Producing Titanium Metal Powder by Selective Chlorination and Preform Reduction Process

Haiyan Zheng¹,* and Toru H. Okabe¹

1 Institute of Industrial Science, The University of Tokyo, Japan
* Currently working at Northeastern University, China
Content of Today’s Topic

1 Introduction
2 Iron removal from Ti ore by selective chlorination using metal chlorides
3 Recovery of Ti metal scrap by utilizing chloride wastes
4 Ti powder production based on calciothermic reduction directly from Ti ore by preform reduction process (PRP)
5 Summary
1 Introduction

![Graph showing the amount of titanium mill products in Japan from 1970 to 2000.](http://www.chemsoc.org/VISELEMENTS/pages/data/titanium_data.html)
The Kroll process

Chlorination: $\text{Ti ore (s)} + C (s) + 2 \text{Cl}_2 (g) \rightarrow \text{TiCl}_4 (l) + \text{MCl}_x (s, g) + \text{CO}_2 (g)$

Reduction: $\text{TiCl}_4 (l, g) + 2 \text{Mg (l)} \rightarrow \text{Ti (s)} + 2 \text{MgCl}_2 (l)$

Electrolysis: $\text{MgCl}_2 (l) \rightarrow \text{Mg (s)} + \text{Cl}_2 (g)$

M: Impurity element in the ore

Essential advantage: High-purity Ti can be obtained.
Problems of the Kroll process

The critical disadvantage of the Kroll process is its “low productivity” because of the following factors:

× High-cost raw material is used.
× Product Ti is massive solid in sponge form.
× Chloride wastes are generated.
  → The usage of expensive titanium concentrates causes high Ti production cost.
  → The generation of chloride wastes causes chlorine loss in the process.
  → Chloride wastes causes environmental burden.
  → Disposal cost of chloride wastes is high.
× Complex, labor consuming, and multi-step batch type.
× Contamination of iron from reaction vessel unavoidable.
× Huge heat generated during the reduction step.
  → It takes time for removing MgCl₂ and cooling the reactor.
× Reduction process is of the batch-type and production rate is low.
  (~ 1 ton / day · reactor)

Production cost of titanium is high.
A new Ti smelting process combined with iron removal from low-grade Ti ore by selective chlorination and efficient recovery of Ti scrap and chloride wastes is investigated with the objective of reducing the production cost and decreasing the environmental burden.
2 Iron removal from Ti ore by selective chlorination

1 Selective chlorination

Low-grade Ti ore (FeTiOₓ) + MClₓ (Cl₂) → Transitional Ti ore (TiO₂) + FeClₓ (e.g. PRP process)

2 Recovery of Ti + Cl

FeClₓ → Fe → TiCl₄

3 Ti smelting

Ti (e.g. PRP process) → Ti

(M = Fe, Al, Si...)
Selective chlorination experiment

Experimental apparatus for the selective chlorination of titanium ore using radio frequency (RF) furnace.
## Experiment conditions

