The Polar™ Titanium process is based on reduction of TiO$_2$ to Ti using molten salt electrochemistry

Cathodic reactions
\[ \text{CaO}_{\text{(in salt)}} + 2e^- = \text{Ca}_{\text{Met (in salt)}} + \text{O}^2- \]
\[ \text{TiO}_2 + 2\text{Ca}_{\text{(in salt)}} = \text{Ti} + 2\text{CaO}_{\text{(in salt)}} \]

Anodic reactions
\[ \text{O}^2- + \text{C}_{\text{(anode)}} = \text{CO}_{\text{(gas)}} + 2e^- \]
\[ 2\text{O}^2- + \text{C}_{\text{(anode)}} = \text{CO}_2_{\text{(gas)}} + 4e^- \]
\[ \text{TiO}_2 + \text{C} = \text{Ti} + \{\text{CO}_{\text{(gas)}} + \text{CO}_2_{\text{(gas)}}\}^* \]

Kinetics of the reaction are important – key parameters for investigation include:
- Reactor temperature,
- Applied voltage,
- Electrolyte composition
- Feed properties

* Stoichiometry not shown, CO/CO$_2$ ratio varies with process conditions
Polar™ Titanium - Project history

Fundamental program

• Elucidated the key reaction mechanisms and provided an IP portfolio base.
• Provided key understanding of reduction kinetics as a function of electrode design, current densities, process voltage, temperature, salt composition, feed morphology & properties.
Attributes of the experimental facilities – main reactor

**REACTORS**

- Containment of up to 1 t of molten salt (CaCl₂).
- CaCl₂ preheating and melting plant for reactor startup (patented).
- Molten CaCl₂ salt temperature up to 150°C of salt superheat (i.e. to 930°C in-salt temperature).
- Variable reduction power to 4800 A, or to a potential of 16 V.
- Off gas handling facilities and reactor shrouding to 28 m³ min⁻¹ (1000 cfm). Off gas scrubbing facilities for HCl, Cl₂, and CaCl₂ fume.
- Inert gas (Ar) shielding for mitigation of metal re-oxidation.

**PROCESS CONTROL & MONITORING**

- Cascaded, multi-zone, flux-limited control for near isothermal furnace heating.
- Individual current and voltage monitoring for every electrode.
- Real-time product gas analysis (CO, CO₂, and O₂).
Titanium produced in recent reactor trials for a range of feed types
Oxygen content in reduced titanium during experimental program
Carbon content in reduced titanium during experimental program
A range of TiO$_2$ feed morphologies have been tested.

Micrographs show fracture surfaces of TiO$_2$ feed forms.

- Increasing sintering temperature
- Increasing BET surface area (m$^2$/g)
- Increasing reactivity
- Increasing physical integrity
The morphology of the final titanium develops to the final form as the oxygen content is progressively reduced.
Typical product chemistry

**Product analysis comments**

- As reduction reactions proceed, the feed form progressively attains final product specifications, moving through a series of transitions to produce Ti:
  \[ \text{TiO}_2 \rightarrow \text{Ti}_4\text{O}_7 \rightarrow \text{Ti}_3\text{O}_5 \rightarrow \text{Ti}_2\text{O}_3 \rightarrow \text{Ca}_x\text{Ti}_y\text{O}_z \rightarrow \text{TiO} \rightarrow \text{Ti metal} \ (0 \text{ to } 15\% \text{ O}) \]

- Potential for a range of products: ingot, sheet, or powder.
- Product quality from the reactor can be varied to suit market requirements.
- Quality achieved to date
  - Oxygen < 0.05%;
  - Carbon < 0.02%;
  - Nitrogen < 0.009%
  - Hydrogen < 0.01%
Titanium metal produced in the Polar™ reactor has been amenable to milling to powder.

- Milling of Ti product accomplished using standard hammer and disc mill equipment with inert gas shroud.
- Milled shape is encouraging for all size distributions.
- Pre-milling morphology of uniformly-distributed microscale pores is preserved within individual particles.
Process and commercial development

- BHP Billiton have committed significant resources to the experimental program for Polar™ Titanium development.

- There has been promising experimental process development, from gram to kilogram scale at BHP Billiton’s Newcastle Technology Centre.

- A program of product characterisation work is underway for all product forms.

- Operation at 10kg/day scale is planned by end of calendar year 2005, with a 0.25 t/day scale demonstration plant under design, dependent upon success of the 10kg/day pilot.

- BHP Billiton interest is ultimately aimed at commodity level production of titanium, and work is continuing to prove the commercial viability of the process.

- A collaboration strategy is being considered, but will be based on all collaborating parties adding value to the business.
If the reduction process takes place via calcium, only negligible rates of reduction will be observed under voltages below ~1.2V.

\[
\text{TiO}_x + xC = \text{Ti} + x\text{CO} \quad \text{(gas)}
\]

\[
\text{CaO} + C = \text{Ca} + \text{CO}
\]

Ca = 0.01 wt.%; CaO = 0.2 wt.%

Ca = 0.00001 wt.%

Ca = 0.0001 wt.%

\(0.001 \quad 0.01 \quad 0.1 \quad 1 \quad 10 \quad 100\)

Oxygen, wt %

\[-2 \quad -1.5 \quad -1 \quad -0.5 \quad 0 \quad 0.5\]

Decomposition potential, V