Chemical Phenomena in Titanium Production

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Outline

- Background
- Routes to produce titanium
- Some basic physical properties
- Main process routes and key physical properties
- Conclusions

South African’s Global Ti Position in 2006

	South Africa	World	Approximate Value	
			South Africa	World
Reserves	220 Mt TiO_2	1300 Mt TiO_2		
Mineral Production	1090 kt TiO_2	5200 kt TiO_2	$ 175m p.a.	$ 840 m.p.a.
Slag Production	1090 kt TiO_2		$ 490m p.a.	$ 2500 p.a.
Pigment Production	~20 kt TiO_2	5100 kt TiO_2	$ 37m p.a.	$ 10000 m.p.a.
Sponge Production	Nil	125 kt p.a. Ti		$ 1250 m.p.a.
Ingot Production	Nil	145 kt p.a. Ti		$ 2600 m.p.a.
Mill Products	Nil	~90 kt p.a. Ti		$ 4500 m.p.a.

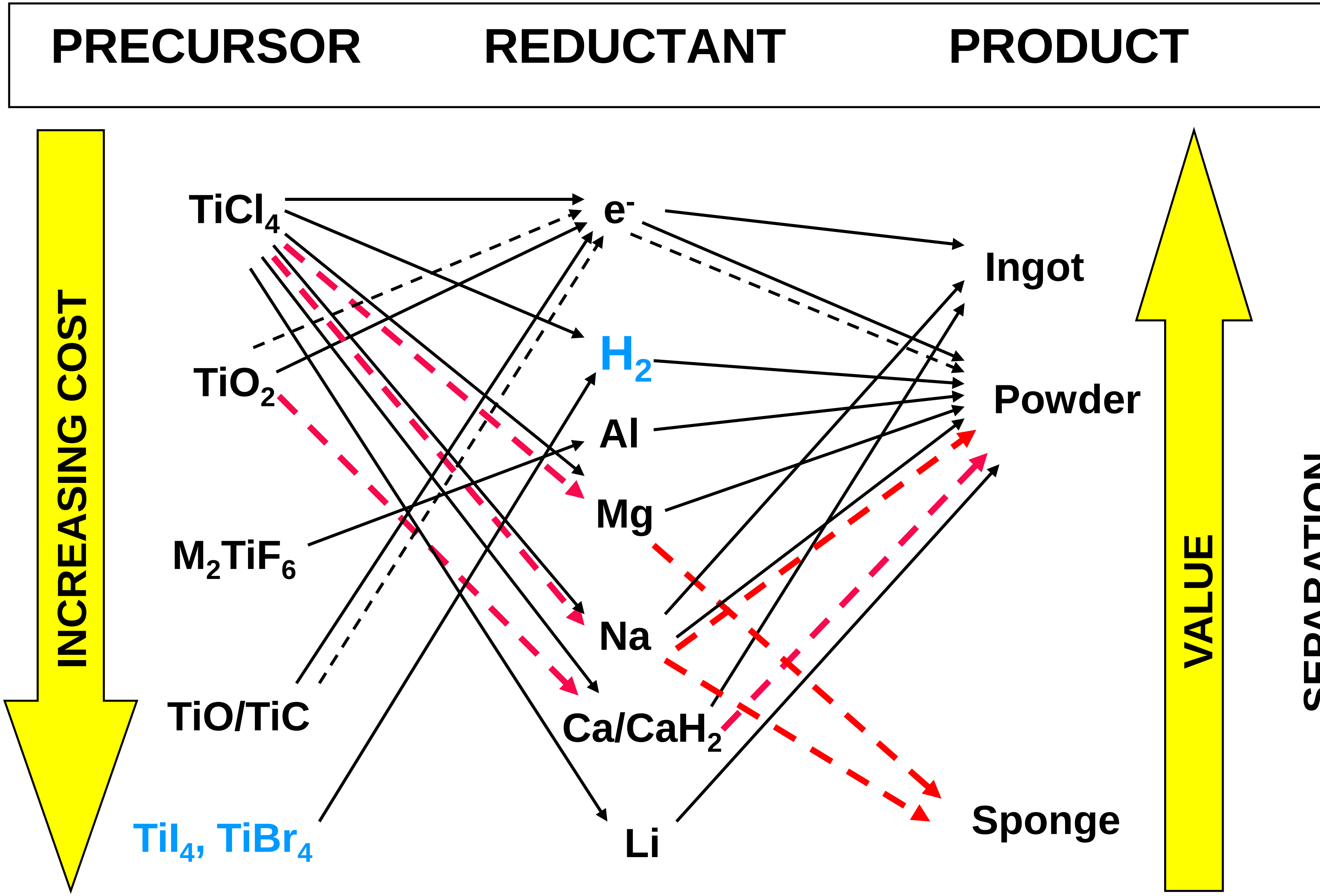
Approximate Physical Properties

	Ti & Alloys	Al & Alloys	Fe & Alloys	Ni & Alloys
Strength (MPa)	1300 max	500 max	1300 max	1400 max
