Recycling Titanium Metal Scraps by Utilizing Chloride Wastes

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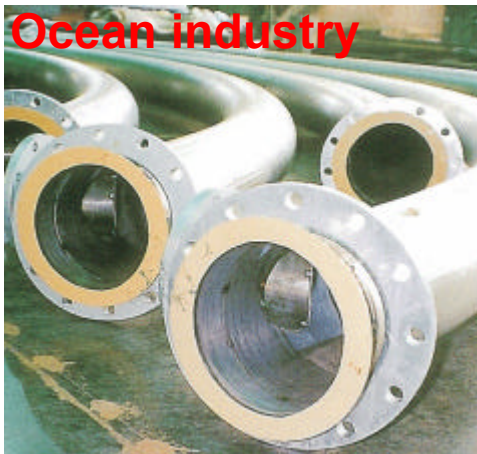The University of Tokyo

Titanium ?

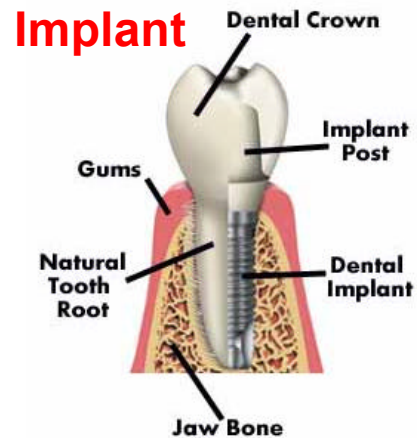**Aerospace industry**

Feature of Titanium

1. Light and high-strength
2. Corrosion resistance
3. Biocompatibility
4. 10th most abundant element in the earth's crust

Japan Aerospace Exploration Agency

Ocean industry

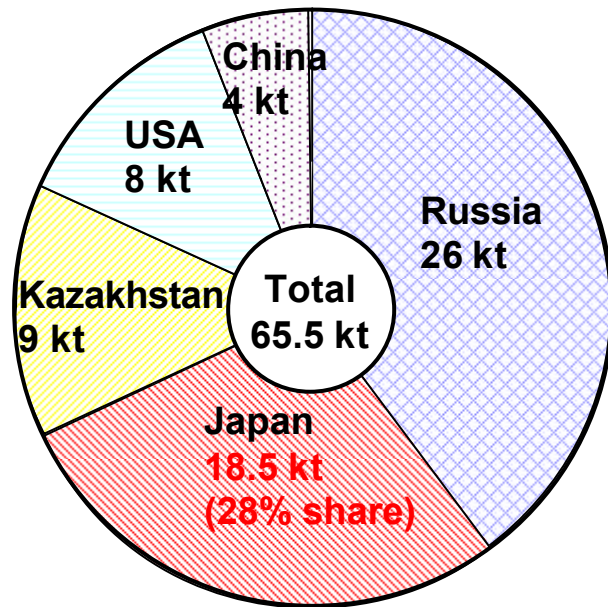The JAPAN TITANIUM SOCIETY

Implant

Dental Crown
Implant Post
Gums
Natural Tooth Root
Dental Implant
Jaw Bone

http://www.atlantadentalimplants.com/

Buildings

TMinato-Machi River Place (Osaka Japan)
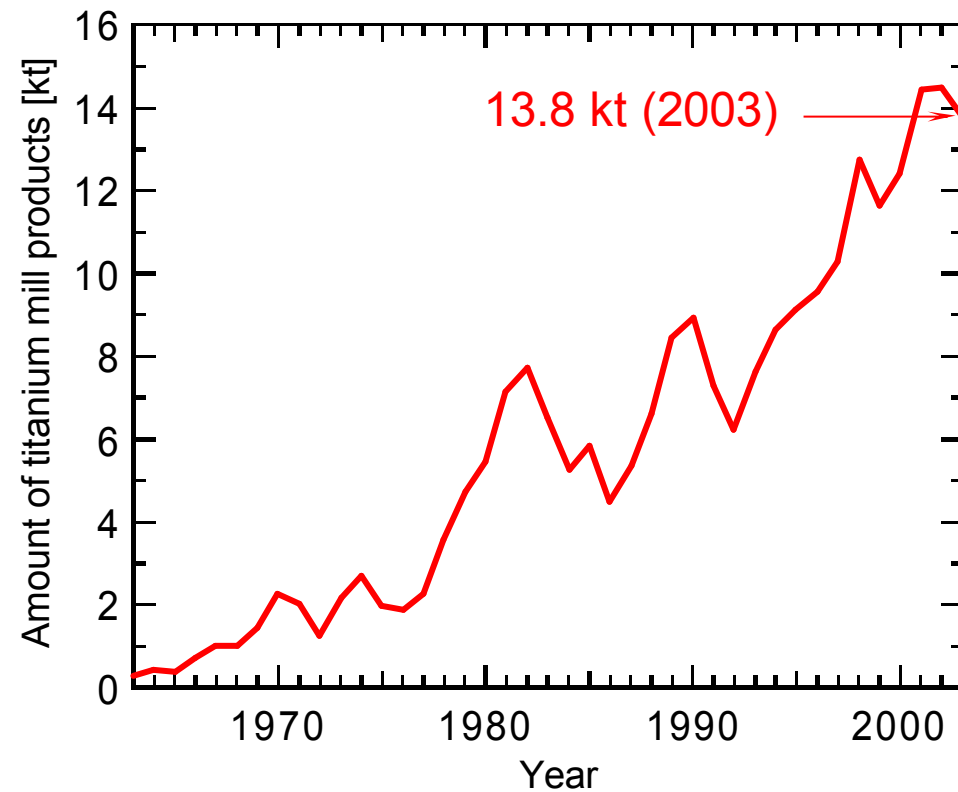http://www.city.osaka.jp/

Current status of titanium production   (2003)

(a) Production of titanium sponge
    in the world
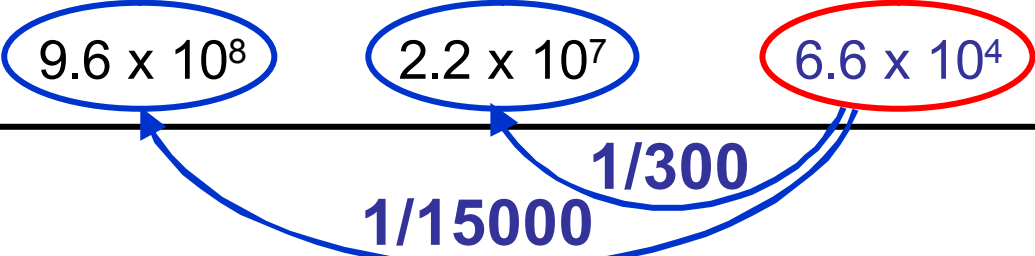
(b) Transition of production volume of
    titanium mill products in Japan

China
4 kt

USA
8 kt

Russia
26 kt

Kazakhstan
9 kt

Total
65.5 kt

Japan
18.5 kt
(28% share)

13.8 kt (2003)

Amount of titanium mill products [kt]

Year

Comparison with common metals

Metal	Iron	Aluminum	Titanium
Symbol	Fe	Al	Ti
Melting point (K)	1943	933	1809
Density (g/cm³@298 K)	7.9	2.7	4.5
Specific strength ((kgf/mm²)/(g/cm³))	4~7	3~6	8~10
Clarke No.	4	3	10
Price (¥/kg)	50	600	3000
Production volume (t/world@2003)	9.6×10^8	2.2×10^7	6.6×10^4

1/300

1/15000

Production volume of metallic titanium

substantially small

Kroll Process

Chlorination: Ti ore (s) + C (s) + 2 Cl$_2$ (g) TiCl$_4$ (l) + CO$_2$ (g)

Reduction: TiCl$_4$ (l) + 2 Mg (s) Ti (s) + 2 MgCl$_2$ (l)

Electrolysis: MgCl$_2$ (l) Mg (s) + Cl$_2$ (g)
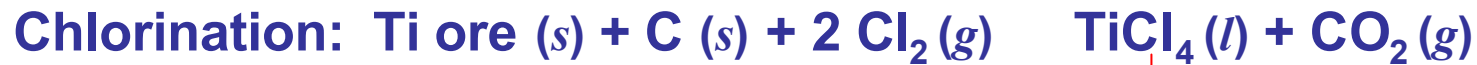
Reduction Reactor for the Kroll Process

Mg & TiCl$_4$ feed port

Mg & MgCl$_2$ recovery port

Metallic reaction vessel

MgCl$_2$ recovery port

Sponge titanium

Ti / Mg / MgCl$_2$ mixture

Furnace
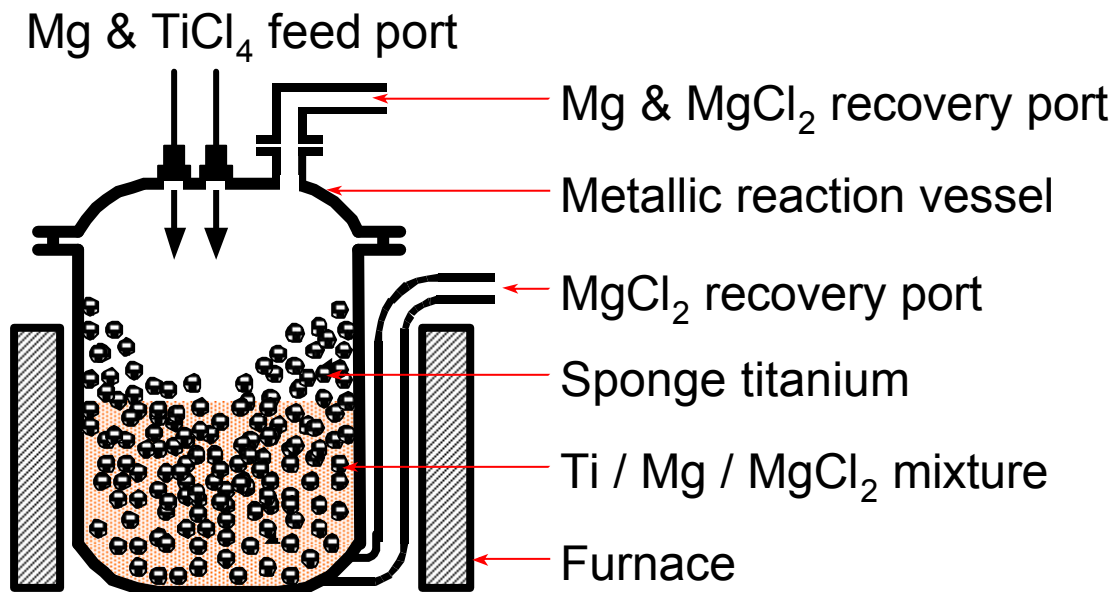
The essential advantage:
High-purity Ti

The critical disadvantage:
Low productivity
    Batch type process
    Slow production speed

Chlorine cycle in the Kroll process

Additional Cl$_2$ supply to compensate for chlorine loss

Cl_2 C Ti ore

Carbo-chlorination

CO_x Chloride wastes

Chlorine loss

$TiCl_4$ Mg

Reduction

$MgCl_2$ Ti

Electrolysis

Cl_2 Mg

Chlorine in the Kroll process is recycled, but the generation of chloride waste causes chlorine loss in the process.
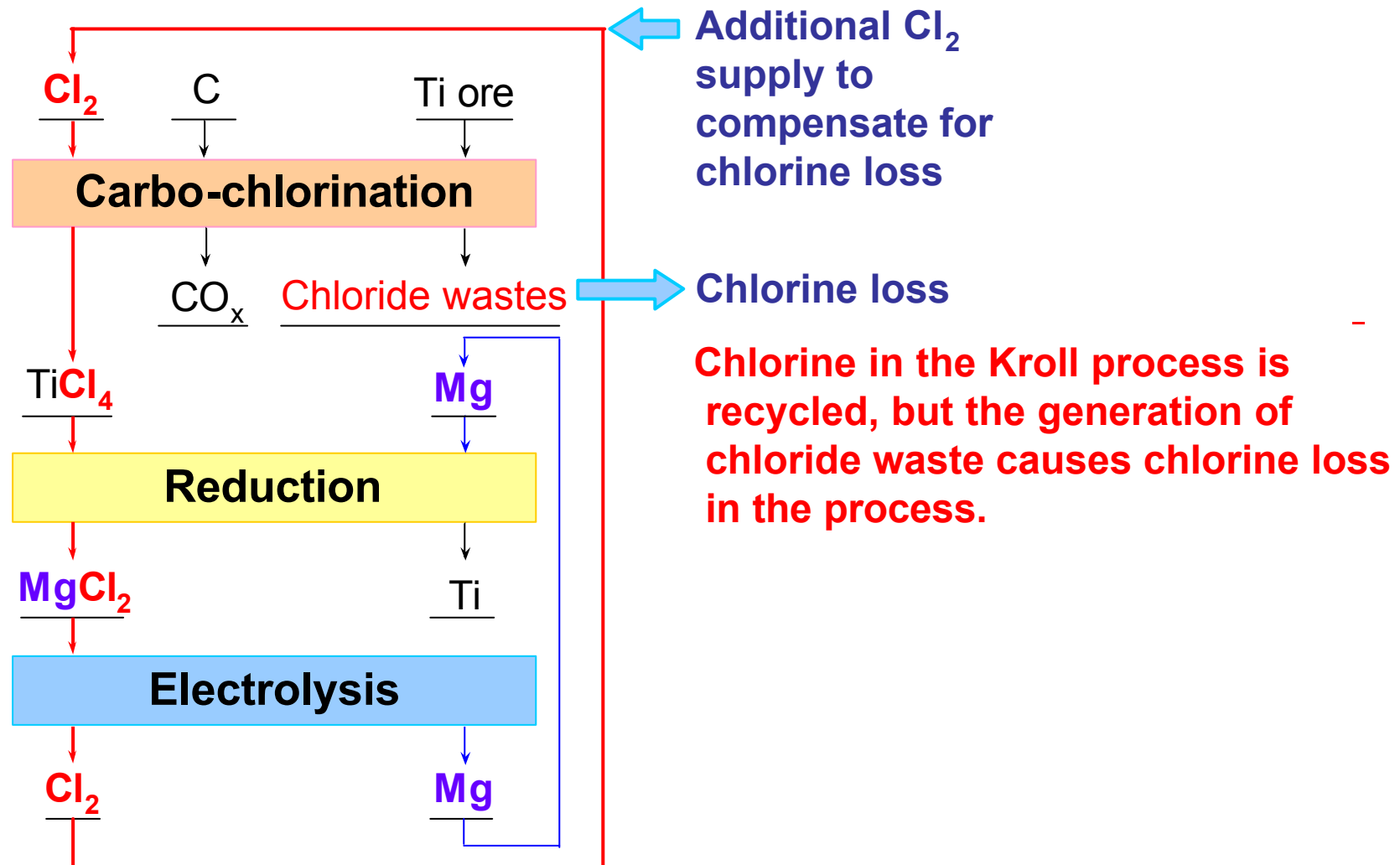
Upgrading Ti ore for minimizing chloride wastes