<table>
<thead>
<tr>
<th>Expt. #</th>
<th>Mass of feed materials, $w / g$</th>
<th>Reaction temp., $T / K$</th>
<th>Reaction time, $t' / hr$</th>
<th>Atmosphere</th>
<th>Flow ratio, v / cc·min$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SCJ</td>
<td>Ilmenite$^a$ 3.00 CaCl$_2$ 1.50 C 0.10</td>
<td>1023</td>
<td>6</td>
<td>N$_2$ + H$_2$O</td>
<td>50</td>
</tr>
<tr>
<td>SCA</td>
<td>3.03 CaCl$_2$ 1.98 -</td>
<td>1073</td>
<td>6</td>
<td>N$_2$ + H$_2$O</td>
<td>full flow$^*$</td>
</tr>
<tr>
<td>SCB</td>
<td>3.00 CaCl$_2$ 2.05 -</td>
<td>1073</td>
<td>6</td>
<td>N$_2$ + H$_2$O</td>
<td>full flow$^*$</td>
</tr>
<tr>
<td>SCH</td>
<td>3.00 CaCl$_2$ 2.00 0.20</td>
<td>1073</td>
<td>6</td>
<td>N$_2$ + H$_2$O</td>
<td>50</td>
</tr>
<tr>
<td>SCI</td>
<td>3.00 CaCl$_2$ 1.50 0.12$^c$</td>
<td>1073</td>
<td>6</td>
<td>N$_2$ + H$_2$O</td>
<td>50</td>
</tr>
<tr>
<td>SCD</td>
<td>3.01 CaCl$_2$ 2.56 -</td>
<td>1173</td>
<td>6</td>
<td>N$_2$ + H$_2$O</td>
<td>full flow$^*$</td>
</tr>
<tr>
<td>SCN</td>
<td>3.00 CaCl$_2$ 3.00 -</td>
<td>1173</td>
<td>3</td>
<td>N$_2$ + H$_2$O</td>
<td>50</td>
</tr>
<tr>
<td>SCO</td>
<td>4.00 CaCl$_2$ 2.00 -</td>
<td>1173</td>
<td>3</td>
<td>N$_2$ + H$_2$O</td>
<td>50</td>
</tr>
<tr>
<td>SCQ</td>
<td>4.00 CaCl$_2$ 2.00 -</td>
<td>1253</td>
<td>3</td>
<td>N$_2$ + H$_2$O</td>
<td>50</td>
</tr>
<tr>
<td>SCR</td>
<td>3.00 CaCl$_2$ 2.00 -</td>
<td>1273</td>
<td>6</td>
<td>N$_2$ + H$_2$O</td>
<td>50</td>
</tr>
<tr>
<td>SCS</td>
<td>3.00 CaCl$_2$ 3.00 -</td>
<td>1293</td>
<td>6</td>
<td>N$_2$ + H$_2$O</td>
<td>50</td>
</tr>
<tr>
<td>SCT</td>
<td>4.00 CaCl$_2$ 2.00 -</td>
<td>1293</td>
<td>12</td>
<td>N$_2$ + H$_2$O</td>
<td>50</td>
</tr>
</tbody>
</table>

$^a$: Natural ilmenite ore produced in Vietnam after pulverization.
$^b$: Experiment date.
$^c$: 0.27 g of H$_2$O was added to the feed materials.
$^*$: Full flow is about 300 cc / min.

Ti ore: Ilmenite; Chlorinating agent: CaCl$_2$; $T$: 1023~1293 K; $t'$: 3~12 h
Results of selective chlorination (1): XRD

CaTiO$_3$ was generated in the sample obtained in the experiment.

FeCl$_2$ was generated and deposited inside the quartz tube in the experiment.

X-ray diffraction patterns of the obtained samples (Expt.S):
(a) Used tape. (b) The residue in the crucible. (c) The residue rinsed by water. (d) The deposit inside the quartz tube.
## Results of selective chlorination (2): XRF