Density (kg/m^3)	4600	2700	7800	8400
Normalized Strength/weight	1	0.85	0.65	0.6
Elasticity (GPa)	115	72	215	200
M.P. (°C)	1668	660	1538	1455
Rel. Corrosion Resistance	Very high	High	Low	Medium
Carbon Compatibility	Resistant	Corrosion		
Bio Compatibility	Excellent			
T Exp. Coeff. (10^{-6}/°C)	±8.5	±20	±12	±11
Conductivity (W/m°C)	7	180	30	40
Color	Aesthetic			

Kyushu National Museum

Photo courtesy of the Kyushu National Museum

http://web-japan.org/nipponia/nipponia38/en/travel/travel03.html



PRECURSOR
REDUCTANT
PRODUCT
INCREASING COST
TiCl4
TiO2
M2TiF6
TiO/TiC
TiI4, TiBr4
e-
H2
Al
Mg
Na
Ca/CaH2
Li
Ingot
Powder
Sponge
VALUE
SEPARATION

The Race

New Primary Metal Technology:

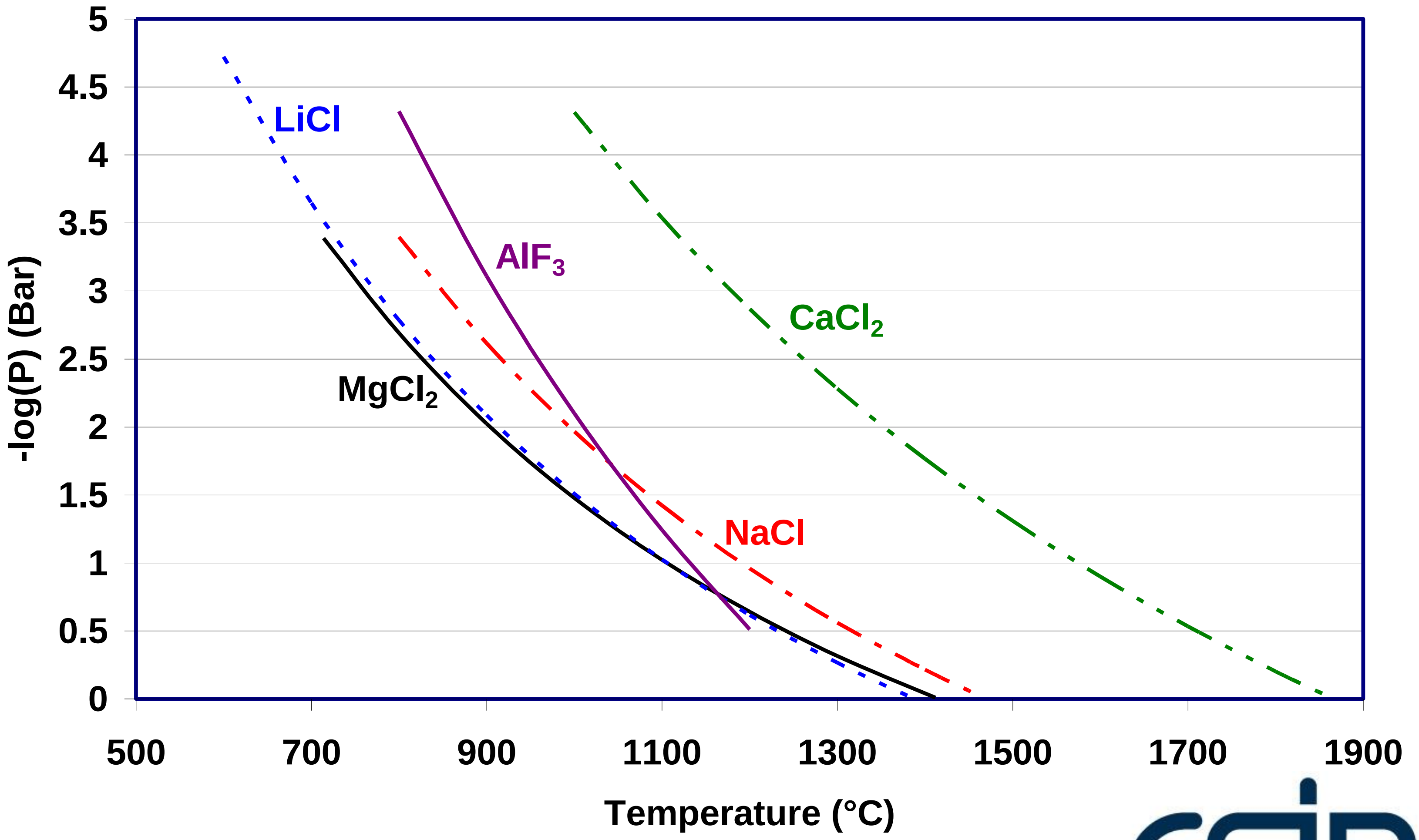
- Europe - Ginatta
- Japan
  - Ono & Suzuki
  - JTS
- USA
  - Armstrong
  - ADMA
- UK – FFC Process
- Australia – TiRO Process
- South Africa
  - Peruke
  - CSIR