Upgrade

Chloride wastes

Ti ore (eg. Ilmenite)

Upgraded Ilmenite (UGI)

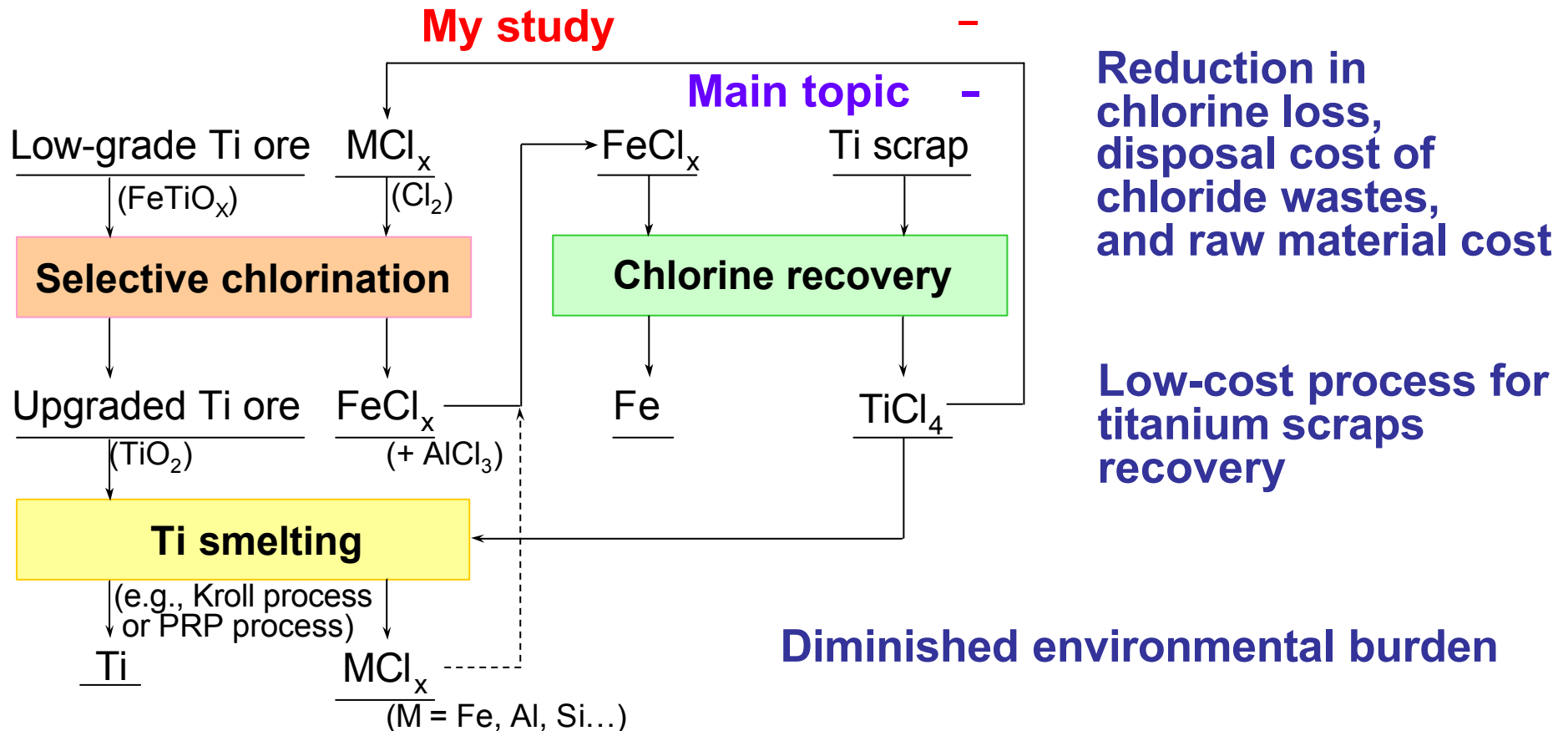**Discarded**
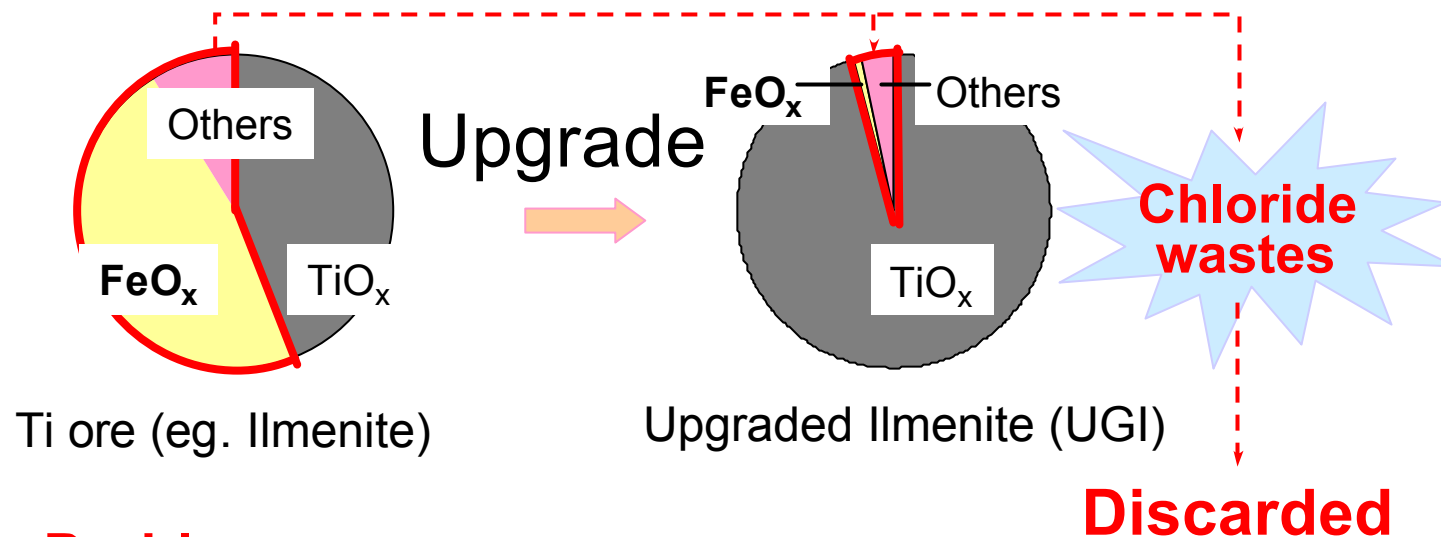
Problems:

When low-grade ore is used, a large amount of chloride wastes (e.g., $FeCl_x$) are generated in the Kroll process.

Disposal cost of chloride wastes
Environmental issues
Causes chlorine loss in the process

➡ **Currently expensive upgraded ilmenite ore (UGI) is used for reducing chloride waste and environmental burden.**

Concept of this study

Possibility of utilizing low-grade titanium ore in the Kroll process or in the new smelting process, such as the PRP

My study

Main topic

Low-grade Ti ore ($FeTiO_x$) → **Selective chlorination** → Upgraded Ti ore (TiO_2) → **Ti smelting** (e.g., Kroll process or PRP process) → Ti

MCl_x (Cl_2)

$FeCl_x$ (+ $AlCl_3$) → MCl_x (M = Fe, Al, Si...)

$FeCl_x$ + Ti scrap → **Chlorine recovery** → Fe, $TiCl_4$

Reduction in chlorine loss, disposal cost of chloride wastes, and raw material cost

Low-cost process for titanium scraps recovery

Diminished environmental burden

Selective chlorination

(Upgrading low-grade titanium ore using $CaCl_2$)

FeO_x (FeTiO$_x$, *s*) + HCl (*g*) $FeCl_x$ (*g*)   + H_2O (*g*)

FeO_x (FeTiO$_x$, *s*) + $CaCl_2$ (*s*, *l*) $FeCl_x$ (*g*)   + CaO (CaTiO$_x$, *s*)

Selective chlorination experiment

Vacuum pump

Deposit obtained after exp.

Chloride Condenser

Stainless steel susceptor

Graphite crucible

Chlorination Reactor

Sample

RF coil

Quartz tube

Ceramic tube

gas

Experimental apparatus for the selective chlorination of titanium ore using Radio Frequency (RF) furnace.

10 cm
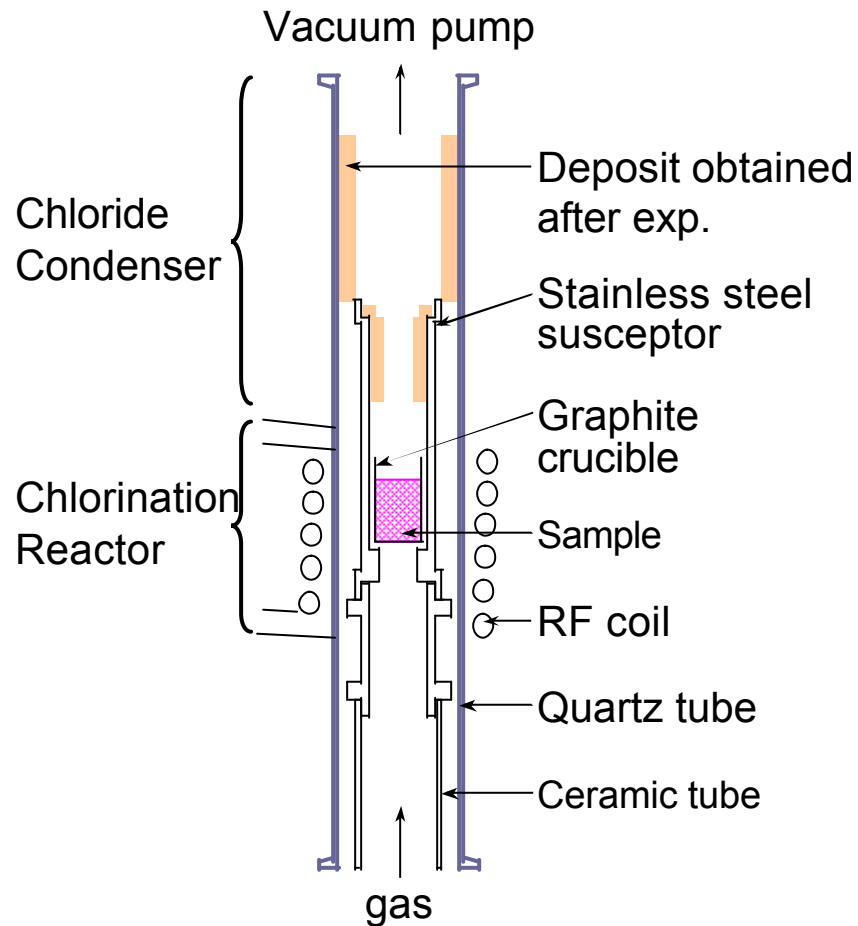
Experimental condition:

Low-grade Ti ore : 3 g,
$CaCl_2$: 2 g,
T = 1100 K,
t' = 6 h,
Graphite crucible,
Atmosphere : N_2 + H_2O.

The concentration of iron in the titanium ore decreased from 54% to 16% (XRF).
Iron removal from the titanium ore was carried out successfully.

Chlorine recovery

(Recovery of chlorine from chloride wastes by utilizing titanium metal scraps)

$$FeCl_x \ (l, g) + Ti \ (s) \quad Fe \ (or \ FeTi, \ s) + TiCl_4 \ (g)$$

Ti-Cl-O system, p_{Cl_2} = 0.1 atm

TiO$_2$ (s)

CO (g)/CO$_2$ (g) eq.

C (s)/CO (g) eq.

C (s)/CO$_2$ (g) eq.

TiCl$_4$ (g)

Oxygen partial pressure, log p_{O_2} (atm)

Temperature T / K

Chemical potential diagram for the Ti-Cl-O system.
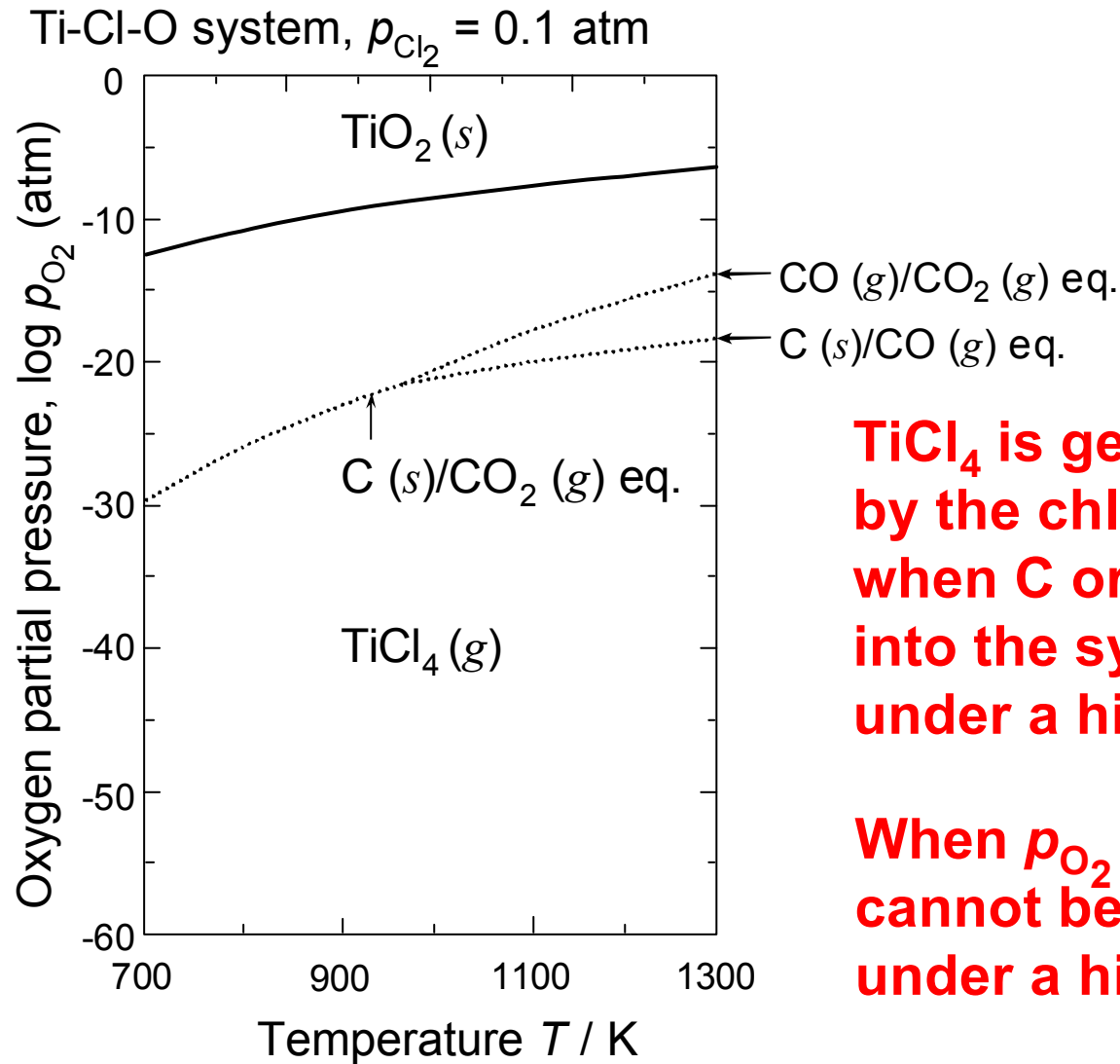
TiCl$_4$ is generated by the chlorination of TiO$_2$ when C or CO is introduced into the system under a high p_{Cl_2} atmosphere.

