and titanite (sphene).
• Among these minerals, only rutile and ilmenite have economic importance
Ilmenite deposit in Chavara, Kerala, India
Applications of TiO₂

- White powder pigment - brightness and very high refractive index - Sunscreens use TiO₂ - high refractive index - protect the skin from UV light.
- TiO₂ – photocatalysts - electrolytic splitting of water into hydrogen and oxygen, - produce electricity in nanoparticle form - light-emitting diodes, etc.
- Paints- paper – catalysts, etc.
Dr Jeya Ephraim, Mineral to Metal

May 11 – 13, 2015  •  Hilton Birmingham Metropole Hotel  •  Birmingham, United Kingdom
Why Titanium Metal

• Titanium is corrosion resistant, very strong and has a high melting point. It has a relatively low density (about 60% that of iron).

• Titanium is used, for example: in the aerospace industry - for in aircraft engines and air frames;

• Implants - replacement hip joints, for pipes, etc, in the nuclear, oil and chemical industries where corrosion is likely to occur.
**Aerospace Applications:** high-temperature performance, creep resistance, strength, and metallurgical structure.

**Jet Engines:** wide chord titanium fan blades increase efficiency while reducing noise.

**Airframes:** innovative alloys replace steel and nickel alloys in landing gear.

**Industrial Applications:** Titanium forms a surface oxide layer, which is an outstanding corrosion inhibitor.

**Human Implants:** Titanium is completely inert to human body fluids, making it ideal for medical replacement structures such as hip and knee implants.
Extraction Methods
CONVENTIONAL ROUTES

ORES: ilmenite, Rutile, Anatase, and Perovskites

Pyrometallurgical Benefication: reduction of iron oxides:
$\text{Fe}_x\text{O}_y + y\text{C} \rightarrow x\text{Fe} + y\text{CO}$

ACID-LEACHING

Chloride Process

Sulphate process

$\text{TiO}_2$ pigment grade
Alkali Roasting

Principle: Ilmenite when roasted with soda ash at high temperature, the iron values in the ore will form sodium ferrite which is soluble in water and the titanium values will form sodium titanate which is insoluble. Therefore preferential separation is possible.
Alkali roasting of ilmenite and anatase ores (Bomar ilmenite)
Temperature - 1073 – 1273 K
Time - 120 min.
Na$_2$CO$_3$ or NaHCO$_3$ in the charge was varied
(Stoichiometric amount required for TiO$_2$, Fe$_2$O$_3$, Al$_2$O$_3$
and SiO$_2$ in the ore)
Alumina
Leaching
Hot water leaching
Acid leaching
5% HCl solution
343 – 353 K temperature
## Analysis of Ilmenite and Anatase

<table>
<thead>
<tr>
<th>Sample</th>
<th>TiO₂</th>
<th>Fe₂O₃</th>
<th>Al₂O₃</th>
<th>SiO₂</th>
<th>P₂O₅</th>
<th>Mn₃O₄</th>
<th>MgO</th>
<th>CaO</th>
<th>Cr₂O₃</th>
<th>LOI *</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anatase</td>
<td>57.8</td>
<td>14.61</td>
<td>7.64</td>
<td>1.65</td>
<td>7.65</td>
<td>0.71</td>
<td>0.36</td>
<td>2.13</td>
<td>0.01</td>
<td>6.19</td>
</tr>
<tr>
<td>Ilmenite</td>
<td>70.65</td>
<td>21.69</td>
<td>2.51</td>
<td>2.13</td>
<td>0.42</td>
<td>0.72</td>
<td>0.37</td>
<td>&lt;0.10</td>
<td>&lt;0.01</td>
<td>2.01</td>
</tr>
</tbody>
</table>
Charaterisation - XRD
The anatase grains (grey colour) are highly porous due to weathering and have light grey colour Fe-rich exsolved phases.