CHINA – Rapid expansion using known technology, cheap labor and large domestic market

Melting & boiling points of some metals and salts ($Ti_{M.P.}$= 1668°C)

Element	Metal	Chloride	Fluoride
Al	660	193	1291 subl.
Li	181	610	848
Na	98	801	996
Mg	650	714	1263
Ca	842	775	1418
Al	2519	447	1291 subl.
Li	1342	1383	1673
Na	883	1465	1704
Mg	1088	1412	2227
Ca	1484	2209	2534

Salt Vapour Pressures



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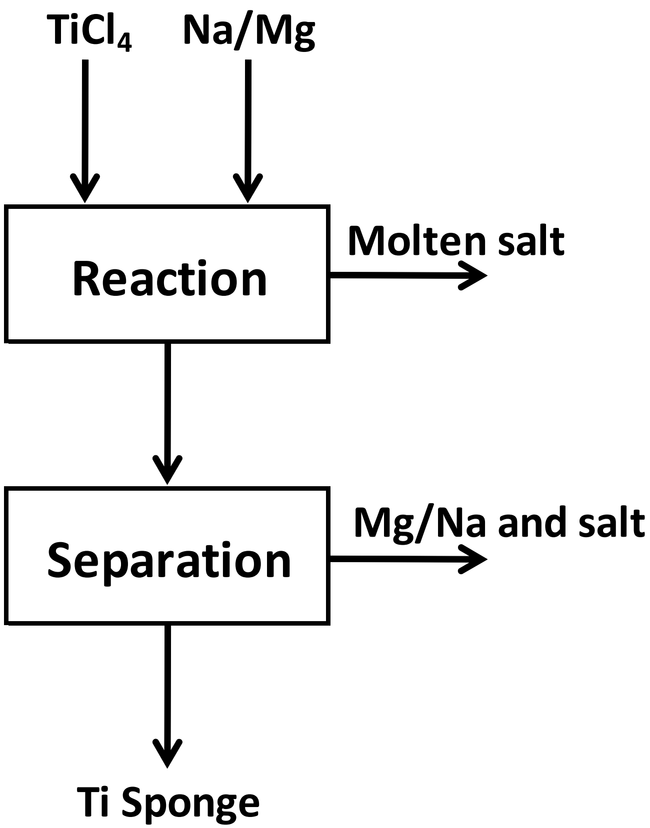
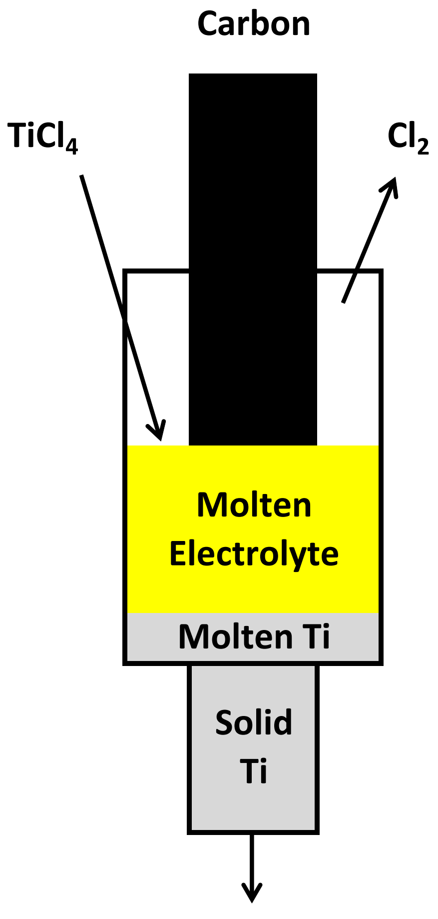
Hunter & Kroll processes