<table>
<thead>
<tr>
<th>Expt. #</th>
<th>Concentration of element $i$, $C_i$ (mass%)$^a$</th>
<th>$C_{Fe}/C_{Ti}$$^b$</th>
<th>Fe removal ratio, $R$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$C_{Fe}^0/C_{Ti}^0$</td>
<td>$C_{Fe}^1/C_{Ti}^1$</td>
<td></td>
</tr>
<tr>
<td>SCJ</td>
<td>Al 4.18  Ca 15.6  Ti 43.8  Fe 36.4</td>
<td>1.17</td>
<td>1.05</td>
</tr>
<tr>
<td>SCA</td>
<td>Al 4.43  Ca 14.2  Ti 48.2  Fe 33.2</td>
<td>1.17</td>
<td>0.73</td>
</tr>
<tr>
<td>SCB</td>
<td>Al 6.45  Ca 11.7  Ti 62.5  Fe 34.9</td>
<td>1.17</td>
<td>0.80</td>
</tr>
<tr>
<td>SCH</td>
<td>Al 2.71  Ca 15.2  Ti 44.9  Fe 37.2</td>
<td>1.17</td>
<td>0.83</td>
</tr>
<tr>
<td>SCI</td>
<td>Al 2.73  Ca 15.3  Ti 54.2  Fe 27.8</td>
<td>1.17</td>
<td>0.51</td>
</tr>
<tr>
<td>SCD</td>
<td>Al 2.91  Ca 20.7  Ti 56.6  Fe 19.8</td>
<td>1.17</td>
<td>0.35</td>
</tr>
<tr>
<td>SCN</td>
<td>Al 0.99  Ca 16.9  Ti 41.6  Fe 40.5</td>
<td>1.17</td>
<td>0.97</td>
</tr>
<tr>
<td>SCO</td>
<td>Al 1.34  Ca 16.8  Ti 40.0  Fe 41.9</td>
<td>1.17</td>
<td>1.05</td>
</tr>
<tr>
<td>SCQ</td>
<td>Al 2.59  Ca 15.2  Ti 47.4  Fe 34.8</td>
<td>1.17</td>
<td>0.73</td>
</tr>
<tr>
<td>SCR</td>
<td>Al 1.97  Ca 18.9  Ti 49.9  Fe 29.2</td>
<td>1.17</td>
<td>0.59</td>
</tr>
<tr>
<td>SCS</td>
<td>Al 1.16  Ca 16.2  Ti 57.2  Fe 25.3</td>
<td>1.17</td>
<td>0.45</td>
</tr>
<tr>
<td>SCT</td>
<td>Al 2.61  Ca 3.36  Ti 77.3  Fe 16.7</td>
<td>1.17</td>
<td>0.22</td>
</tr>
</tbody>
</table>

*a: Determined by ICP-AES.

*b: $C_{Fe}^0$, $C_{Fe}^1$: the concentration of iron in the sample before and after experiment, respectively; $C_{Ti}^0$, $C_{Ti}^1$: the concentration of titanium in the sample before and after experiment, respectively. $C_{Ti}^0 = 0.438$, $C_{Fe}^0 = 0.513$.

$^*$: $R = 100 \times \{1 - (C_{Fe}^1/C_{Ti}^1) / (C_{Fe}^0/C_{Ti}^0)\}$.

### After experiment:

- $C_{Fe}: 51.3\% \rightarrow 16.7\%$
- $C_{Ti}: 43.8\% \rightarrow 77.3\%$

$R = 100 \times \{1 - (C_{Fe}^1/C_{Ti}^1) / (C_{Fe}^0/C_{Ti}^0)\} > 0$

Fe was selectively removed from Ti ore.
Combined chemical potential diagram of the Fe-Cl-O (dotted line) and Ti-Cl-O (solid line) systems at 1100 K.

Discussion: Mechanism of selective chlorination

Region for selective chlorination of iron

<table>
<thead>
<tr>
<th>Reactions</th>
<th>Gibbs Free Energy (kJ)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>a:</strong> FeO (s) + TiO₂ (s) + CaCl₂ (s, l) = FeCl₂ (g, l) + CaTiO₃ (s)</td>
<td>( \Delta G^o_r = 8.33 ) at 1100 K</td>
</tr>
<tr>
<td><strong>b:</strong> H₂O (g) + CaCl₂ (l) = 2 HCl (g) + CaO (s)</td>
<td>( \Delta G^o_r = 92.67 ) at 1100 K</td>
</tr>
<tr>
<td>FeO(s) + TiO₂(s) + 2 HCl(g) + CaO(s) = FeCl₂(l, g) + CaTiO₃(s) + H₂O(g)</td>
<td>( \Delta G^o_r = -84.34 ) at 1100 K</td>
</tr>
</tbody>
</table>

- The generation of HCl during the selective chlorination was demonstrated and no Ti element was detected in the bubbler water.
- FeCl₂ and CaTiO₃ were identified by XRD.