When p_{O_2} is high, TiCl$_4$ cannot be obtained even under a high p_{Cl_2} atmosphere.

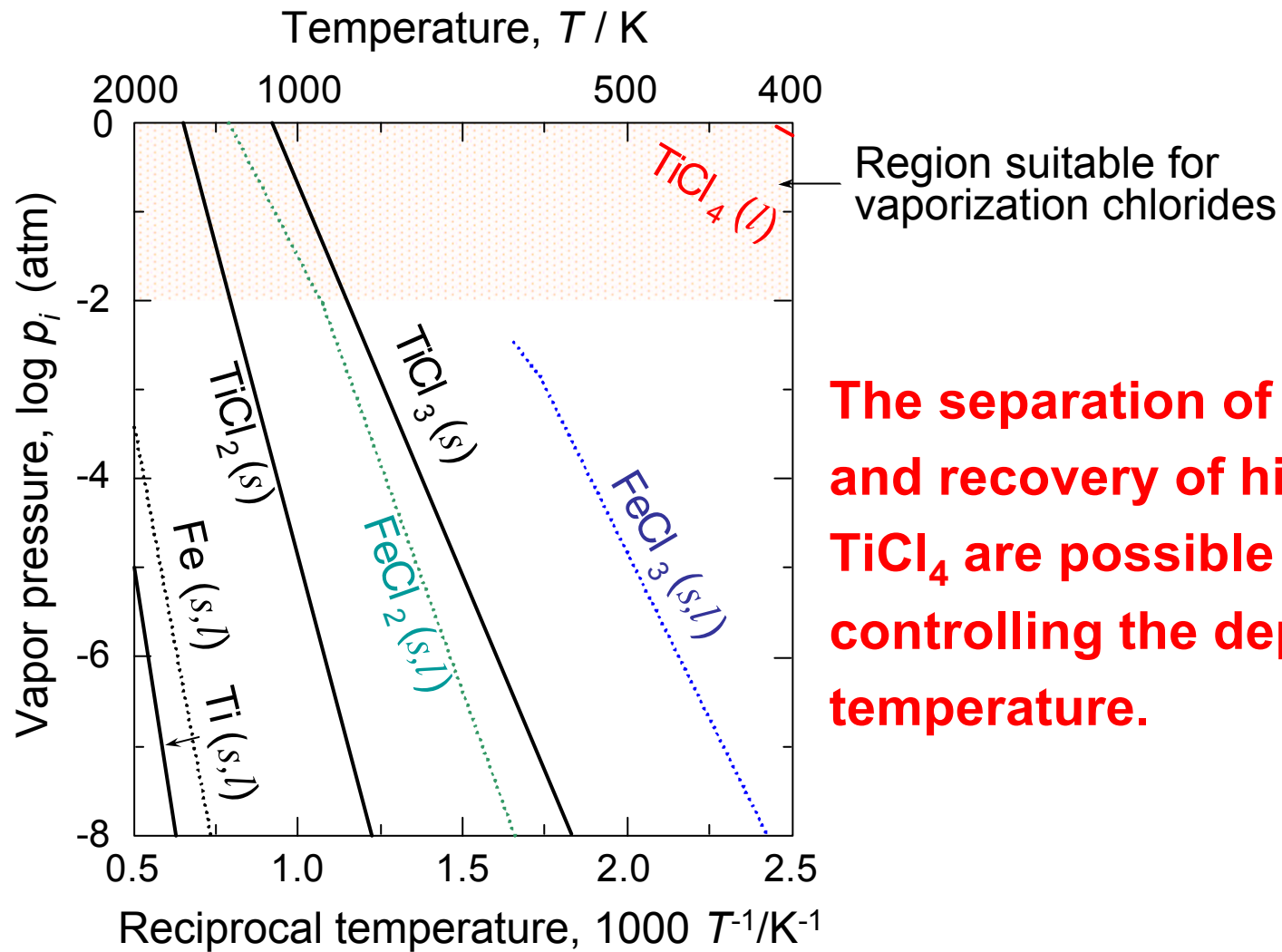## Ti (s) + FeCl$_x$ (l, g) ⇌ TiCl$_4$ (g) + Fe (or FeTi, s)

Fe-Ti-Cl system, T = 1100 K
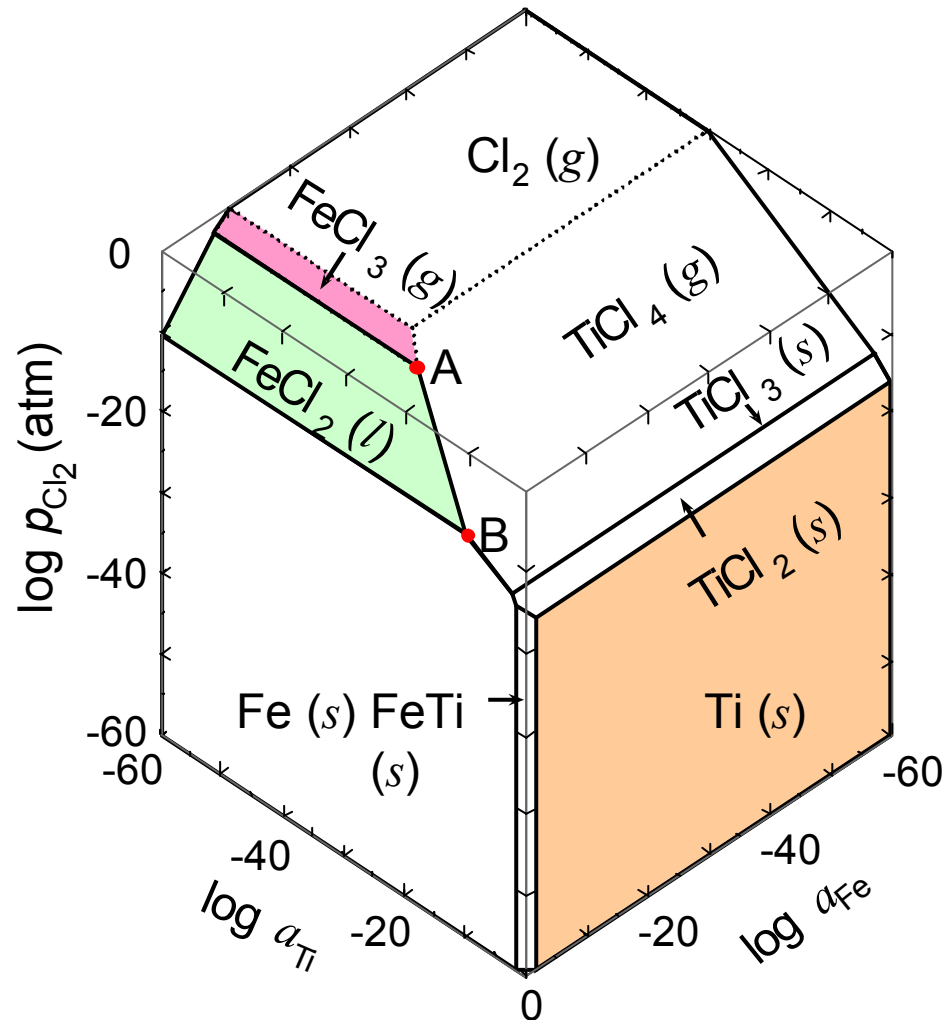
Chlorine present in the iron chlorides can be extracted by metallic titanium.

TiCl$_4$ can be obtained.
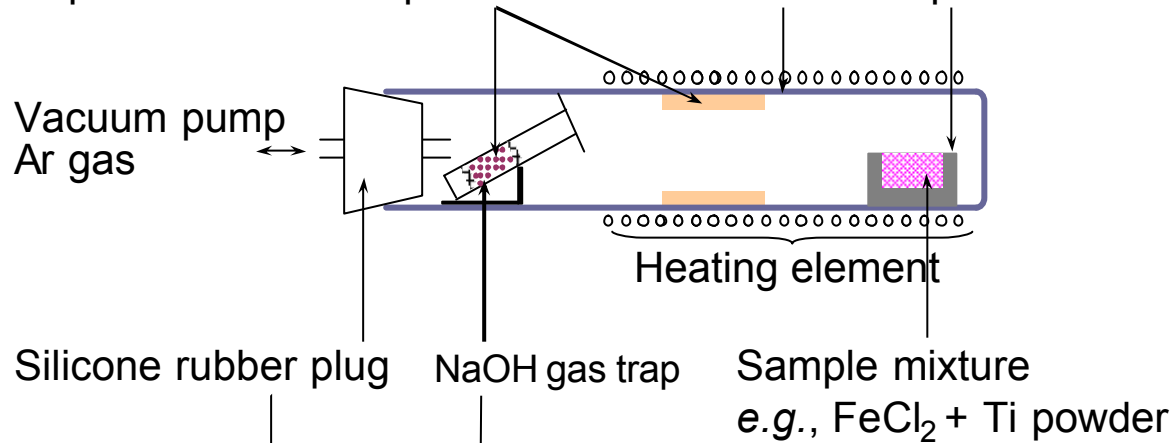
Chemical potential diagram for the Fe-Ti-Cl system at 1100 K.

Vapor pressure of some chlorides as a function of reciprocal temperature.

The separation of chlorides and recovery of high-purity TiCl$_4$ are possible by controlling the deposition temperature.

Chlorine recovery experiment

$$Ti\ (s) + 2\ FeCl_2\ (s, l) \quad TiCl_4\ (g) + 2\ Fe\ (s)$$

Deposits after the experiment   Quartz tube   Graphite crucible

Vacuum pump
Ar gas

Heating element

Silicone rubber plug   NaOH gas trap   Sample mixture
                                          e.g., FeCl$_2$ + Ti powder

Experimental condition:

Ti: 0.3 g, FeCl$_2$: 2 g
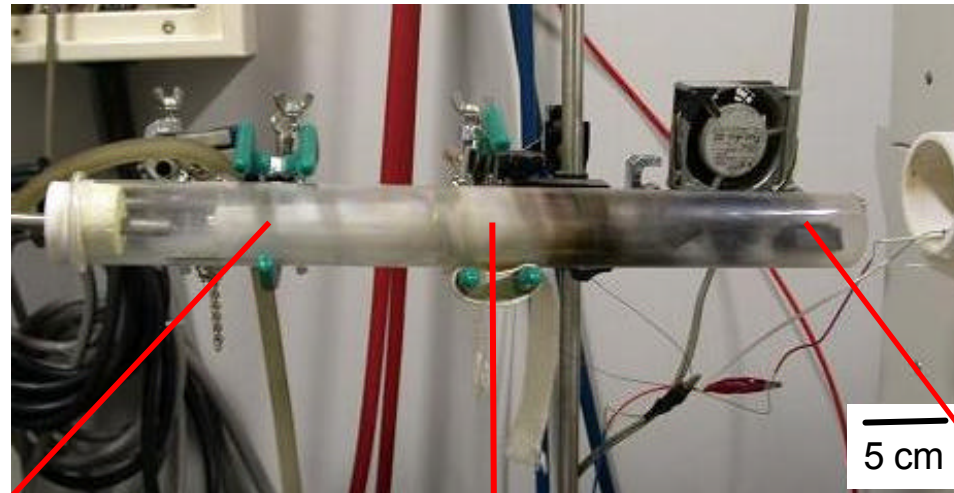
T = 1100 K,

t' = 6 h,

Graphite crucible,

Atmosphere : Ar.

5 cm
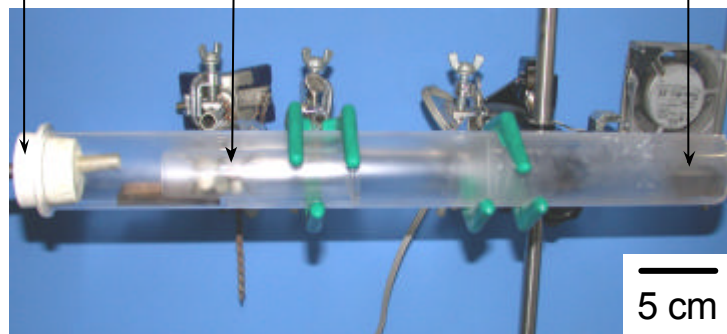
Experimental apparatus for chlorination of titanium using FeCl$_2$ as chlorine source.

Results of chlorine recovery (1)

Assembled Quartz tube after experiment.

5 cm

The form of the obtained residue and deposit after experiment.

Solid (White)

Deposit on the surface of the NaOH gas trap (A)

Flake (Brown)

Deposit inside the quartz tube (B)

Powder (Black)

Residue in the graphite Crucible after heating (C)

The product/mixture of TiCl$_4$ + NaOH

Results of chlorine recovery (2)

Table: Analytical results of the samples before and after heating, and the deposits btained within the quartz tube and on the surface of the NaOH gas trap after heating.