Hunter: Substoichiometric
Kroll: Excess Mg

Hunter: Aqueous leach
Kroll: Vacuum distillation

Ginatta Process



Temperature > 1670°C

Electrolyte

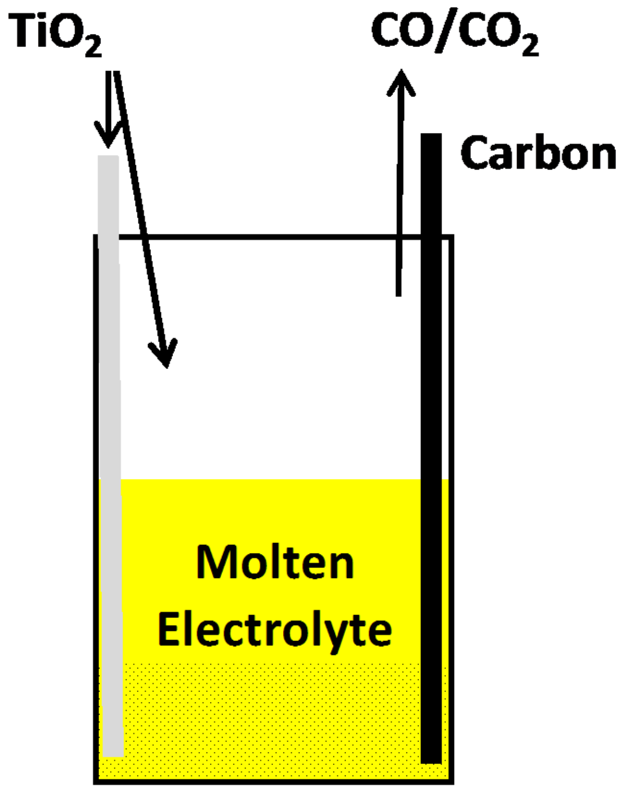
- Chlorides: Only Ca & Ba
- Fluorides: Mg, Ca, Sr, Y

