Synthetic Rutile – not just Fe Reduction

Nick Bernard
Technical Development Manager
1-2 February 2016

Synthetic Rutile

- What is it?
- What is it for?
- Process outline
- Pigment industry
- Sulphate process
- TiO_2 solubility
- Reaction pathways
- M_3O_5 Crystal Form

What is SR and what is it used for?

- SR = high grade TiO_2 made from ilmenite ($FeO.TiO_2$)
  - Fe extraction from Ilmenite
  - Becher Process
    - exclusively in Western Australia.
    - 5 plants
    - ~14Mt of SR

- Hardware based on DRI technology
  - higher temperature - 1100-1140°C

What is the process?

- Fe metallisation of ilmenite + hydrometallurgical extraction of the Fe(m)
  - ➢ Results in a porous TiO_2 grain:

Ilmenite $FeO.TiO_2 + (1+x)CO(g) \rightarrow Fe(m) + TiO_{2-x} + (1+x)CO_2(g)$

Ilmenite – solid solution series of ferrotitanates e.g.

Pseudorutile $Fe_2O_3.3TiO_2 + CO(g) \rightarrow 2FeO.TiO_2 + TiO_2 + CO_2(g)$

- Pseudorutile preferred:
  - – more porous and thus more amenable to the Fe extraction process (the hydrometallurgy stage).
- Minerals are never pure!
  - – Mixture of ilmenite and altered ilmenites
  - – other elements – Mn, Mg, Al, Cr, V

Mineralogy

The reduction process is not clear cut

- TiO_2 is partly reduced
  - TiO_2 to Ti_3O_5 (anosovite) and Ti_2O_3.
- Trace elements present
  - M_3O_5 and M_2O_3 forms.
- Chloride pigment process
  - chlorination at 1000°C to form metal chlorides
  - mineralogy of the TiO_2 mineral irrelevant
- M_3O_5 (Pseudobrookite) avoided
  - trace elements are locked in it

    = lower TiO_2 grade in SR.
- HTPS 2015 Dr Ian Grey CSIRO Key Note presentation
  - high levels of MgO in Victorian ilmenite $\neq$ SR production
  - H_2 based process to overcome this

Pigment Industry

- Two pigment processes
  - Chloride process

    $TiO_2 + 2Cl_2(g) + C = TiCl_4(g) + CO_2(g)$ 900-1000°C

    $TiCl_4(g) + O_2(g) = TiO_2 + 2Cl_2(g)$

  - Sulphate process

    $FeO.TiO_2 + 2H_2SO_4 = TiOSO_4 + FeSO_4 + 2H_2O$ 190-230°C

    $TiOSO_4 + H_2O = TiO(OH)_2 + H_2SO_4$

    $TiO(OH)_2 = TiO_2 + H_2O\ (g)$ 900-1000°C

- Market Share ~50:50
- SR only addresses half the market

What is the Sulphate Process?

- Digestion of mineral with concentrated sulphuric acid –

  $FeO.TiO_2 + H_2SO_4 \rightarrow TiOSO_4 + FeSO_4 + H_2O$

  - $FeSO_4$ precipitated by chilling
  - TiO_2 precipitate by heating Δ

  $TiOSO_4 + H_2O \rightarrow TiO(OH)_2 + H_2SO_4$
- Issues: waste
  - $FeSO_4.7H_2O$
  - waste H_2SO_4 neutralised to $CaSO_4$
- Two feeds
  - Ilmenite (49-54% TiO_2)
  - Ti slag (76-81% TiO_2)
- Ti Slag - electric smelting,
  - rock ilmenites in Canada and Norway
  - High MgO contents (>3%) - unacceptable for chloride pigment

What makes TiO_2 Slag soluble?

- MgO = solubility
- Slag is predominantly M_3O_5 (pseudobrookite)

  $(Fe, Mn, Mg)O.2TiO_2$

  MgO is particularly effective at stabilising this phase
- Some of the more highly reduced rutiles are also soluble:

Ti_4O_7	$2TiO_2.Ti_2O_3$	
Ti_5O_9	$3TiO_2.Ti_2O_3$	Magnelli phases
Ti_6O_{11}	$4TiO_2.Ti_2O_3$	

Challenge

- Becher SR acid soluble?
- CSIRO and Iluka - since the 1970's
  - behaviour of titanium minerals in reducing environments
    - Ian Grey et al at CSIRO over the last 40 years
- Ferrous pseudobrookite ($FeO.2TiO_2$) – easy to make
  - max achievable grade is 69% TiO_2
  - too much Fe in the mineral.
- Ferrous pseudobrookite further reduced
  - $TiO_2 \rightarrow$ rutile and reduced rutiles = insoluble
- Trace elements (Mg, Mn)
  - stabilises pseudobrookite