Exp. # CB	Concentration of element i, C_i (mass%)[a]		
	Ti	Fe	Cl
Initial sample in the graphite crucible before heating	23.0	49.5	27.5
Residue in the graphite crucible after heating (C)	9.9	90.1	n.d.
Deposit inside the quartz tube (B)	2.7	54.6	42.7
Deposit on the surface of the NaOH gas trap (A)	43.3	3.3	53.4

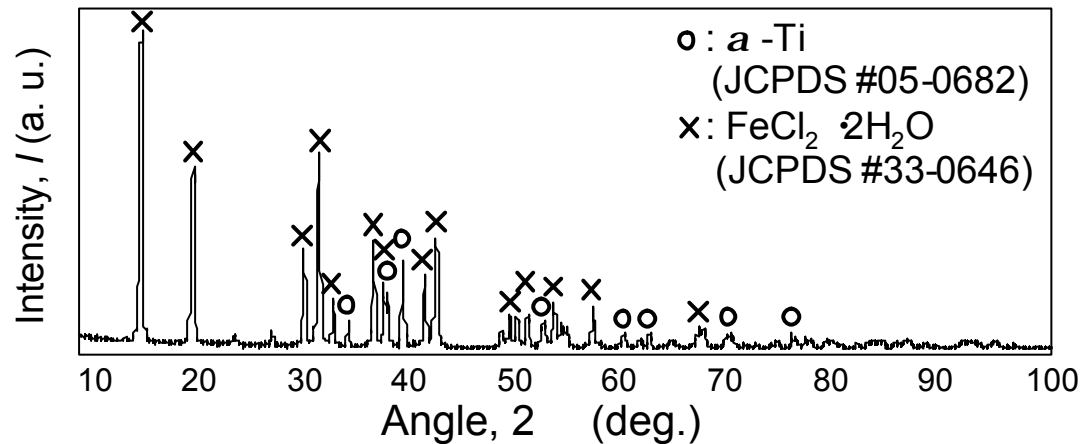a: Determined by XRF analysis, n.d. = not detected (below 0.1%).

Chlorine in $FeCl_2$ was extracted as $TiCl_4$ by metallic Ti .

Fe was generated at heating zone.

Chlorine in $FeCl_x$ was extracted by metallic Ti.

Results of chlorine recovery (3)

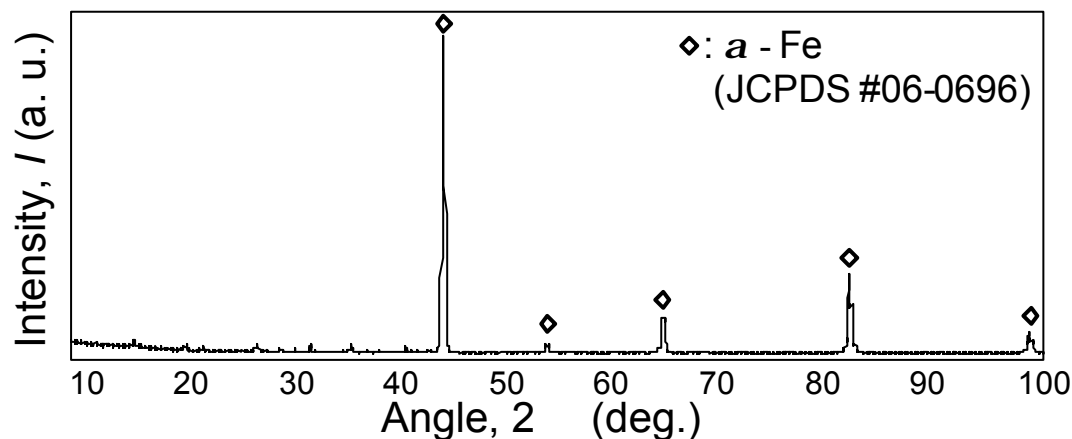THE UNIVERSITY OF TOKYO

XRD patterns of the sample before experiment (a)
and the residue after experiment (b) (Exp. # CB)

(a) Sample mixture before experiment

o : a -Ti (JCPDS #05-0682)
x : $FeCl_2 \cdot 2H_2O$ (JCPDS #33-0646)

$Ti\ (s) + FeCl_2\ (s, l)$

$TiCl_4\ (g) + Fe\ (s)$

(b) Residue obtained after experiment

◇: a - Fe (JCPDS #06-0696)

Fe was generated at heating zone.
Chlorine in $FeCl_x$ was extracted by metallic Ti.

Summary

My study

Main topic

Low-grade Ti ore
(FeTiO$_X$)

MCl$_X$
(Cl$_2$)

FeCl$_X$

Ti scrap

| **Selective chlorination** | | **Chlorine recovery** | |

Upgraded Ti ore
(TiO$_2$)

FeCl$_X$
(+ AlCl$_3$)

Fe

TiCl$_4$

Ti smelting
(e.g., Kroll process or PRP process)

Ti

MCl$_X$
(M = Fe, Al, Si…)
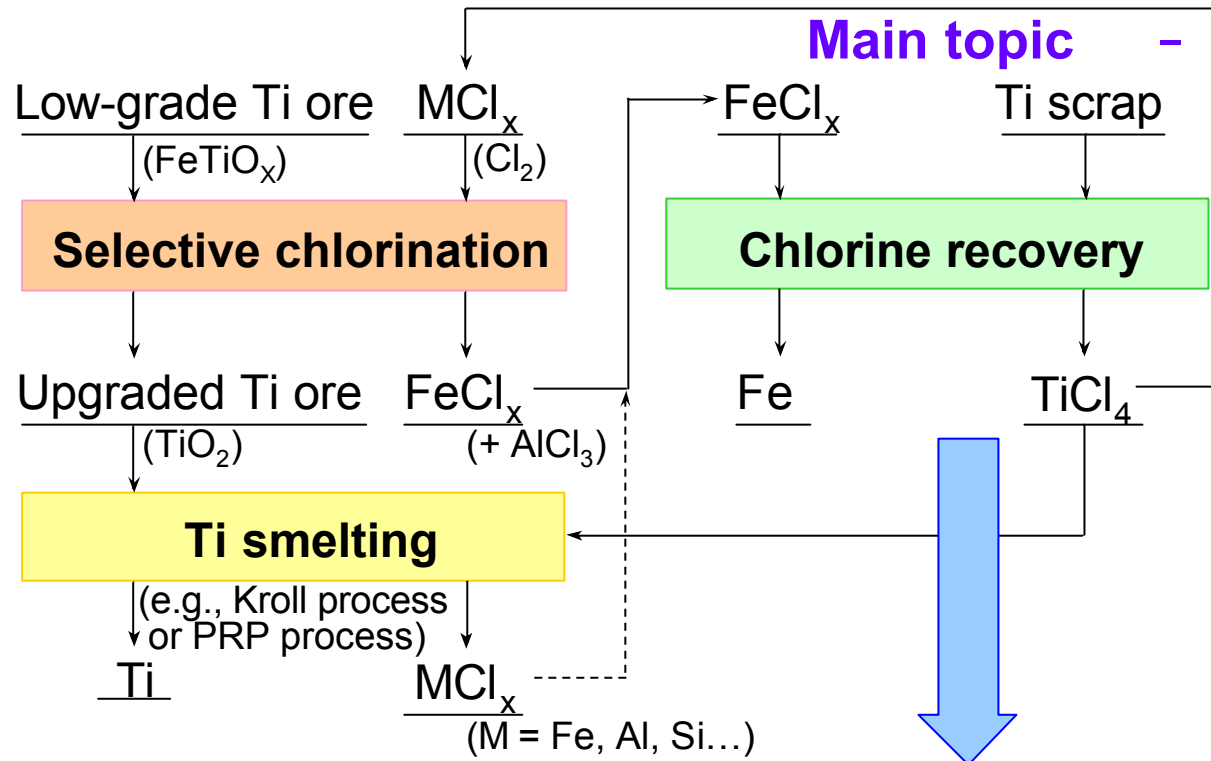
- **The feasibility of the new recycling process of chlorine in the chloride waste by metallic Ti is demonstrated from the thermodynamic viewpoint.**

- **According to the experiment, chlorine recovery from FeCl$_2$ using Ti was demonstrated and TiCl$_4$ can be obtained**

Future Work

1. **The detailed mechanism and the mass balance of the chlorination reactions are under investigation.**

2. **Chloride wastes from the Kroll process will be investigated in the future.**

3. **The recycling process of other reactive metal scraps by chloride waste will be investigated.**

Recycling Titanium Metal Scraps by Utilizing Chloride Wastes

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The University of Tokyo

For Questions

1791

First discovered by William Gregor, a clergyman and amateur geologist in Cornwall, England

1795

Klaproth, a German chemist, gave the name titanium to an element re-discovered in Rutile ore.

1887

Nilson and Pettersson produced metallic titanium containing large amounts of impurities

1910

M. A. Hunter produced titanium with 99.9% purity by the sodiothermic reduction of $TiCl_4$ in a steel vessel.

 (119 years after the discovery of the element)

1946

W. Kroll developed a commercial process for the production of titanium: Magnesiothermic reduction of $TiCl_4$.

Titanium was not purified until 1910, and was not produced commercially until the early 1950s.

Titanium is the 10th most abundant element in the earth's crust

Rank	Element	Clark #.
1	^{8}O	49.50
2	^{14}Si	25.80
3	^{13}Al	7.56
4	^{26}Fe	4.70
5	^{20}Ca	3.39
6	^{11}Na	2.63
7	^{19}K	2.40
8	^{12}Mg	1.93
9	^{1}H	0.87
10	**^{22}Ti**	**0.46**
11	^{17}Cl	0.19
12	^{25}Mn	0.09
13	^{15}P	0.08
14	^{6}C	0.08
15	^{16}S	0.03

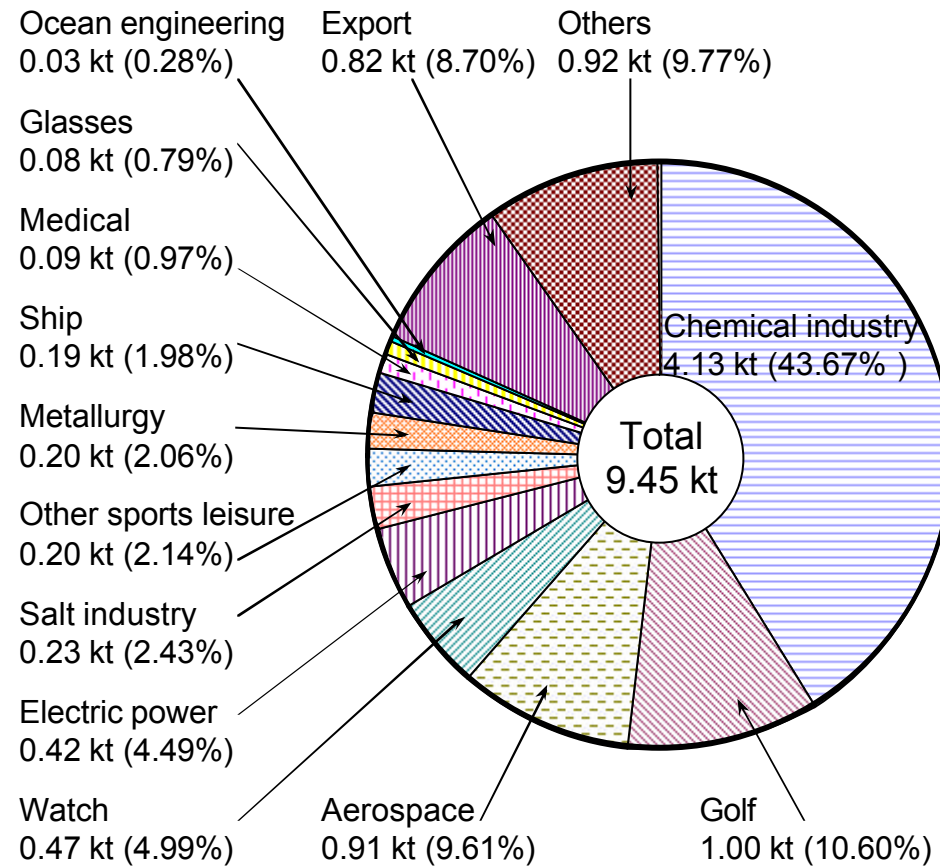| Rank	Element	Clark #.
16	^{7}N	0.03
17	^{9}F	0.03
18	^{39}Rb	0.03
19	^{56}Ba	0.02
20	^{40}Zr	0.02
21	^{24}Cr	0.02
22	^{38}Sr	0.02
23	^{23}V	0.02
24	^{28}Ni	0.01
25	^{29}Cu	0.01
26	^{74}W	6×10^{-3}
27	^{3}Li	6×10^{-3}
28	^{58}Ce	4.5×10^{-3}
29	^{27}Co	4×10^{-3}
30	^{50}Sn	4×10^{-3}