Probable reactions for selective chlorination:

\[
\begin{align*}
\text{FeO (s) + TiO₂ (s) + CaCl₂ (s, l)} & = \text{FeCl₂ (g, l) + CaTiO₃ (s)} \\
\text{or} & \\
\text{FeO (s) + TiO₂ (s) + 2 HCl (l) + CaO (s)} & = \text{FeCl₂ (l, g) + CaTiO₃ (s) + H₂O (g)}
\end{align*}
\]
Summary on iron removal from low-grade Ti ore by selective chlorination

1. Iron removal directly from Ti ore was successfully carried out.

   In a certain experimental condition: \( C_{Fe} \): 51.3% → 16.7%

2. The mechanism of the selective chlorination reactions was considered as follows:

   \[
   \text{FeO (s) + TiO}_2 \text{ (s) + CaCl}_2 \text{ (s,l) = FeCl}_2 \text{ (g,l) + CaTiO}_3 \text{ (s)} } \\
   \text{or} \\
   \text{FeO (s) + TiO}_2 \text{ (s) + 2 HCl (l) + CaO (s) = FeCl}_2 \text{ (l,g) + CaTiO}_3 \text{ (s) + H}_2\text{O (g)}}
   \]
3 Recovery of Ti scrap by utilizing chloride wastes

1 Selective chlorination

Low-grade Ti ore
(FeTiO$_x$)

Upgraded Ti ore
(TiO$_2$)

2 Recovery of Ti + Cl

MCl$_x$
(Cl$_2$)

FeCl$_x$
(FeTiO$_x$)

FeCl$_x$
(+ AlCl$_3$)

Fe

TiCl$_4$

Ti scrap

3 Ti smelting

(e.g. PRP process)

Ti

MCl$_x$
(M = Fe, Al, Si…)

The 4th Workshop on Reactive Meal Processing, March 13-15, 2008, MIT, Cambridge, MA, USA
Recovery experiment

\[ \text{Ti (s)} + 2 \text{FeCl}_2 (l, g) \rightarrow \text{TiCl}_4 (g) \uparrow + 2 \text{Fe (s)} \]

( Deposits after the experiment )

Quartz tube  
Graphite crucible

Vacuum pump  
Ar gas

Silicone rubber plug  
NaOH gas trap

Heating element  
Sample mixture  
e.g., FeCl\(_2\) + Ti powder

Experimental apparatus for the recovery of Ti and Cl.
## Experiment conditions

<table>
<thead>
<tr>
<th>Expt. #</th>
<th>Form of Ti feed</th>
<th>Mass of feed materials, ( w / g )</th>
<th>Concentration of element ( i ), ( C_i ) (mass%)&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Reaction temp., ( T / K )</th>
<th>Reaction time, ( t' / h )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Ti scrap</td>
<td>FeCl(_2) (Powder)</td>
<td>NaOH</td>
<td>Ti</td>
</tr>
<tr>
<td>CG</td>
<td>Powder</td>
<td>0.36</td>
<td>1.94</td>
<td>6.03</td>
<td>15.6</td>
</tr>
<tr>
<td>CH</td>
<td>Powder</td>
<td>0.36</td>
<td>1.94</td>
<td>5.95</td>
<td>15.6</td>
</tr>
<tr>
<td>CA</td>
<td>Powder</td>
<td>0.33</td>
<td>1.90</td>
<td>5.27</td>
<td>14.8</td>
</tr>
<tr>
<td>CJ</td>
<td>Powder</td>
<td>0.37</td>
<td>1.94</td>
<td>5.97</td>
<td>16.0</td>
</tr>
<tr>
<td>CI</td>
<td>Powder</td>
<td>0.36</td>
<td>1.94</td>
<td>-</td>
<td>15.6</td>
</tr>
<tr>
<td>CE</td>
<td>Granule</td>
<td>0.50</td>
<td>2.82</td>
<td>5.47</td>
<td>15.1</td>
</tr>
<tr>
<td>CF</td>
<td>Turning</td>
<td>0.50</td>
<td>3.19</td>
<td>5.38</td>
<td>13.6</td>
</tr>
</tbody>
</table>

<sup>a</sup>: Atmosphere of reaction: argon (Ar) gas, pressure before the experiment: \( p_{\text{initial}} = 0.2 \) atm, maximum pressure during the experiment: \( p_{\text{Max}} = 0.4 \) atm.  
<sup>b</sup>: Calculated based on the mass of feed materials.