The dark grey colour phase is rutile, the light grey colour phases are pseudorutile/brookite (Ti-Fe-O) phases and bright colour grain is zircon mineral.


Chemical reactions during Alkali Roasting

\[ \text{Na}_2\text{CO}_3 \ (s) \rightarrow \text{Na}_2\text{O} \ (s) \ + \ \text{CO}_2 \ (g) \]

\[ \text{TiO}_2 \ (s) \ + \ 2 \text{Na}_2\text{CO}_3 \ (s) \rightarrow \text{Na}_4\text{TiO}_4 \ (s) \ + \ 2 \text{CO}_2 \ (g) \]

\[ \text{TiO}_2 \ (s) \ + \ \text{Na}_2\text{CO}_3 \ (s) \rightarrow \text{Na}_2\text{TiO}_3 \ (s) \ + \ \text{CO}_2 \ (g) \]

\[ 5 \text{TiO}_2 \ (s) \ + \ 4 \text{Na}_2\text{CO}_3 \ (s) \rightarrow \text{Na}_8\text{Ti}_5\text{O}_{14} \ (s) \ + \ 4 \text{CO}_2 \ (g) \]

\[ 3 \text{TiO}_2 \ (s) \ + \ \text{Na}_2\text{CO}_3 \ (s) \rightarrow \text{Na}_2\text{Ti}_3\text{O}_7 \ (s) \ + \ \text{CO}_2 \ (g) \]

\[ 6 \text{TiO}_2 \ (s) \ + \ \text{Na}_2\text{CO}_3 \ (s) \rightarrow \text{Na}_2\text{Ti}_6\text{O}_{13} \ (s) \ + \ \text{CO}_2 \ (g) \]

\[ \text{Fe}_2\text{O}_3 \ (s) \ + \ \text{Na}_2\text{CO}_3 \ (s) \rightarrow \text{Na}_2\text{Fe}_2\text{O}_4 \ (s) \ + \ \text{CO}_2 \ (g) \]

\[ \text{SiO}_2 \ (s) \ + \ \text{Na}_2\text{CO}_3 \ (s) \rightarrow \text{Na}_2\text{SiO}_3 \ (s) \ + \ \text{CO}_2 \ (g) \]

\[ \text{Al}_2\text{O}_3 \ (s) \ + \ \text{Na}_2\text{CO}_3 \ (s) \rightarrow \text{Na}_2\text{Al}_2\text{O}_4 \ (s) \ + \ \text{CO}_2 \ (g) \]

\[ \text{Fe}_2\text{TiO}_5 \ (s) \rightarrow \text{TiO}_2 \ (s) \ + \ \text{Fe}_2\text{O}_3 \ (s) \]
Alkali Roasting: The plot of Gibbs free energy change verses temperature for the reactions of various oxide constituents in TiO$_2$ ores.
Microstructure of ilmenite ore after alkali roasting

The micrograph of anatase ore after alkali roasting at 850°C for 4 hours. The X-ray elemental map of grain A shows the formation of Na-Al-Fe-Si-O complex phase.
The Eh-pH diagram of Na – Ti – Fe – O system calculated by using FACT-Sage programme. The hatched areas show the water and acid leaching conditions.
**Water leaching:**

\[3\text{Na}_2\text{TiO}_3 + 2\text{H}_2\text{O} \rightarrow \text{Na}_2\text{Ti}_3\text{O}_7 + 4[\text{Na}^+] + 4[\text{OH}^-]\]

\[2\text{Na}_2\text{Ti}_3\text{O}_7 + \text{H}_2\text{O} \rightarrow \text{Na}_2\text{Ti}_6\text{O}_{13} + 2[\text{Na}^+] + 2[\text{OH}^-]\]

**Acid leaching:**

\[\text{Na}_2\text{Ti}_6\text{O}_{13} + 2\text{HCl} \rightarrow \text{TiO}_2 + 2\text{NaCl} + \text{H}_2\text{O}\]
XRD of ilmenite and anatase roasted with soda-ash + alumina at 900°C for 4 hrs