The tenth most abundant element
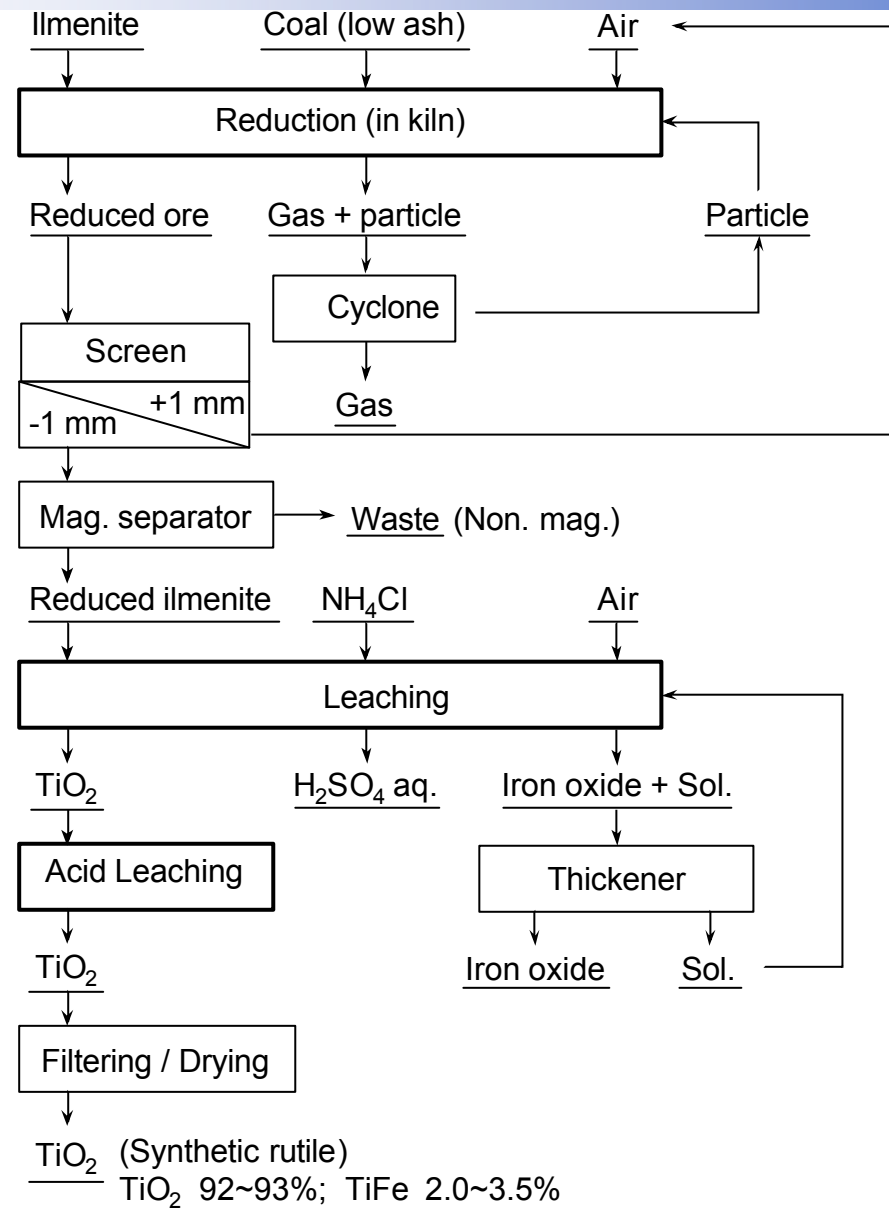
Exhausting element…
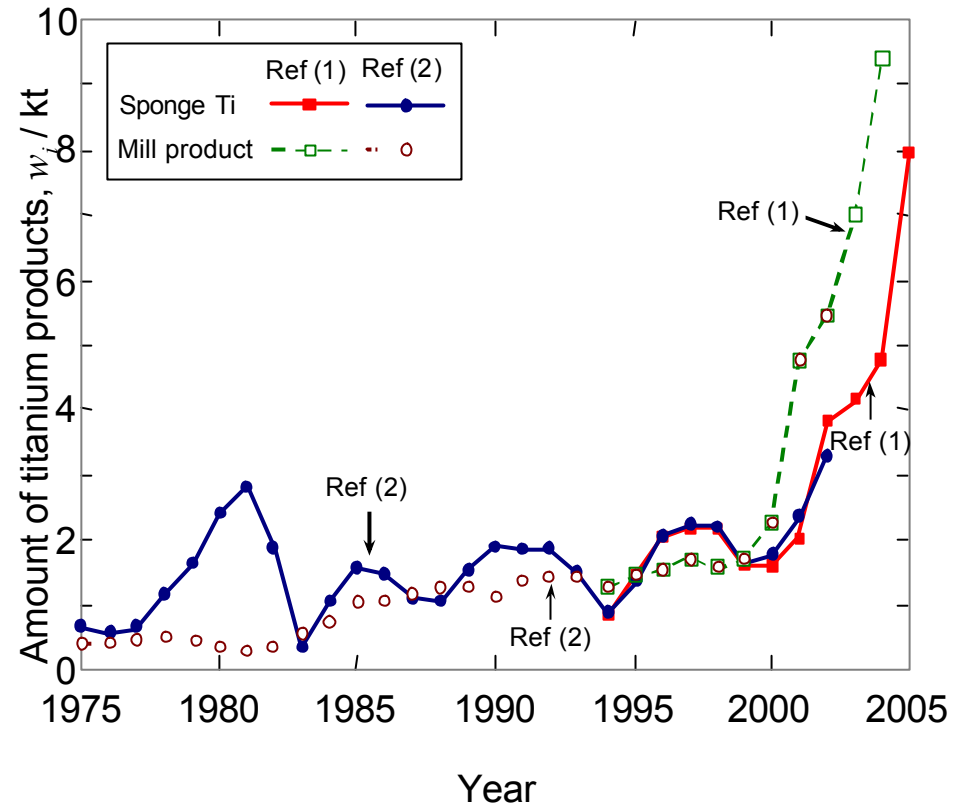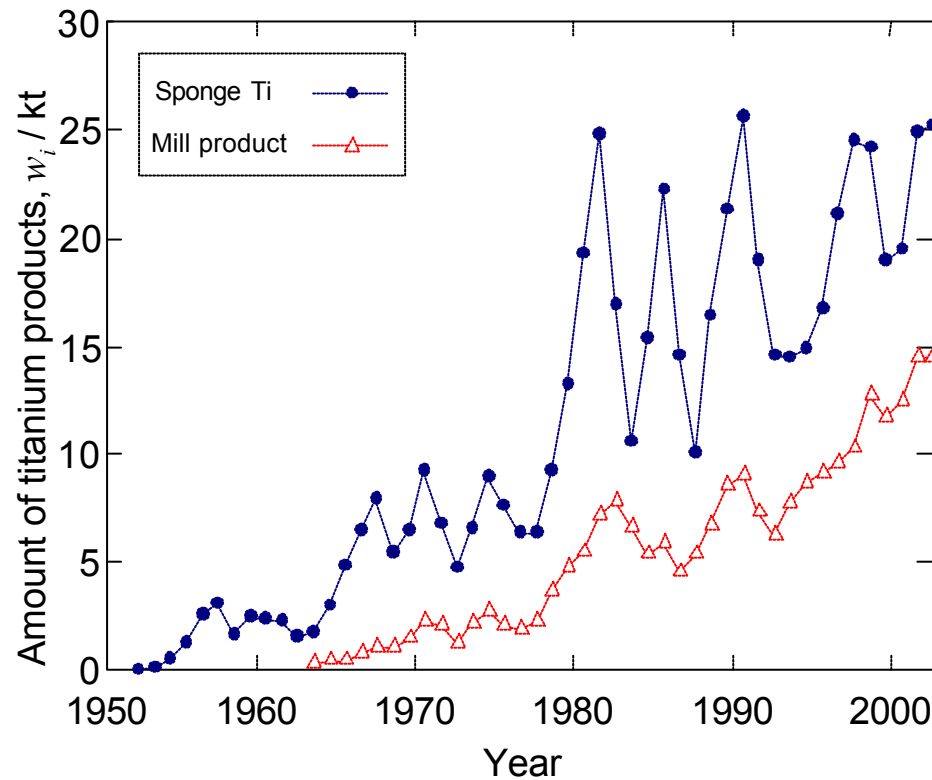
Transition of production volume of titanium sponge and mill products in China.
Ref(1): China Titanium Association (Courtesy of Mr. Akiyama, JTS)
Ref(2): China Titanium Association (H. Z., Private communication)

Ocean engineering
0.03 kt (0.28%)

Export
0.82 kt (8.70%)

Others
0.92 kt (9.77%)

Glasses
0.08 kt (0.79%)

Medical
0.09 kt (0.97%)

Ship
0.19 kt (1.98%)

Metallurgy
0.20 kt (2.06%)

Other sports leisure
0.20 kt (2.14%)

Salt industry
0.23 kt (2.43%)

Electric power
0.42 kt (4.49%)

Watch
0.47 kt (4.99%)

Aerospace
0.91 kt (9.61%)

Golf
1.00 kt (10.60%)

Chemical industry
4.13 kt (43.67%)

Total
9.45 kt

Shipments of titanium mill product in various field's application in China (2004).

Ilmenite   Coal (low ash)   Air

Reduction (in kiln)

Reduced ore   Gas + particle   Particle

Cyclone

Screen

+1 mm
-1 mm

Gas

Mag. separator → Waste (Non. mag.)

Reduced ilmenite NH_4Cl Air

Leaching

TiO_2 H_2SO_4 aq.   Iron oxide + Sol.

Acid Leaching

Thickener

TiO_2 Iron oxide   Sol.

Filtering / Drying

TiO_2 (Synthetic rutile)
TiO_2 92~93%; TiFe 2.0~3.5%

Flowchart of the Beacher process.

Ilmenite   Reductant (Heavy oil etc.)
                            Fe^{2+} / TFe = 80~95%

┌───┐
│   Reduction (in kiln)   │   (18~20% HCl)
└───┘

Reduced ore   HCl aq.   HCl vapor

┌───┐
│   Leaching (in digestor)   │
└───┘

145C° (2.5 kg/cm^2) *4 hr
                    *2 step

Leached ilmenite   Water   Spray acid   Fuel

┌──────────────────────────┐   ┌──────────────────────────┐
│   Filtration   │   │   Roasting   │
└──────────────────────────┘   └──────────────────────────┘

TiO$_2$ Sol.   Iron oxide   HCl
                                     (90% purity)

┌──────────────────────────┐   ┌──────────────────────────┐
│   Calcination   │   │   Absorber   │
└──────────────────────────┘   └──────────────────────────┘

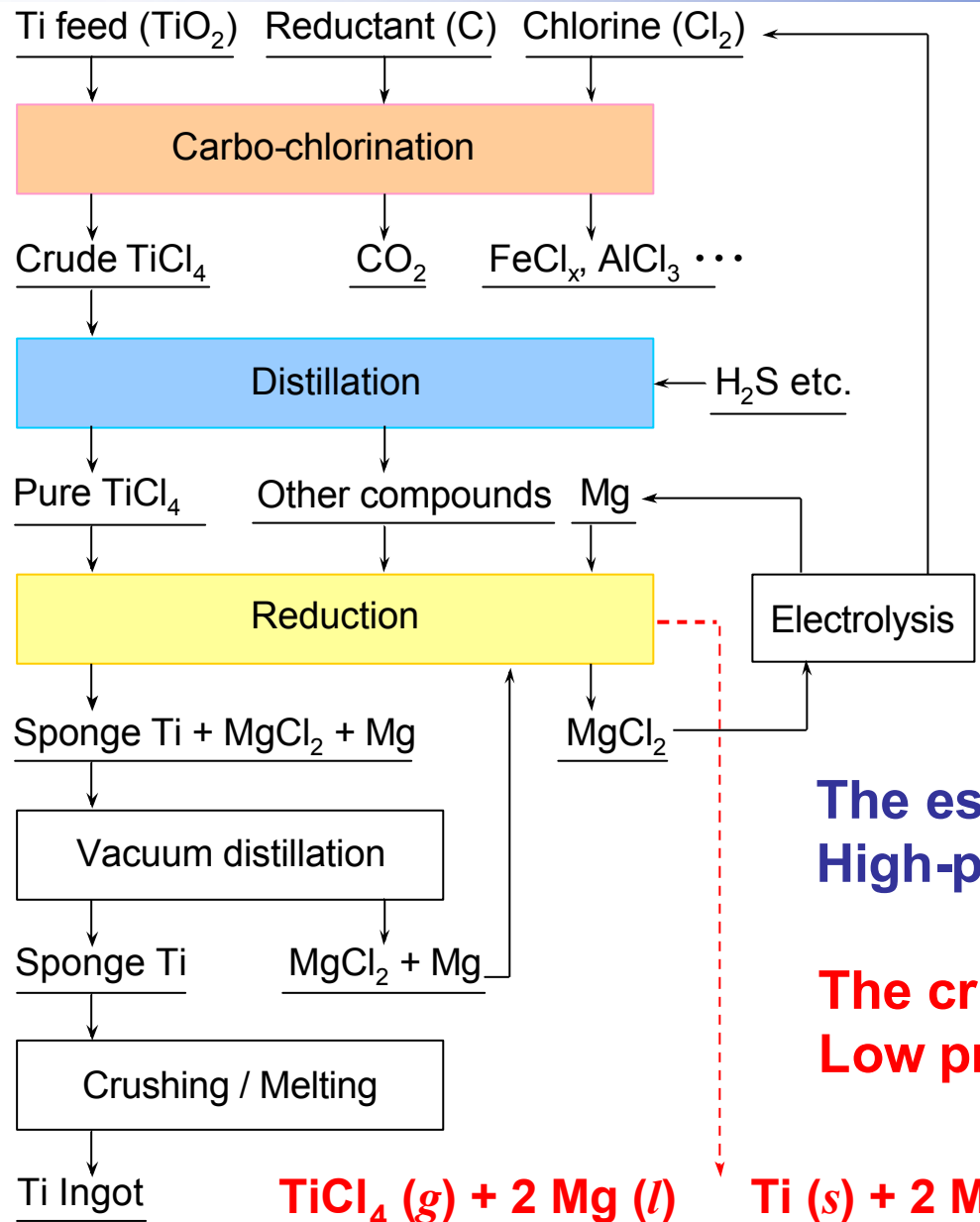TiO$_2$ (Synthetic rutile)   HCl aq.
     95%   TiO$_2$
     1%   TiFe
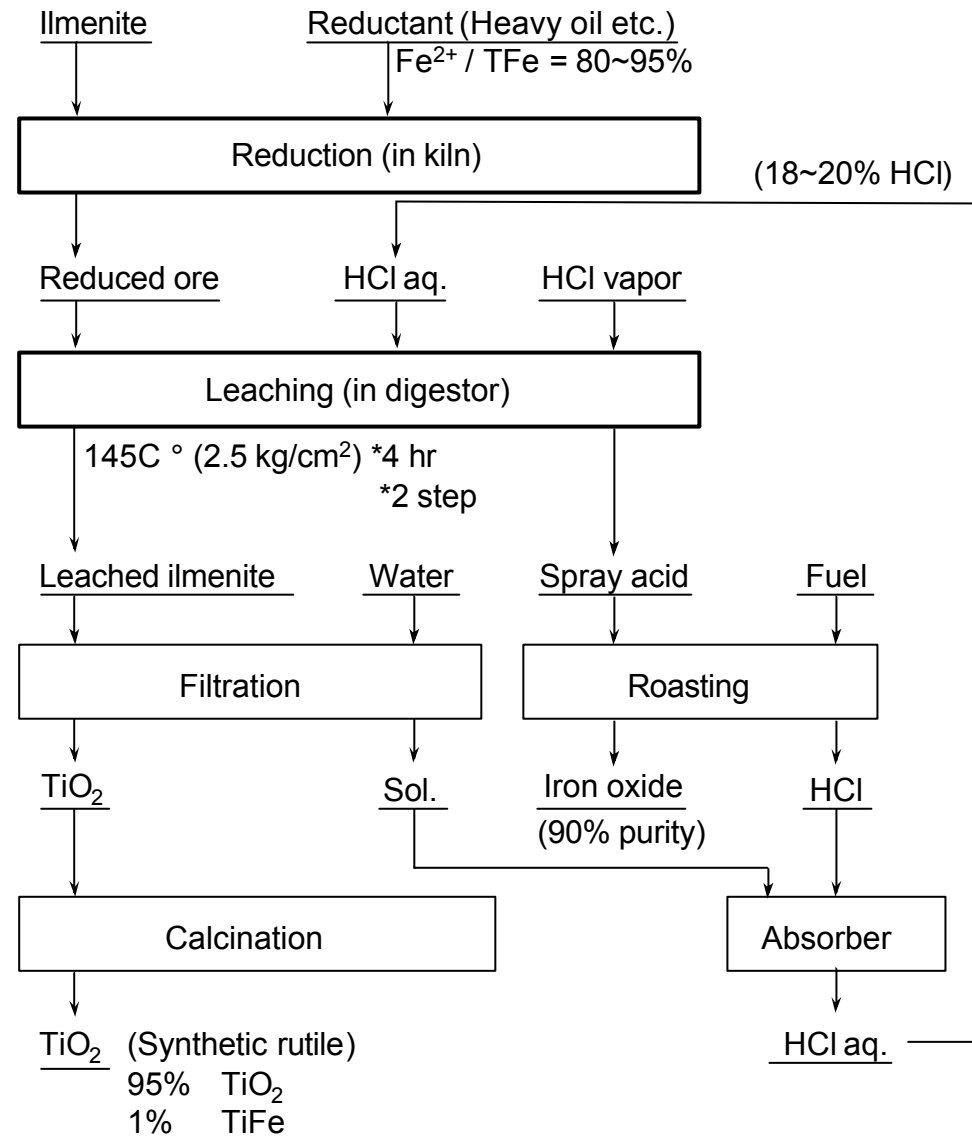
Flowchart of the Benilite process.