**Ti scrap**: Ti powder, Ti granule, or Ti turning;  
**Chlorinating agent**: FeCl\(_2\);  
**\( T \)**: 900~1200 K;  
**\( t' \)**: 1~3 h.
Results of Ti + Cl recovery (1): Observation (Ti powder)

Assembled quartz tube after experiment.

The form of the obtained residue and deposit after experiment.

**Solid (White)**
- Deposit on the surface of the NaOH gas trap
- [Image]

**Flake (Brown)**
- Deposit inside the quartz tube
- [Image]

**Powder (Black)**
- Residue in the graphite crucible after heating
- [Image]

Melting point of FeCl₂: 950 K @ 1 atm
Melting point of TiCl₄: 408 K @ 1 atm
Results of Ti + Cl recovery (2): XRF (Ti powder)

Analytical results of the samples before and after the recovery experiment.

<table>
<thead>
<tr>
<th>Expt. # CA</th>
<th>Concentration of element $i$, $C_i$ (mass%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ti</td>
</tr>
<tr>
<td>Sample in the graphite crucible before experiment</td>
<td>14.8$^a$</td>
</tr>
<tr>
<td>Residue in the graphite crucible after experiment</td>
<td>1.6$^b$</td>
</tr>
<tr>
<td>Deposit inside the quartz tube</td>
<td>2.7$^d$</td>
</tr>
<tr>
<td>Deposit on the surface of NaOH gas trap</td>
<td>(41.3)$^d$</td>
</tr>
</tbody>
</table>

$^a$: Calculated based on the mass of Ti and FeCl$_2$.
$^b$: Determined by ICP–AES.
$^c$: Determined by potentiometric titration method.
$^d$: Determined by XRF, and the value excludes carbon, sodium and gaseous elements (except chlorine element).

$C_{Fe}^\ast$: 37.5% $\rightarrow$ 98.0%.

$C_{Ti}^\ast$: 14.8% $\rightarrow$ 1.6%.

TiCl$_x$ was obtained and considered as TiCl$_4$. 
Results of Ti + Cl recovery (3): XRD (Ti powder)

XRD patterns of the sample before experiment (a) and the residue after experiment (b) (Expt. CA)

Fe was generated at heating zone.

Starting materials: Ti + FeCl₂
Obtained sample: Fe + TiCl₄

$$\text{Ti (s)} + 2 \text{FeCl}_2 (s, l) \rightarrow \text{TiCl}_4 (g) + 2 \text{Fe (s)}$$
## Results of Ti + Cl recovery (4): Mass balance and reaction ratio

Mass balance of samples before and after the experiment and analytical results of the residue obtained in the graphite crucible after the experiment.

<table>
<thead>
<tr>
<th>Expt. #</th>
<th>Mass of samples in the graphite crucible</th>
<th>Concentration of element $i$, $C_i$ (mass%)</th>
<th>Reaction ratio, $R$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CG</td>
<td>2.30</td>
<td>2.04</td>
<td>13.4</td>
</tr>
<tr>
<td>CH</td>
<td>2.30</td>
<td>0.79</td>
<td>2.8</td>
</tr>
<tr>
<td>CA</td>
<td>2.23</td>
<td>0.56</td>
<td>1.6</td>
</tr>
<tr>
<td>CJ</td>
<td>2.31</td>
<td>0.70</td>
<td>0.7</td>
</tr>
<tr>
<td>CI</td>
<td>2.30</td>
<td>0.62</td>
<td>4.2</td>
</tr>
<tr>
<td>CE</td>
<td>3.32</td>
<td>0.62</td>
<td>46.1</td>
</tr>
<tr>
<td>CF</td>
<td>3.69</td>
<td>0.58</td>
<td>82.0</td>
</tr>
</tbody>
</table>

$a$: Determined by ICP–AES; $b$: Determined by potentiometric titration method.

$$R = 100 - C_{Ti}^1 \cdot \frac{M_s^1}{M_{Ti}^0} (\%)$$

- Ti in Ti scrap was recovered as TiCl$_4$ by reacting with FeCl$_2$.
- Reaction ratio reached to 99% at 1200 K when Ti powder was used as the starting material.
- Higher temperatures improve the efficiency of the recycling of Ti and Cl.
Summary on Ti + Cl recovery