  Density of Ba, La & Ce too high

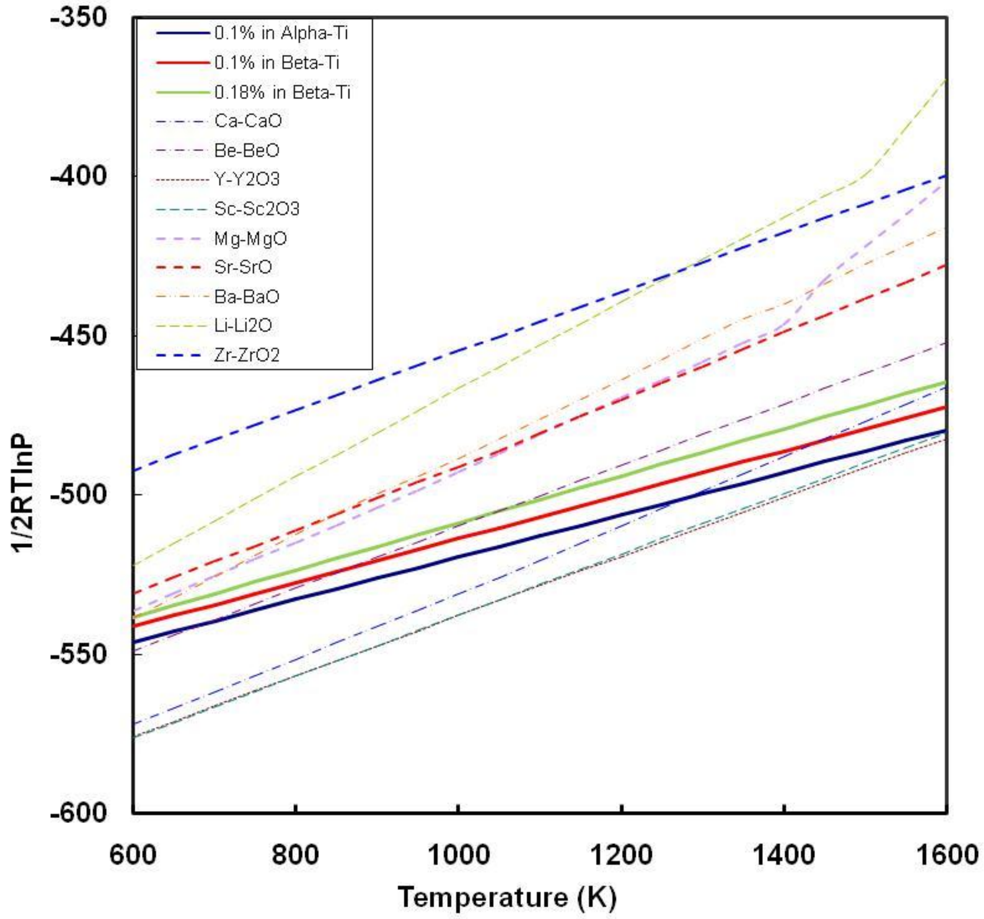
Lining

- Oxides: Only Y & Sc
- Freeze lining

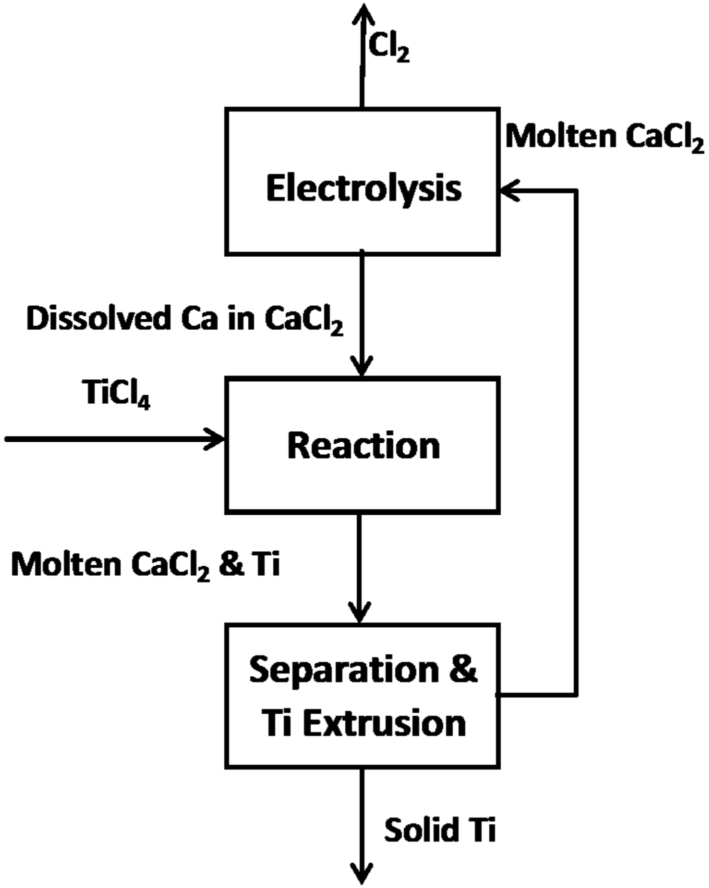
FFC and Ono & Suzuki Processes



Low oxygen potential of metal of the salt cation



JTS Process

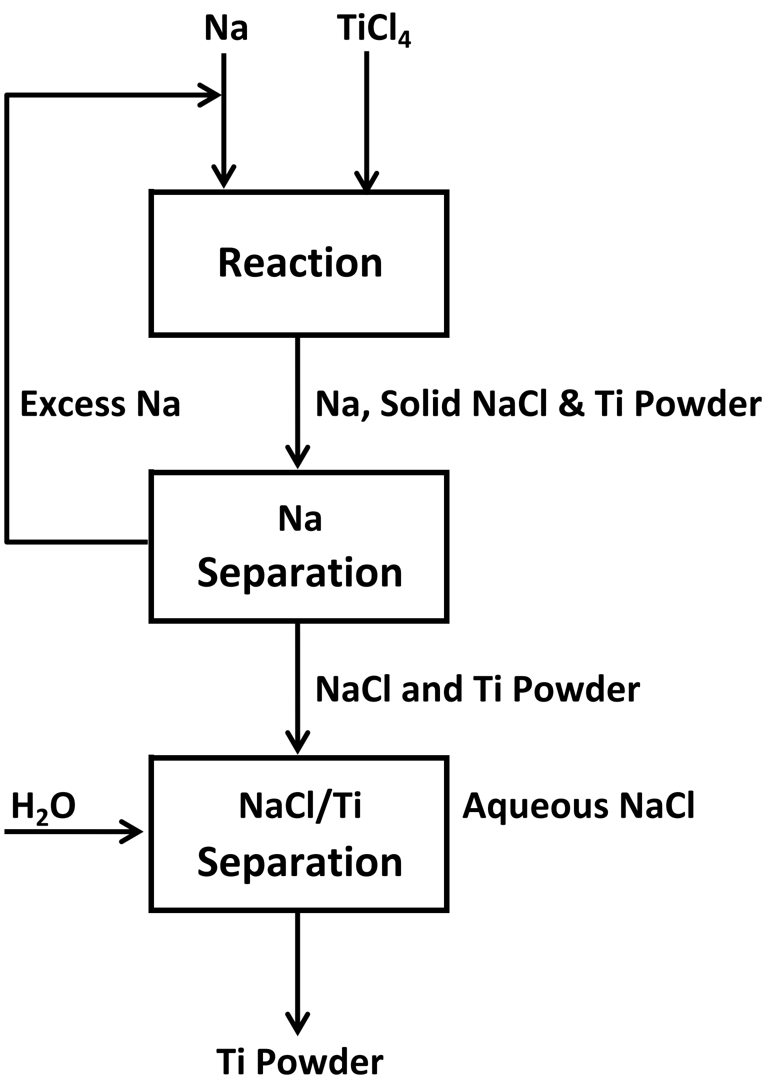


High solubility of Ca in $CaCl_2$

B.P. of $CaCl_2$ > M.P. of Ti

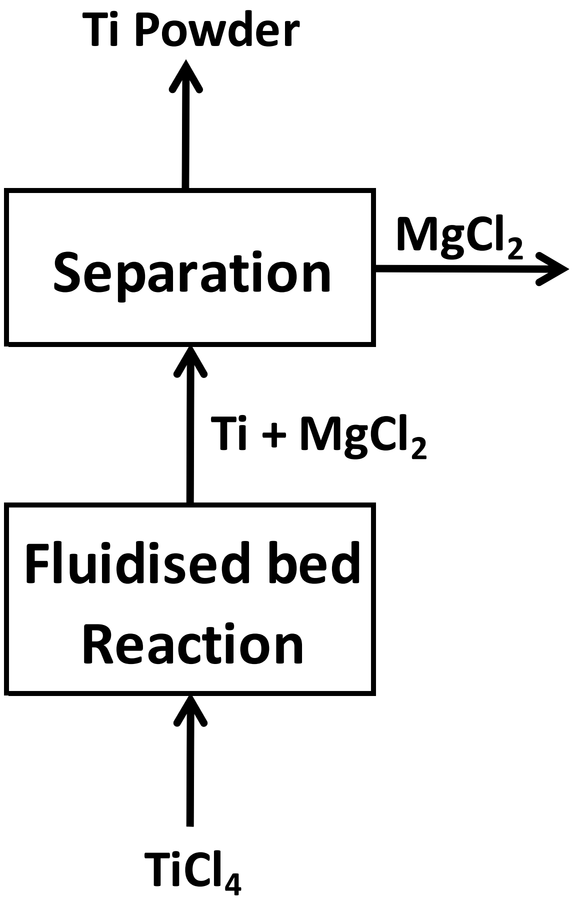
$\rho_{CaCl2} < \rho_{Ti}$