Features of reductant and feed materials in metallothermic reduction process.

	$TiCl_4$	TiO_2
Mg	Possible to remove Mg and $MgCl_2$ by distillation. Possible to efficiently eletrosis $MgCl_2$ Easy to control purity (strong contamination of carbon)	× Impossible to remove oxygen
Na	Difficult to remove Na Difficult to control the temperature Easy to purity control (strong resistance to Ni contamination)	× Impossible to remove oxygen
Ca	High enegy loss Difficult to remove Ca or $CaCl_2$ Cost of the reductant production Process with strong resistace to Oxygen	Difficult to purity control Difficult to remove Ca or $CaCl_2$ Cost of the reductant production

The Kroll process

Ti feed (TiO_2)   Reductant (C)   Chlorine (Cl_2)

Carbo-chlorination

Crude $TiCl_4$ CO_2 $FeCl_x$, $AlCl_3$

Distillation ← H_2S etc.

Pure $TiCl_4$ Other compounds   Mg

Reduction ---- Electrolysis

Sponge Ti + $MgCl_2$ + Mg $MgCl_2$

Vacuum distillation

Sponge Ti $MgCl_2$ + Mg

Crushing / Melting

Ti Ingot

**The essential advantage:
High-purity titanium available.**

**The critical disadvantage:
Low productivity.**

$TiCl_4$ (g) + 2 Mg (l)   Ti (s) + 2 $MgCl_2$ (l)

Table Gibbs energy change of formation and reaction in the Fe-Ti-O system.

Reactions	Gibbs energy change,		G°_f or	G°_r (kJ/mol)	Ref.
	1100 K	1200 K	1300 K	1273 K[a]	
Fe (s) + 0.5 O$_2$ (g) = FeO (s)	-200.709	-194.362	-187.999	-189.717	1
	-192.476	-185.817	-179.133	-180.937	2
	-200.670	-271.184	-270.265	-189.667	4
	-190.021	-183.792	-177.563	-179.244	8
Ti (s) + O$_2$ (g) = TiO$_2$ (s)	-744.912	-727.229	-709.392	-714.208	1
	-745.367	-727.312	-709.436	-714.262	2
	-744.807	-727.113	-709.265	-714.084	4
	-742.567	-724.883	-707.200	-711.975	7
	-717.417	-700.250	-683.083	-687.718	8
Fe (s) + Ti (s) + 1.5 O$_2$ (g) = FeTiO$_3$ (s)	-956.608	-931.690	-906.600	-913.374	1
2 Fe (s) + Ti (s) + 2 O$_2$ (g) = Fe$_2$TiO$_4$ (s)	-1164.697	-1133.483	-1102.214	-1110.66	1
	-1164.870	-1133.57	-1102.23	-1110.69	2
TiO$_2$ (s) + Fe (s) + 0.5 O$_2$ (g) = FeTiO$_3$ (s)	-211.696	-204.461	-197.208	-199.166	1
				-202.3	5
	-209.946	-204.558	-199.171	-200.625	8
TiO$_2$ (s) + 2 Fe (s) + O$_2$ (g) = Fe$_2$TiO$_4$ (s)	-417.785	-406.254	-392.822	-396.452	1
	-419.503	-406.258	-392.794	-396.428	2
				-393.2	5
TiO$_2$ (s) + FeO (s) = FeTiO$_3$ (s)	-10.987	-10.099	-9.209	-9.449	1
	-26.462	-25.05	-24.638	-24.749	3
	-17.829	-18.955	-20.081	-19.777	6
	-20.042	-18.833	-17.625	-17.951	7
				-12.6	1, 5
				-21.4	2, 5
				-12.6	4, 5
				-23.1	5, 8
				-21.381	8
TiO$_2$ (s) + 2 FeO (s) = Fe$_2$TiO$_4$ (s)	-18.367	-17.53	-17.022	-17.018	1
	-34.551	-34.707	-34.528	-34.554	2
				-13.8	1, 5
				-31.3	2, 5
				-13.9	4, 5
				-34.7	5, 8

a: interpolated

References

[1] I. Barin, Thermochemical Data of Pure Substances, 3rd ed., (Weinheim, Federal Republic of Germany, VCH Verlagsgesellschaft mbH, 1997).

[2] Outokumpu HSC Chemistry® for Windows, Version 5.0, (Finland, Outokumpu Research Oy Information Service, 2002).

[3] O. Knacke, O. Kubaschewski, and K. Hesselmann, Thermochemical Properties of Inorganic Substances, 2nd ed., (Berlin, Federal Republic of Germany, Springer-Verlag, 1991).

[4] NIST-JANAF Thermochemical Tables 4th ed., U.S. Bureau of Standards (1998).

[5] S. Ito, Phase Equilibria of the Titanium-Iron-Oxygen system as 1,273 K on Titanium Extraction Processing, (Journal of the Mining and Materials Processing Institute of Japan (Vol. 112, p.867-972, 1996).

[6] J. S. J. Van Devender, Kinetics of Selective Chlorination of ilmenite, (Thermochimica Acta, vol. 124, p. 205-215, 1988).

[7] Special Lecture for the Process Design of the Recycling Material, Distributed Documents, (Summer term, 2003)

[8] O. Kubaschewski, High Temp. High pressures 4.1 (1972).

a: Interpolated
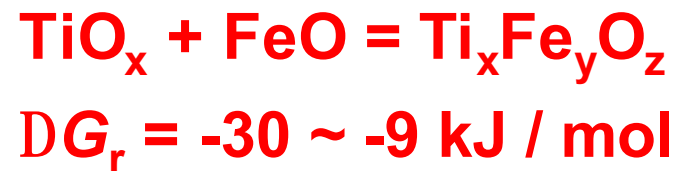
$$TiO_x + FeO = Ti_xFe_yO_z$$

$$\Delta G_r = -30 \sim -9 \text{ kJ / mol}$$

. Selective chlorination

(Upgrading low-grade titanium ore using $CaCl_2$)

FeO_x ($FeTiO_x$, s) + HCl (g) $FeCl_x$ (g)   + H_2O (g)

FeO_x ($FeTiO_x$, s) + $CaCl_2$ (s, l) $FeCl_x$ (g)   + CaO ($CaTiO_x$, s)

. Chlorine recovery

(Recovery of chlorine from chloride wastes by utilizing titanium scraps)

$FeCl_x$ (l, g) + Ti (s)   Fe (or FeTi, s)+ $TiCl_4$ (g)

. Selective chlorination

(Upgrading low-grade titanium ore using $CaCl_2$)

FeO_x ($FeTiO_x$, s) + HCl (g)　　　$FeCl_x$ (g)　+ H_2O (g)

FeO_x ($FeTiO_x$, s) + $CaCl_2$ (s, l)　　$FeCl_x$ (g)　+ CaO ($CaTiO_x$, s)

FeO$_x$ chlorination (Ti ore: mixture of TiO$_x$ and FeO$_x$.)

Fe-Cl-O system, T = 1100 K

CaO (s) / CaCl$_2$ (l) eq.
H$_2$O (g) / HCl (g) eq.

Fe$_2$O$_3$ (s)

Fe$_3$O$_4$ (s)

FeO (s)

CO (g) / CO$_2$ (g) eq.
C (s) / CO (g) eq.

Fe(s)

FeCl$_3$ (g)

FeCl$_2$ (l)

H$_2$O (g) + CaCl$_2$ (l)
2 HCl (g) + CaO (s)

FeO$_x$ (FeTiOx, s) + HCl (g)
FeCl$_2$ (l, g) + H$_2$O (g)

or

FeO$_x$ (FeTiO$_x$, s) + CaCl$_2$ (l)
FeCl$_x$ (g) + CaO (CaTiO$_x$, s)
$a_{CaO} \ll 1$

FeO$_x$ can be chlorinated
using CaCl$_2$ + H$_2$O.
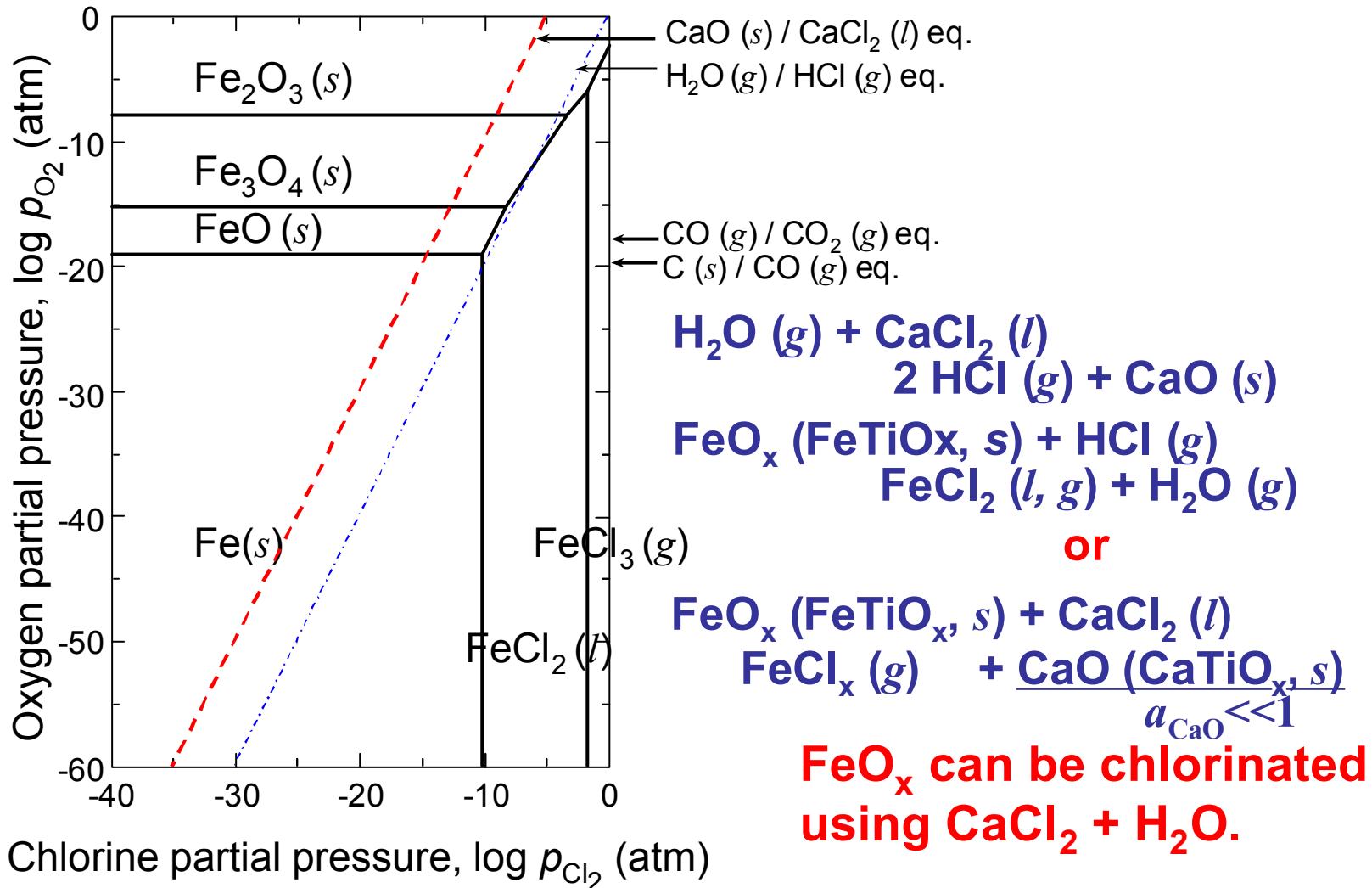
Chemical potential diagram for Fe-Cl-O system at 1100 K.

TiO$_x$ chlorination (Ti ore: mixture of TiO$_x$ and FeO$_x$.)

Ti-Cl-O system, T = 1100 K

CaO (s) / CaCl$_2$ (l) eq.

H$_2$O (g) / HCl (g) eq.

CO (g) / CO$_2$ (g) eq.
C (s) / CO (g) eq.