1. Metallic Ti was recovered in the form of TiCl$_4$ by FeCl$_2$.

2. Fe was generated at heating zone.

3. The obtained experimental results indicate that the reaction during the experiment is

   \[ \text{Ti} (s) + 2 \text{FeCl}_2 (s, l) = \text{TiCl}_4 (g) + 2 \text{Fe} (s) \]

4. Higher temperatures improve the efficiency of the recycling of Ti and Cl.
4 Ti powder production by preform reduction process (PRP)

1 Selective chlorination

Low-grade Ti ore \((\text{FeTiO}_x)\) → Upgraded Ti ore \((\text{TiO}_2)\) → Ti

MCI\(_x\) \((\text{Cl}_2)\) → FeCl\(_x\) \((+ \text{AlCl}_3)\) → FeCl\(_x\) \((\text{Cl}_2)\) → Recovery of Ti + Cl

2 Recovery of Ti + Cl

Ti scrap → FeCl\(_x\) \((\text{Cl}_2)\) → TiCl\(_4\) → Fe

3 Ti smelting

Upgraded Ti ore \((\text{TiO}_2)\) → Ti (e.g. PRP process) → Ti

MCI\(_x\) \((\text{Cl}_2)\) → MCl\(_x\) \((\text{Cl}_2)\) → MCl\(_x\) \((\text{M} = \text{Fe, Al, Si}...)\)
The 4th Workshop on Reactive Meal Processing, March 13-15, 2008, MIT, Cambridge, MA, USA

PRP

**Ti ore**  
**Flux**  
**Binder**  
Mixing  
Slurry

Rutile + CaCl$_2$ + Binder  
$T$: Room temp., $t'$: 6 h  
e.g. 40mm × 20mm × 8mm  
**Preform fabrication**

Feed preform  
Calcination/iron removal  
FeCl$_x$↑  
$T$: 1273 K, $t'$: 1 ~ 2 h

Sintered feed preform  
Reduction  
Ti + CaO + Ca

Calcium vapor  
$T$: 1273 K, $t'$: 6 ~ 10 h

Reduced preform  
Leaching  
Waste solution  
Ti powder  
Vacuum drying

**Ti ore**: Rutile  
**Flux**: CaCl$_2$  
**Binder**: Collodion

Ti ore + flux  
TiO$_2$ feed in flux

**TiO$_2$ (s, in feed preform) + 2 Ca (g) = Ti (s, powder) + 2 CaO (s, flux)**

Ti ore

Flux

Binder

Mixing

Slurry

Preform fabrication

Feed preform

Calcination/iron removal

Sintered feed preform

Reduction

Reduced preform

Leaching

Waste solution

Vacuum drying

Powder

Ti powder

Ti ore: Rutile  
Flux: CaCl$_2$  
Binder: Collodion
Reduction experiment in PRP

Schematic illustration of the experimental apparatus for the reduction experiment.

\[
\text{TiO}_2 (s, \text{in feed preform}) + 2 \text{Ca} (g) = \text{Ti} (s) + 2 \text{CaO} (s, \text{in flux})
\]

\[
T: 1273 \text{ K}
\]