Armstrong Process



Advantage of low M.P. of Na

TiRO Process



$T_{M.P.Mg} < T_{reactor} < T_{M.P.MgCl2}$

Leaching:

Effluent, H_2 formation, re-crystallization of anhydrous $MgCl_2$

$MgCl_2.H_2O \leftrightarrow MgO+2HCl$

Evaporation

Large mass/energy

Continuous operation under vacuum

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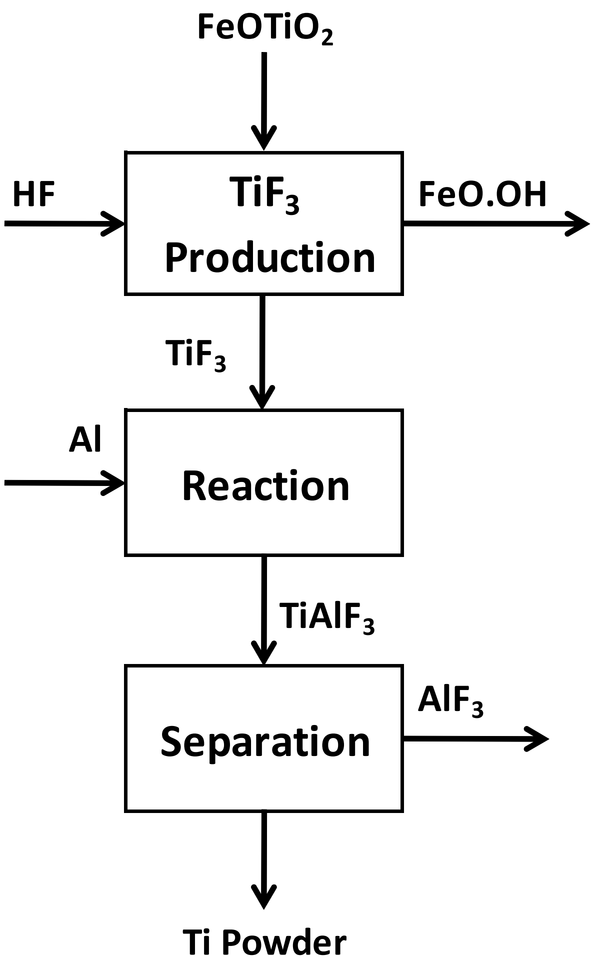
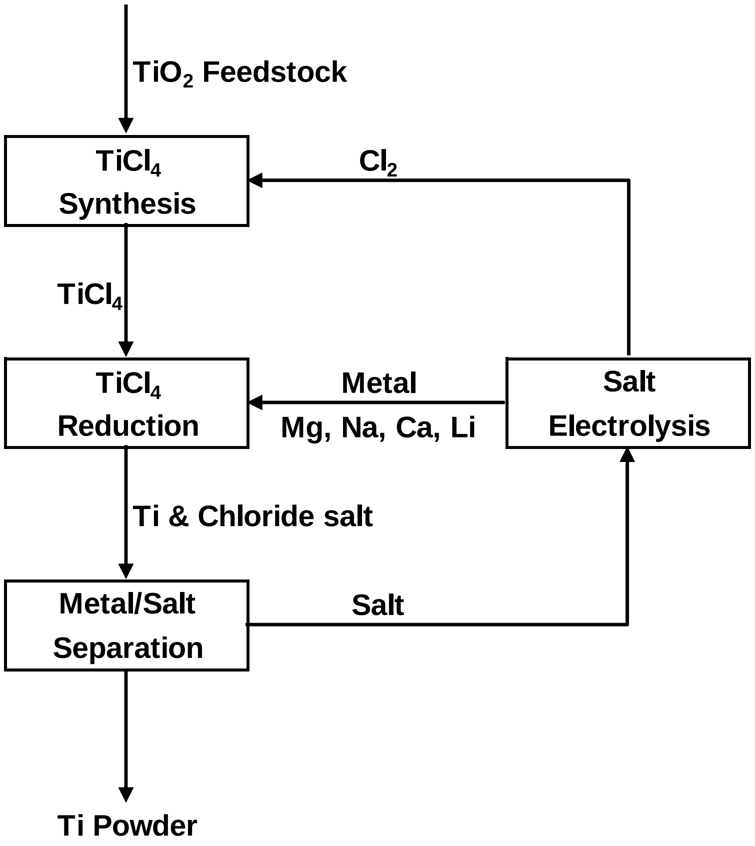
Peruke Process