Stability Regions

CSIRO O_2 fugacity/T diagram

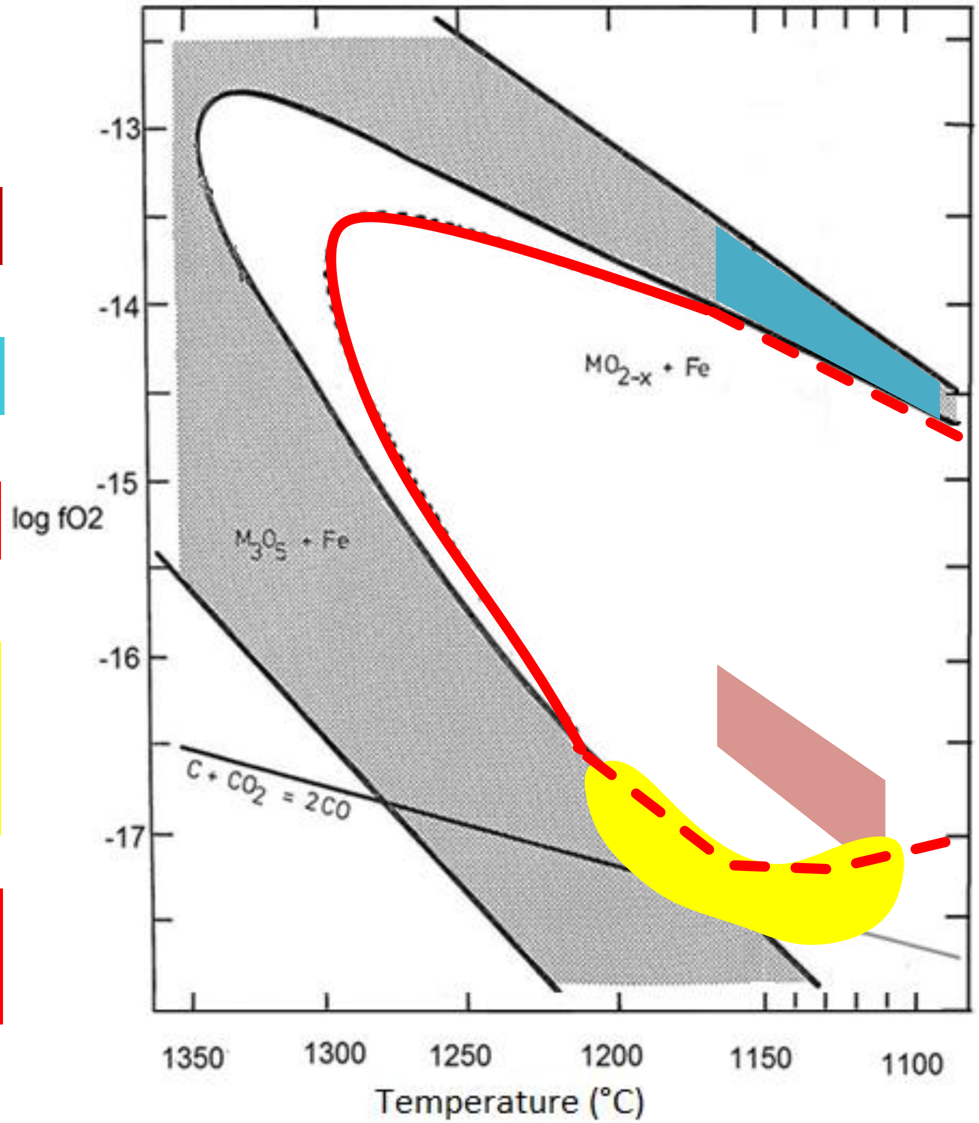
Typical operating region for SR Kiln

Low TiO_2 ferrous pseudobrookite

Impact of trace elements on M_3O_5

Pseudobrookite & reduced rutiles –
high TiO_2 grade in product
>90% solubility in H_2SO_4

Impact of trace elements on M_3O_5
<1200°C postulate from current work



So how?

- Challenge is to operate the kiln in this preferred region

AND

- <1200°C (upper limit for refractory integrity/life)
- 1980's focussed on
  - additives - Mg
  - 1200°C temperatures
- 2010's work
  - lower temperatures and
  - ilmenite with the Mg is already present in the mineral.