ST – sodium titanate, SAF – Sodium aluminium ferrite
A XRD of processed ilmenite after aeration leaching. B XRD of synthetic rutile after acid wash. Phases such as anatase, pseudobrookite and rutile are present after acid wash.
Water and Acid leaching

(a) After water leaching

(b) After acid leaching

The microstructure of ilmenite ore after alkali roasting at 950°C for 4 hours followed by water and acid leaching. Dark grey phase on the surface of the grey colour sodium titanate grain in (a) is complex Na-Fe-Si-O salt phase which is not dissolved in the aqueous medium, whereas the bright phase in the core is unreacted pseudorutile phase. The grey colour grains in (b) are of rutile with small bright colour particles of unreacted ore particles.
Rare earth particle separated un-attacked by the chemical processing steps
## Processing of Kerala Ilmenite (CSIR-NIIST, Trivandrum, Kerala, India) PhD work

### Analysis of Kerala ilmenite

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂</td>
<td>60.60</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>26.10</td>
</tr>
<tr>
<td>FeO</td>
<td>9.60</td>
</tr>
<tr>
<td>MnO</td>
<td>0.50</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>0.40</td>
</tr>
<tr>
<td>V₂O₅</td>
<td>0.12</td>
</tr>
<tr>
<td>MgO</td>
<td>0.15</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.50</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>0.15</td>
</tr>
<tr>
<td>SiO₂</td>
<td>0.40</td>
</tr>
<tr>
<td>Rare Earths</td>
<td>0.80</td>
</tr>
</tbody>
</table>
**Principle**

Ilmenite – carbothermic reduction – metallic iron formed – rusted in the presence of NH₄Cl – iron hydroxide formed – iron hydroxide slurry is separated from TiO₂ by repeated washing. Analyse the samples for TiO₂ and total iron.

- Reduction at high temperature
- Rusting
- Rutilation
- Acid wash

Problem: Rusting step takes about 16 – 20 hrs for completion making the process uneconomical for the industries
Composition of a reduced ilmenite

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂</td>
<td>62.64</td>
</tr>
<tr>
<td>Total Iron</td>
<td>28.32</td>
</tr>
<tr>
<td>Metallic Iron</td>
<td>24.03</td>
</tr>
<tr>
<td>P</td>
<td>0.12</td>
</tr>
<tr>
<td>C</td>
<td>1.00</td>
</tr>
<tr>
<td>S</td>
<td>0.15</td>
</tr>
<tr>
<td>MgO</td>
<td>2.80</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>0.80</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>1.50</td>
</tr>
<tr>
<td>MnO</td>
<td>0.45</td>
</tr>
<tr>
<td>SiO₂</td>
<td>1.00</td>
</tr>
<tr>
<td>Others</td>
<td>0.26</td>
</tr>
<tr>
<td>(V, Zr, etc.)</td>
<td></td>
</tr>
</tbody>
</table>
Experimental set up used for Rusting

Solid – liquid ratio 1:4
RPM – 800 per minute
Air: 4 – 5 lit/min
<table>
<thead>
<tr>
<th>Time (hr)</th>
<th>NH₄Cl</th>
<th>NH₄Cl + fructose</th>
<th>NH₄Cl + glucose</th>
<th>NH₄Cl + glyoxal</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>12.2</td>
<td>38.3</td>
<td>39.2</td>
<td>40.01</td>
</tr>
<tr>
<td>2</td>
<td>23</td>
<td>64.2</td>
<td>65.3</td>
<td>66.5</td>
</tr>
<tr>
<td>3</td>
<td>33</td>
<td>82.3</td>
<td>83.2</td>
<td>84.3</td>
</tr>
<tr>
<td>4</td>
<td>44.3</td>
<td>91.3</td>
<td>92.4</td>
<td>93.2</td>
</tr>
<tr>
<td>5</td>
<td>45.2</td>
<td>92.5</td>
<td>93.8</td>
<td>94.5</td>
</tr>
</tbody>
</table>
Percentage Iron Removal