\[
\tau: 6 \text{ or } 10 \text{ h}
\]
### Experiment conditions

<table>
<thead>
<tr>
<th>Expt. #</th>
<th>Mass of feed materials in preform, $w_i / g$</th>
<th>Cationic molar ratio, $R_{\text{Cat.}} / Ti^b$</th>
<th>Calcination</th>
<th>Reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Feed Ti ore$^a$</td>
<td>Flux CaCl$_2$</td>
<td>Binder Collodion</td>
<td>Additive C powder</td>
</tr>
<tr>
<td>PH-1</td>
<td>6.26</td>
<td>1.74</td>
<td>4.86</td>
<td>-</td>
</tr>
<tr>
<td>PH-2</td>
<td>6.26</td>
<td>1.74</td>
<td>4.91</td>
<td>-</td>
</tr>
<tr>
<td>PH-3</td>
<td>5.65</td>
<td>2.35</td>
<td>5.20</td>
<td>-</td>
</tr>
<tr>
<td>PH-4</td>
<td>5.65</td>
<td>2.35</td>
<td>5.28</td>
<td>-</td>
</tr>
<tr>
<td>PCE-1</td>
<td>6.26</td>
<td>1.74</td>
<td>4.85</td>
<td>0.20</td>
</tr>
<tr>
<td>PCE-2</td>
<td>6.26</td>
<td>1.74</td>
<td>4.59</td>
<td>0.20</td>
</tr>
<tr>
<td>PCE-3</td>
<td>5.65</td>
<td>2.35</td>
<td>5.34</td>
<td>0.20</td>
</tr>
<tr>
<td>PCE-4</td>
<td>5.65</td>
<td>2.35</td>
<td>4.95</td>
<td>0.20</td>
</tr>
<tr>
<td>PCD-1</td>
<td>6.26</td>
<td>1.74</td>
<td>4.93</td>
<td>0.20</td>
</tr>
<tr>
<td>PCD-2</td>
<td>6.26</td>
<td>1.74</td>
<td>4.26</td>
<td>0.20</td>
</tr>
<tr>
<td>PCD-3</td>
<td>5.65</td>
<td>2.35</td>
<td>5.54</td>
<td>0.20</td>
</tr>
<tr>
<td>PCD-4</td>
<td>5.65</td>
<td>2.35</td>
<td>5.79</td>
<td>0.20</td>
</tr>
</tbody>
</table>

---

*a: Natural rutile ore produced in South Africa after pulverization.

*b: Cationic molar ratio, $R_{\text{Cat.}} / Ti = N_{\text{Cat.}} / N_{\text{Ti}}$, where $N_{\text{Cat.}}$ and $N_{\text{Ti}}$ are mole amount of cation in flux and that of titanium, respectively.

Fe removal: $\text{FeO}_x (s, \text{in Ti ore}) + 2/y \text{MCl}_y (g, l) = \text{FeCl}_2 (g) + 2/y \text{MO}_{xy/2}$

Reduction: $\text{TiO}_2 (s) + 2 \text{Ca} (g) = \text{Ti} (s) + 2 \text{CaO} (s)$ in flux
The generation of CaTiO$_3$ was considered to be beneficial for the iron removal. Metallic titanium was successfully produced “directly” from “natural titanium ore” by the PRP.
## Results of PRP (2): Composition and yield

<table>
<thead>
<tr>
<th>Expt. #.</th>
<th>Al</th>
<th>Cl</th>
<th>Ca</th>
<th>Ti</th>
<th>Fe</th>
<th>Y (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PH-1</td>
<td>0.46</td>
<td>&lt;0.01</td>
<td>2.05</td>
<td>97.1</td>
<td>0.41</td>
<td>60</td>
</tr>
<tr>
<td>PH-2</td>
<td>0.76</td>
<td>&lt;0.01</td>
<td>2.57</td>
<td>96.1</td>
<td>0.53</td>
<td>63</td>
</tr>
<tr>
<td>PH-3</td>
<td>0.52</td>
<td>&lt;0.01</td>
<td>0.20</td>
<td>98.7</td>
<td>0.59</td>
<td>73</td>
</tr>
<tr>
<td>PH-4</td>
<td>0.79</td>
<td>&lt;0.01</td>
<td>1.30</td>
<td>97.8</td>
<td>0.13</td>
<td>76</td>
</tr>
<tr>
<td>PCE-1</td>
<td>0.45</td>
<td>0.14</td>
<td>0.52</td>
<td>98.9</td>
<td>0.03</td>
<td>76</td>
</tr>
<tr>
<td>PCE-2</td>
<td>0.48</td>
<td>0.16</td>
<td>2.27</td>
<td>97.1</td>
<td>&lt;0.01</td>
<td>86</td>
</tr>
<tr>
<td>PCE-3</td>
<td>0.57</td>
<td>0.08</td>
<td>1.97</td>
<td>97.3</td>
<td>0.06</td>
<td>79</td>
</tr>
<tr>
<td>PCE-4</td>
<td>0.29</td>
<td>0.13</td>
<td>0.75</td>
<td>98.8</td>
<td>0.04</td>
<td>80</td>
</tr>
<tr>
<td>PCD-1</td>
<td>0.81</td>
<td>&lt;0.01</td>
<td>3.86</td>
<td>95.2</td>
<td>0.15</td>
<td>99</td>
</tr>
<tr>
<td>PCD-2</td>
<td>0.56</td>
<td>&lt;0.01</td>
<td>0.98</td>
<td>98.2</td>
<td>0.23</td>
<td>79</td>
</tr>
<tr>
<td>PCD-3</td>
<td>0.86</td>
<td>&lt;0.01</td>
<td>0.97</td>
<td>98.0</td>
<td>0.18</td>
<td>92</td>
</tr>
<tr>
<td>PCD-4</td>
<td>0.73</td>
<td>&lt;0.01</td>
<td>0.68</td>
<td>98.4</td>
<td>0.14</td>
<td>88</td>
</tr>
</tbody>
</table>