TiO$_2$ (s) Ti$_4$O$_7$ (s)

Ti$_3$O$_5$ (s)

Ti$_2$O$_3$ (s)

TiO (s)   TiCl$_4$ (g)

TiCl$_3$ (s)

Ti (s)   TiCl$_2$ (s)

Oxygen partial pressure, log p_{O_2} (atm)

Chlorine partial pressure, log p_{Cl_2} (atm)
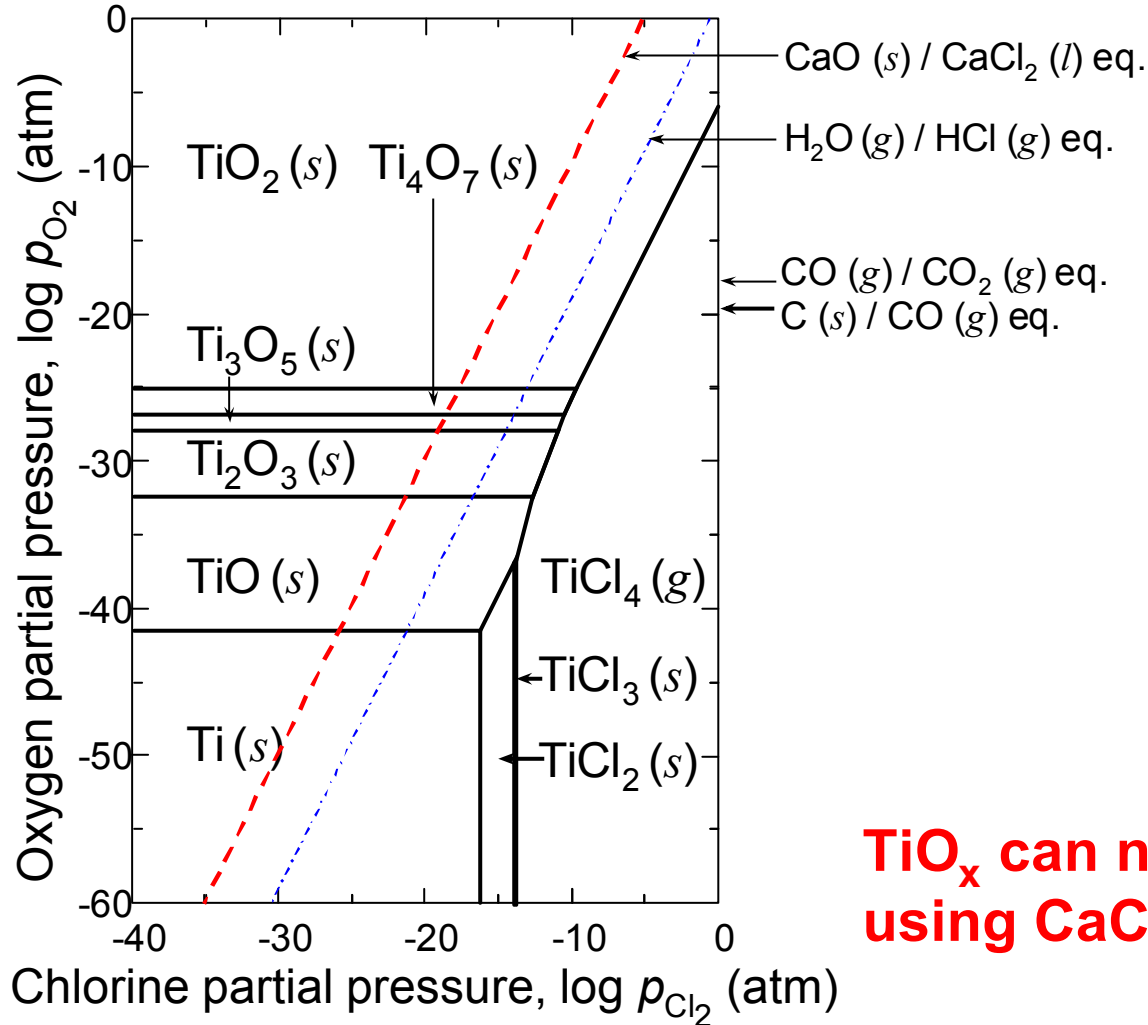
TiO$_x$ can not be chlorinated using CaCl$_2$, nor CaCl$_2$+H$_2$O.

Chemical potential diagram for Ti-Cl-O system at 1100 K.

Ti ore chlorination (Ti ore: mixture of TiO_x and $FeO_{x.}$)

Fe-Cl-O system and Ti-Cl-O system, T = 1100 K

H$_2$O (g) / HCl (g) eq.

CaO (s) / CaCl$_2$ (l) eq.

Potential region for selective chlorination of iron

CO (g) / CO$_2$ (g) eq.
C (s) / CO (g) eq.

FeO_x ($FeTiO_x$, s) + HCl (g)
$FeCl_x$ (g) + H$_2$O (g)

FeO_x ($FeTiO_x$, s) + CaCl$_2$ (l)
$FeCl_x$ (g) + $\underline{CaO (CaTiO_x, s)}$
$a_{CaO} \ll 1$
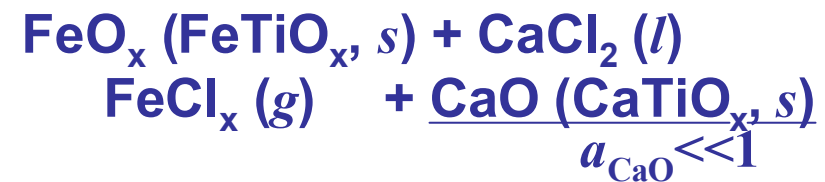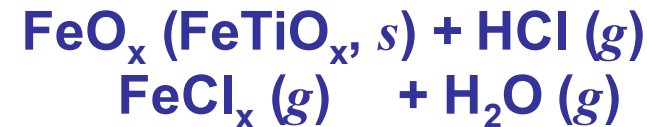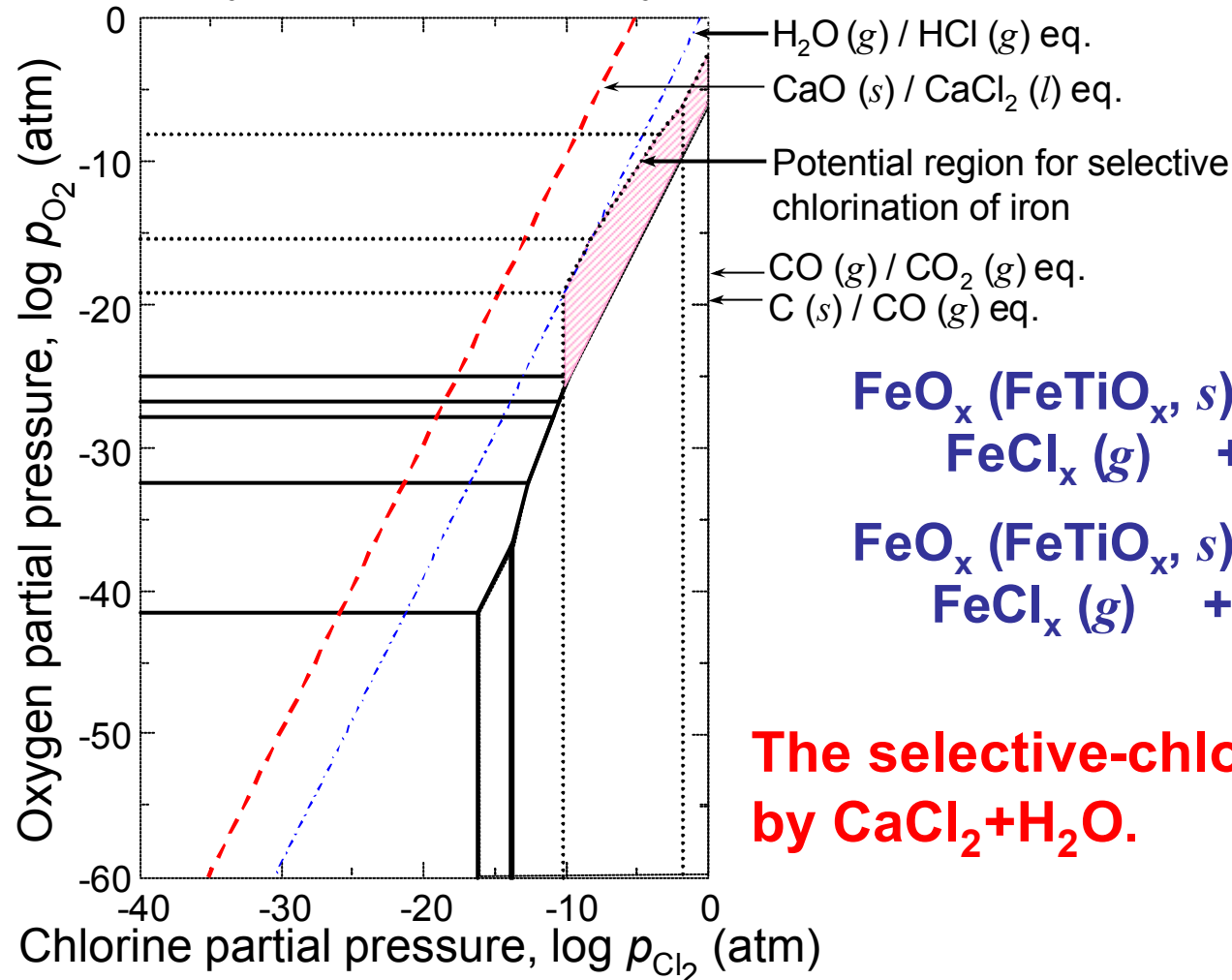
The selective-chlorination of Ti ore by CaCl$_2$+H$_2$O.

Combine d chemical potential diagram for Fe-Cl-O (dotted line) system and Ti-Cl-O system (solid line) at 1100 K.

Results of selective chlorination
(chlorine source: $CaCl_2 + H_2O$)

$$H_2O\ (g) + CaCl_2\ (l) \longrightarrow 2\ HCl\ (g) + CaO\ (s)$$

$$FeO_x\ (s) + HCl\ (g) \longrightarrow FeCl_2\ (l, g) + H_2O\ (g)$$

or

$$FeO_x\ (FeTiO_x,\ s) + CaCl_2\ (l) \longrightarrow FeCl_x\ (g) + CaO\ (CaTiO_x,\ s)$$
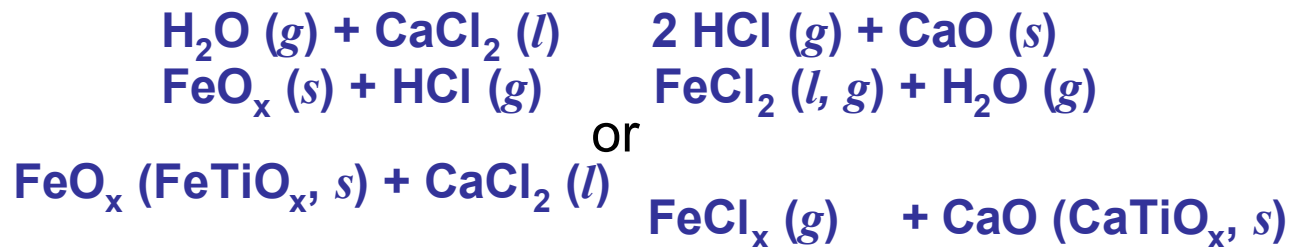
Table: Analytical results of titanium ore and the residue obtained from the selective chlorination of titanium ore. (Exp. # SA)

Sample	Concentration of element i, C_i (mass%)[a]				
	Ti	Fe	Al	Si	V
Ti ore [b]	45.42	53.68	0.07	0.45	0.38
After exp.	77.97	16.32	0.04	4.00	1.66

a: Value determined by XRF analysis.
b: Ilmenite from Vietnam.

Fe was selectively chlorinated.
(Iron removal from the titanium ore was carried out successfully.)

Furthermore, iron concentration levels below 8 % is currently under investigation.

Fe-Cl-O system, T = 900 K
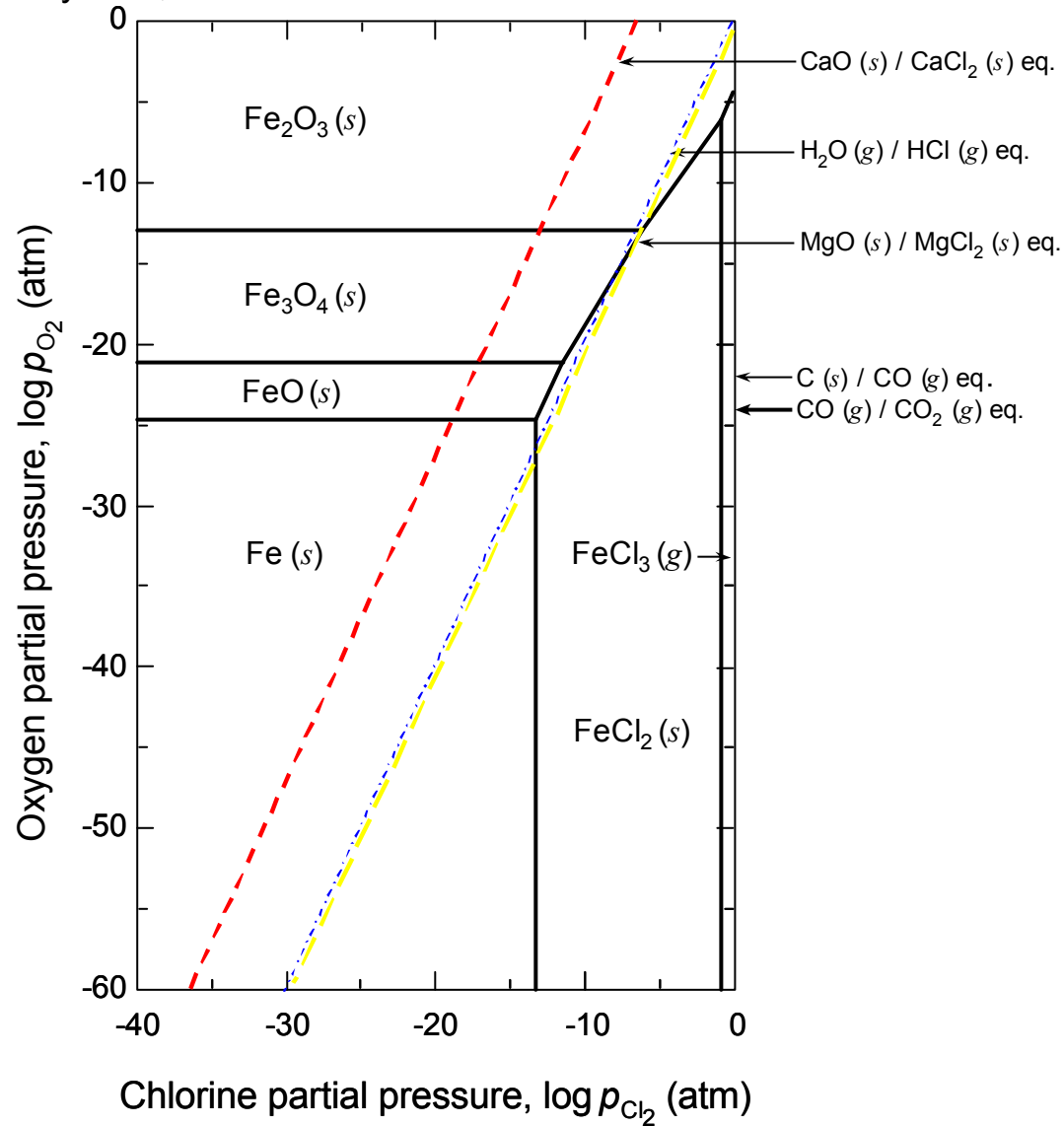
Chemical potential diagram for Fe-Cl-O system at 900 K.