- M.P. of Al determines $T_{Reactor}$
- Low solubility of AlF_3 in water≈5.6g/lit
- AlF_3 does not melt: Physical separation does not work well
- Separation by sublimation
  - Large mass/energy
  - Continuous operation under vacuum (low vapour pressure)

Continuous metallothermic reduction in molten salt (CSIR)



M.P. of salt determines reactor temperature, construction materials & heat exchanger design.

M.P. of salt and metal affects electrolyser temperature.

Oxide/chloride equilibrium of salt determines salt recovery process.

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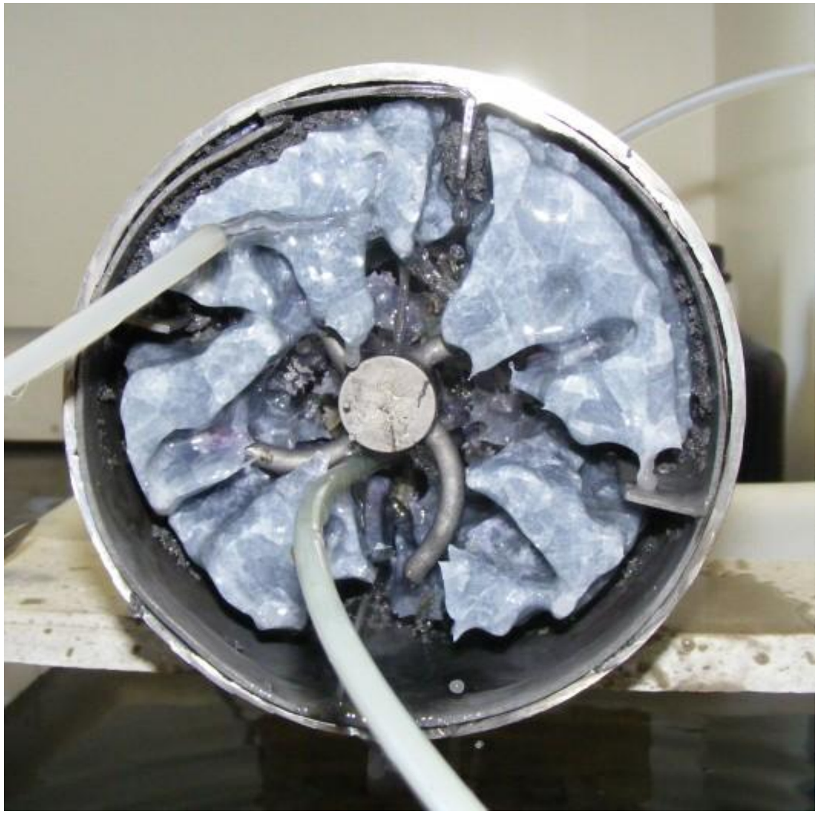
Product Removal