* Determined by XRF, and the value excludes carbon and gaseous elements except chlorine element.

Loss occurred mainly at leaching process. Still high Fe content considering the practical application, but can be improved to lower level.
Results of PRP (3): Comparison of the SEM images

Ti powder obtained after leaching

Expt. PCD-2, Cationic molar ratio, $R_{\text{Cat/Ti}} = 0.2$, Carbon powder: 0.2 g

- TiO$_2$: 6.26 g
- CaCl$_2$: 1.74 g
- $T = 1273$ K
- $t' = 9.7$ h

Expt. PCD-4, Cationic molar ratio, $R_{\text{Cat/Ti}} = 0.3$, Carbon powder: 0.2 g

- TiO$_2$: 5.65 g
- CaCl$_2$: 2.35 g
- $T = 1273$ K
- $t' = 9.7$ h

More amount of the flux, larger size of the primary particle.

Cationic molar ratio, $R_{\text{Cat/Ti}} = N_{\text{Cat}} / N_{\text{Ti}}$, where $N_{\text{Cat}}$ and $N_{\text{Ti}}$ are mole amount of cation in flux and that of titanium, respectively.
Summary on Ti powder production by PRP

1. Metallic Ti powder with 98% purity and 88% yield was obtained directly from natural Ti ore (rutile ore) using Ca vapor by PRP.

2. Generation of CaTiO$_3$ was considered to be beneficial for removing iron from Ti ore.

3. More amount of the flux, larger size of the primary particle.
1. Iron was successfully removed from the low-grade Ti ore by selective chlorination using metal chlorides.

\[
\begin{align*}
\text{FeO} \ (s) + \text{TiO}_2 \ (s) + \text{CaCl}_2 \ ((s,l)) &= \text{FeCl}_2 \ ((g,l)) + \text{CaTiO}_3 \ (s) \\
\text{FeO} \ (s) + \text{TiO}_2 \ (s) + 2 \text{HCl} \ (g) + \text{CaO} \ (s) &= \text{FeCl}_2 \ ((l,g)) + \text{CaTiO}_3 \ (s) + \text{H}_2\text{O} \ (g)
\end{align*}
\]

2. The feasibility of the new recycling process of metallic Ti by FeCl₂ is demonstrated and higher temperatures improve the efficiency of the recycling of Ti and Cl.

\[
\text{Ti} \ (s) + 2 \text{FeCl}_2 \ ((s,l)) = \text{TiCl}_4 \ (g) + 2 \text{Fe} \ (s)
\]

3. Metallic Ti powder with 98% or more was obtained directly from rutile ore by PRP. It is demonstrated that PRP is suitable for producing high purity titanium powder directly from titanium ore.

\[
\text{TiO}_2 \ (s, \text{in feed preform}) + 2 \text{Ca} \ (g) = \text{Ti} \ (s, \text{powder}) + 2 \text{CaO} \ (s, \text{flux})
\]