- NH4Cl
- NH4Cl+Fructose
- NH4Cl+glucose
- NH4Cl+glyoxal

Iron Removal vs. Time (hr)

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SEM of a Reduced ilmenite
High grade synthetic rutile (TiO₂) having >97.5%
### Surface area analysis of reduced ilmenite and synthetic rutile

<table>
<thead>
<tr>
<th>Name of the sample</th>
<th>Surface area (sq.m/g) using 75% metallisation</th>
<th>Surface area (sq.m/g) using 85% metallisation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reduced ilmenite (RI)</td>
<td>2.3597</td>
<td>2.8757</td>
</tr>
<tr>
<td>Synthetic rutile (NH₄Cl + glucose)</td>
<td>2.4742</td>
<td>3.2462</td>
</tr>
<tr>
<td>Synthetic rutile (NH₄Cl + Fructose)</td>
<td>3.1433</td>
<td>3.157</td>
</tr>
<tr>
<td>Synthetic rutile (NH₄Cl + glyoxal)</td>
<td>2.4824</td>
<td>3.2622</td>
</tr>
</tbody>
</table>
Conclusion

• The oxidative alkali roasting process can be used for the production of synthetic rutile from different types of TiO₂ ores.

• The formation of complex alkali salt phase during roasting process helps to separate the Fe₂O₃ and other impurities oxides from the ores, which are removed subsequently in the water and acid leaching processes.

• The increasing the roasting temperature up to 1223 K improved the separation of the impurities. However above 1223 K, the roasted mass fused with the crucible due to the formation of large volumes of liquid phase.
• The excess addition of alkali in the roasting reaction improved the purity of synthetic rutile to around 92%. But the particle size of the synthetic rutile reduced significantly (< 100μm).

• The impurities such as Cr₂O₃, Al₂O₃, CaO, and V₂O₅, which are undesirable for pigment manufacturing process, were also successfully removed by the oxidative alkali roasting techniques.
Carbothermic reduction followed by rusting helps the removal of iron in an accommodative method.

High grade synthetic rutile (TiO$_2$) of $>97.5\%$ is obtained.

The surface area or the particle size is retained so that the SR can be used for chlorination in FBCR.
Commercialisation

Highlights:

• NH$_4$Cl was replaced by another inorganic catalyst
• Set of additional catalysts developed
• Iron oxide obtained during rusting was reduced to sponge iron and sold thus making totally a green process

The technology developed by the CSIR-NIIST, Trivandrum, has been commercialised to the Cochin Minerals & Rutile Ltd. (http://www.cmrlindia.com/) after two pilot plant level studies.
Present and Future work

Following the success of isolation of high pure titanium metal powder from titanium dioxide, we are in the process of optimising the conditions to isolate titanium metal powder from Rutile.

\[
\text{TiO}_2 + 2\text{Ca} \rightarrow 2\text{CaO} + \text{Ti}
\]

Bradford Metallurgy Plc: We are in the process of setting up of a pilot plant to reduce (1 – 5 kg) of titanium dioxide powder.
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Ti – 98.46% Ca – 1.54%
Dr Jeya Ephraim, Mineral to Metal

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- I thank EPSRC & IMR, University of Leeds for providing funding and facilities
- I thank CSIR for providing Senior Research Fellowship and NIIST for providing facilities
- We thank RKTS, University of Bradford for providing funding for the production of titanium metal powder from titanium dioxide
Team Members of Titanium Metallurgy Group

Dr Raj Patel
Dr Russel Hodgetts
Mr Matthew Palmer
Mr Andrew Birch
Mr Stuart Fox
Thank You & Any Questions???