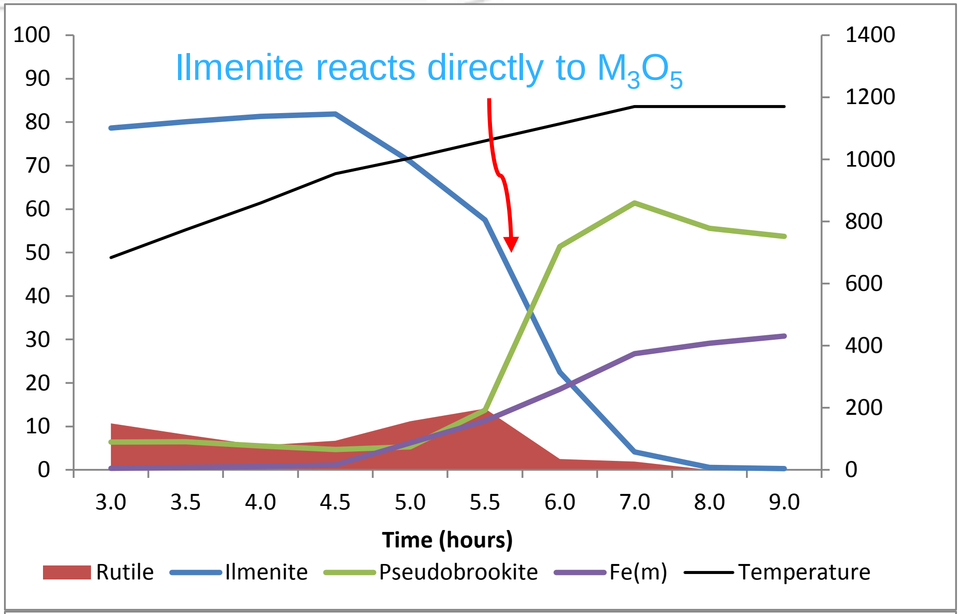
Reaction Pathways

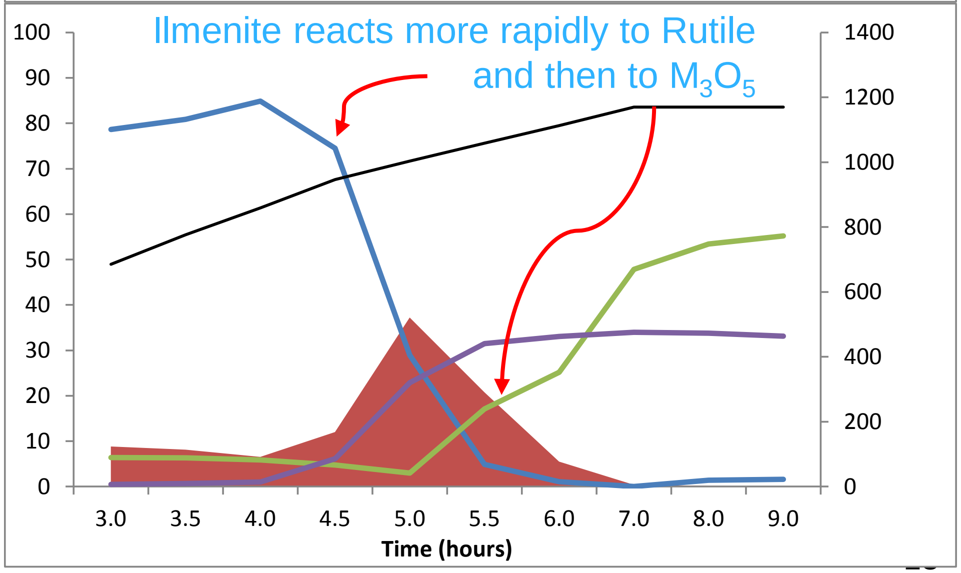
- Match high temperature metallurgy to hydrometallurgical behaviour of the product
- Starting material influences the final outcome e.g.
  - $FeO.TiO_2 \rightarrow FeO.2TiO_2 + Fe(m) \rightarrow 2TiO_2 + Fe(m)$
  - $FeO.TiO_2 \rightarrow TiO_2 + Fe(m) \rightarrow Ti_3O_5 + Fe(m)$
  - $Fe_2O_3.3TiO_2 \rightarrow 2FeO.TiO_2 + TiO_2 \rightarrow 2TiO_2 + 2Fe(m)$
- Same final mineralogy composition exhibit different solubility
  - a consequence of which mineral phases were present part way through the reaction sequence

Reaction pathway - coal

- Coal can impact reaction pathway.
- Normal coal
  - ilmenite directly to Pseudobrookite and Fe(m)
- High reductive coal
  - ilmenite reacts more quickly to rutile and Fe(m)
  - further reduction forms Pseudobrookite

⇒ Increasing reactivity changes the reaction pathway





M_3O_5 Crystal Form

- Monoclinic – Orthorhombic forms of Pseudobrookite
  - differences in solubility
  - feducing ilmenites with low levels of MgO.
  - this has been previously reported by Ian Grey in Al, Fe and Mg systems:
    - $MgTi_2O_5$-Ti_3O_5 – orthorhombic to monoclinic below $Mg_{0.28}Ti_{2.72}O_5$
    - $FeTi_2O_5$-Ti_3O_5 – orthorhombic to monoclinic below $Fe_{0.35}Ti_{2.65}O_5$
    - $Al_2Ti_2O_5$-Ti_3O_5 – orthorhombic to monoclinic below $Al_{0.45}Ti_{2.55}O_5$
    - this may explain differences in solubility but still to be confirmed

State of Development

- Requirements demonstrated in the laboratory
- Demonstrated on pilot kiln + reactive coal
- Trials on 200kt/y commercial kiln planned for end of Q1 2016
- Continued laboratory test work to understand the mechanisms and the impact of the ilmenite mineralogy

Learnings

- Mineralogy is far more complex than is apparent
- Mineralogy of the final product is dependent on
  - starting mineral composition
  - reaction pathway which is itself influenced by the reduction reaction kinetics.
- Expect to be able to achieve the desired mineralogy at temperatures acceptable in the commercial kiln

Thank You & Questions

ILUKA

Iluka Resources Limited

www.iluka.com

For more information, contact:

nick.bernard@iluka.com

+61 (0) 419 918 143