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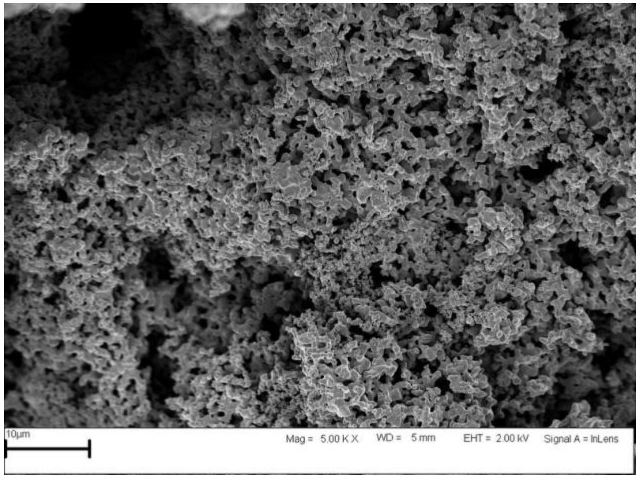
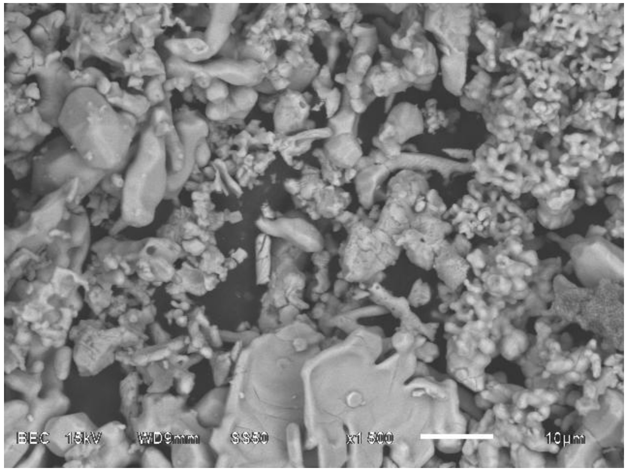
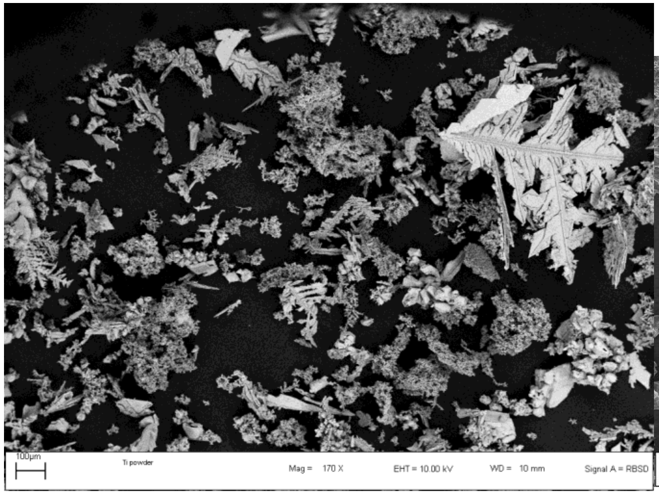
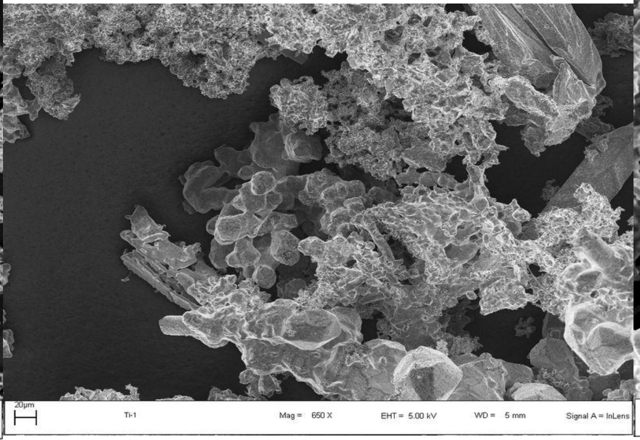
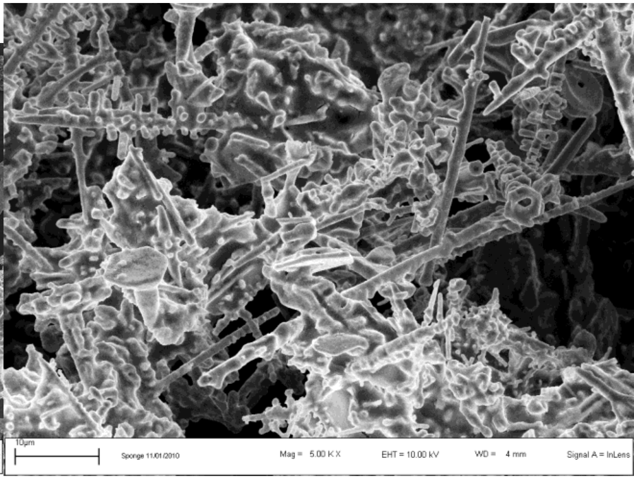
Product Morphology











Conclusions

- The obvious: Basic physical properties of the relevant chemicals have major effects on the selection of the chemical route to produce titanium and on the associated process and equipment designs.
- However, there is no consensus as to what process would be better than the Kroll process and many different approaches are being pursued by different organisations around the world.

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THANK YOU

The support of the DST is sincerely appreciated

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