Fe-Cl-O system, T = 1300 K

Chemical potential diagram for Fe-Cl-O system at 1300 K.
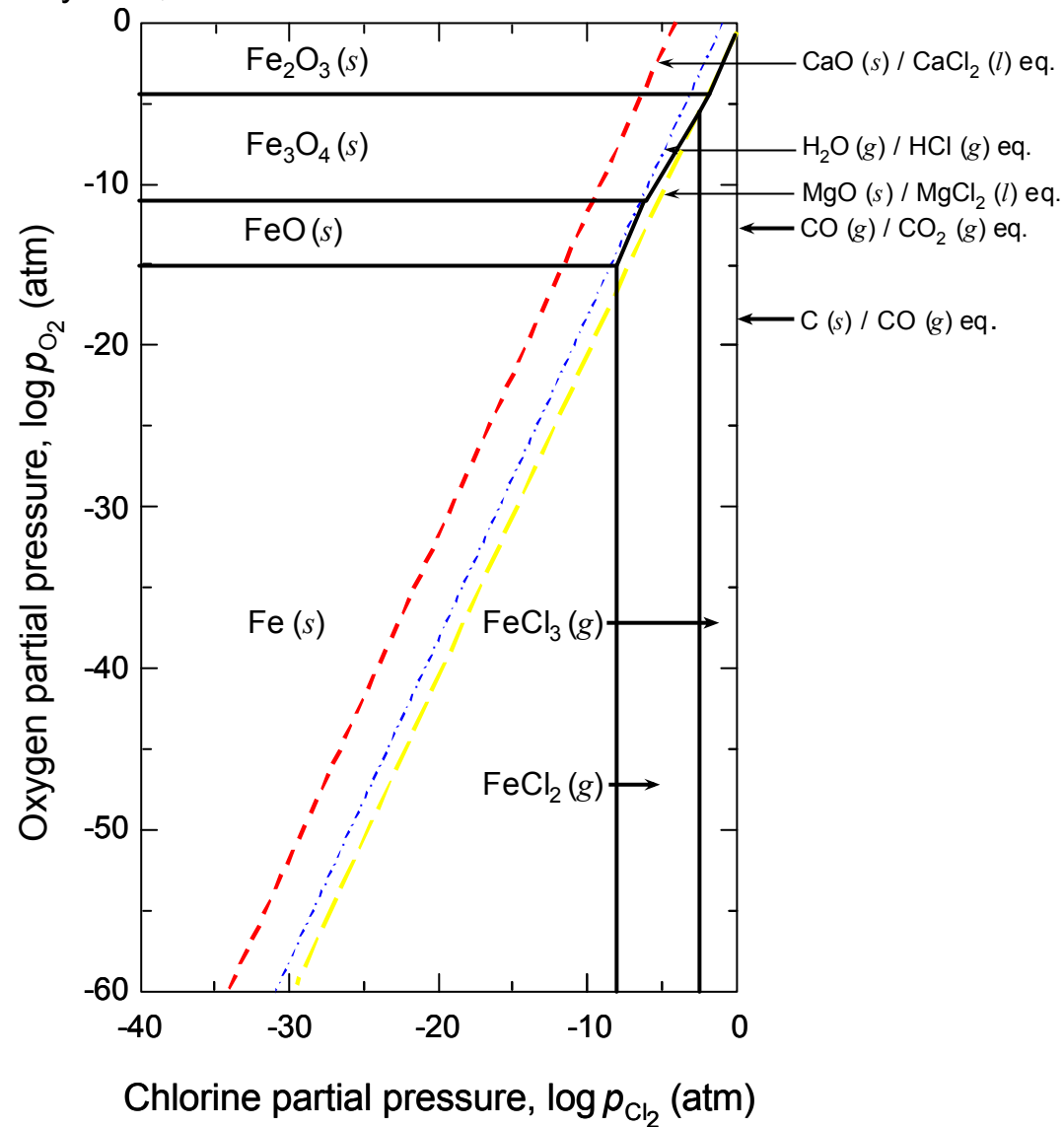
Chemical potential diagram for Ti-Cl-O system at 900 K.
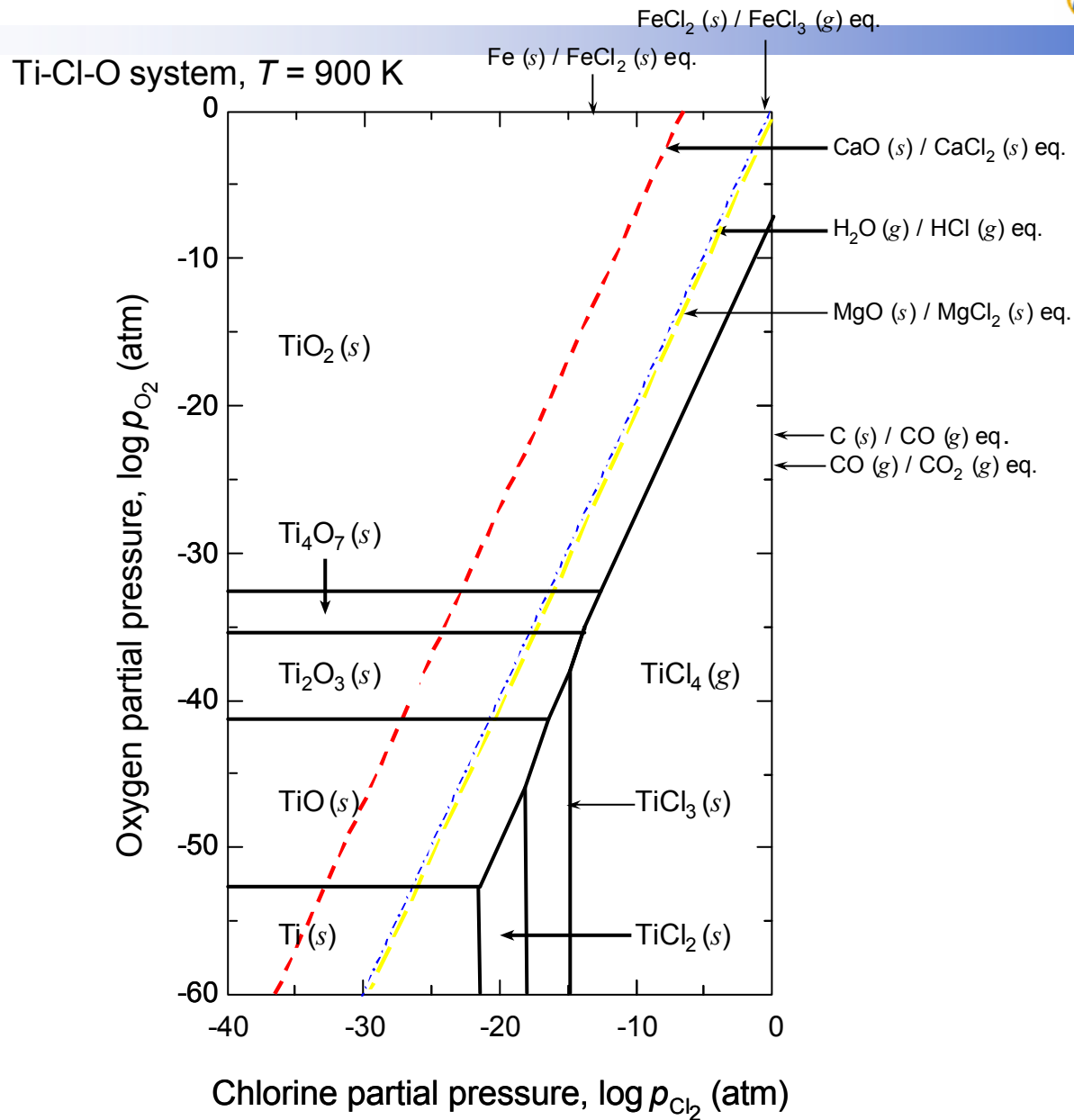
Ti-Cl-O system, *T* = 1300 K
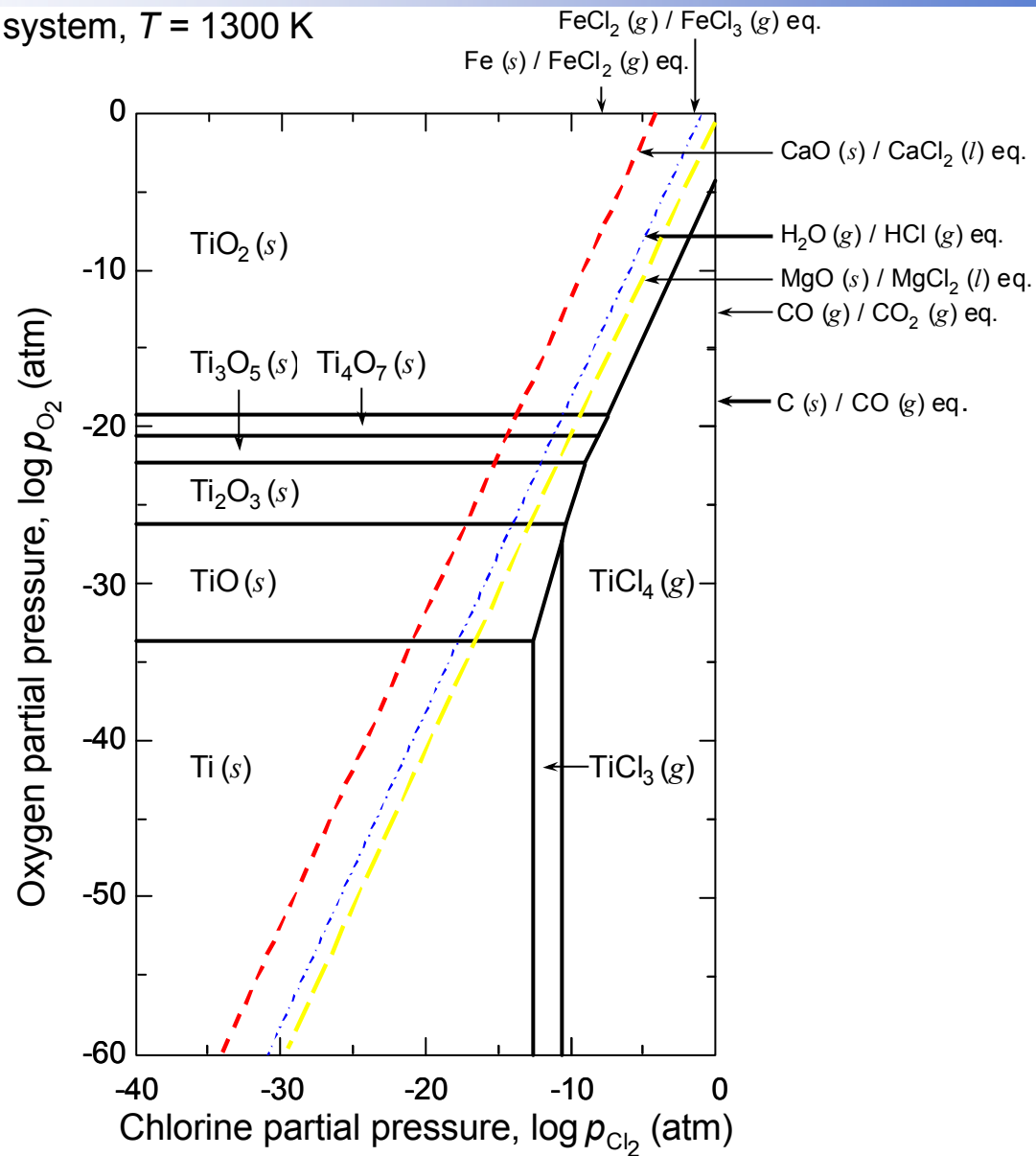
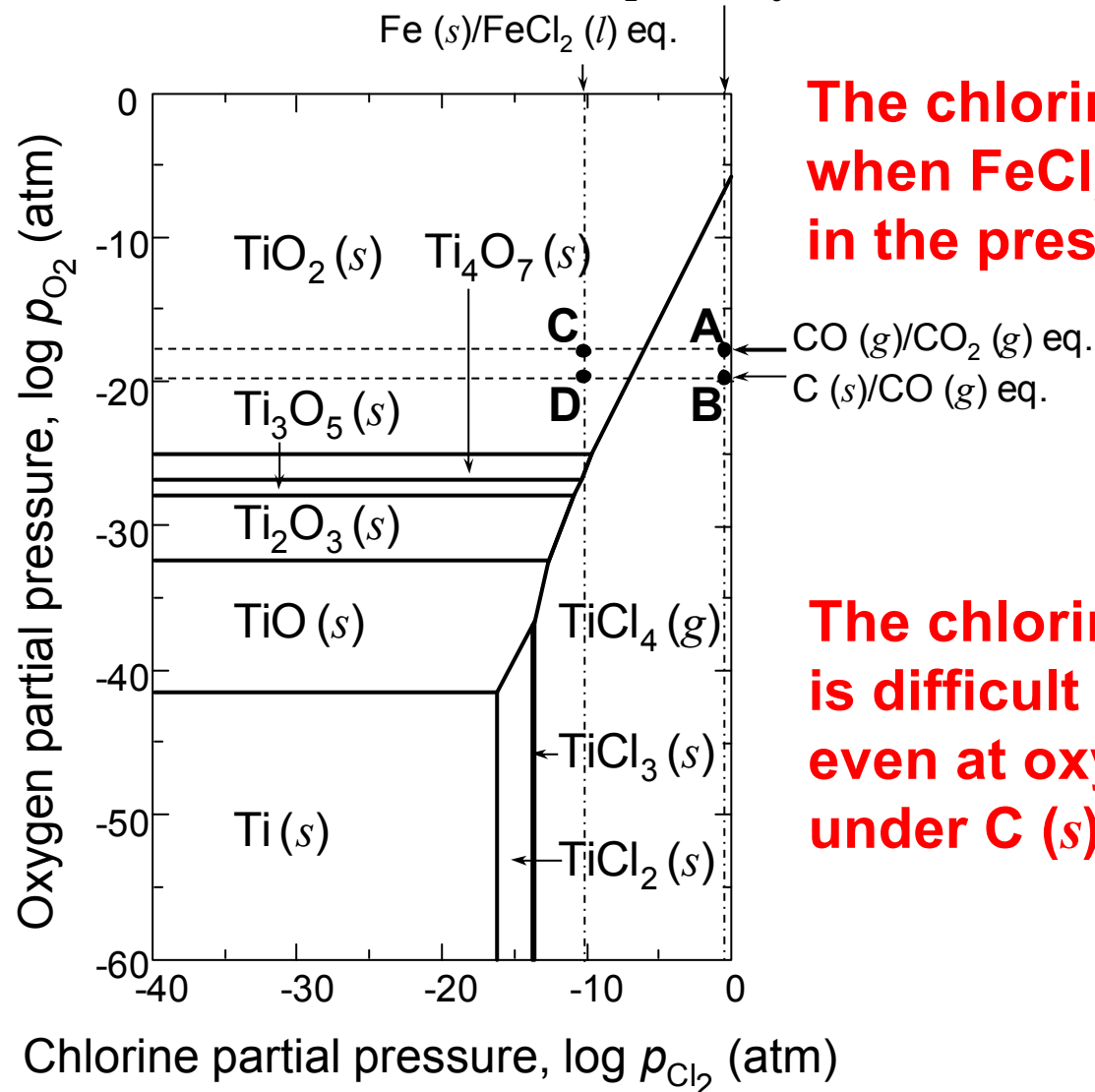
Chemical potential diagram for Ti-Cl-O system at 1300 K.
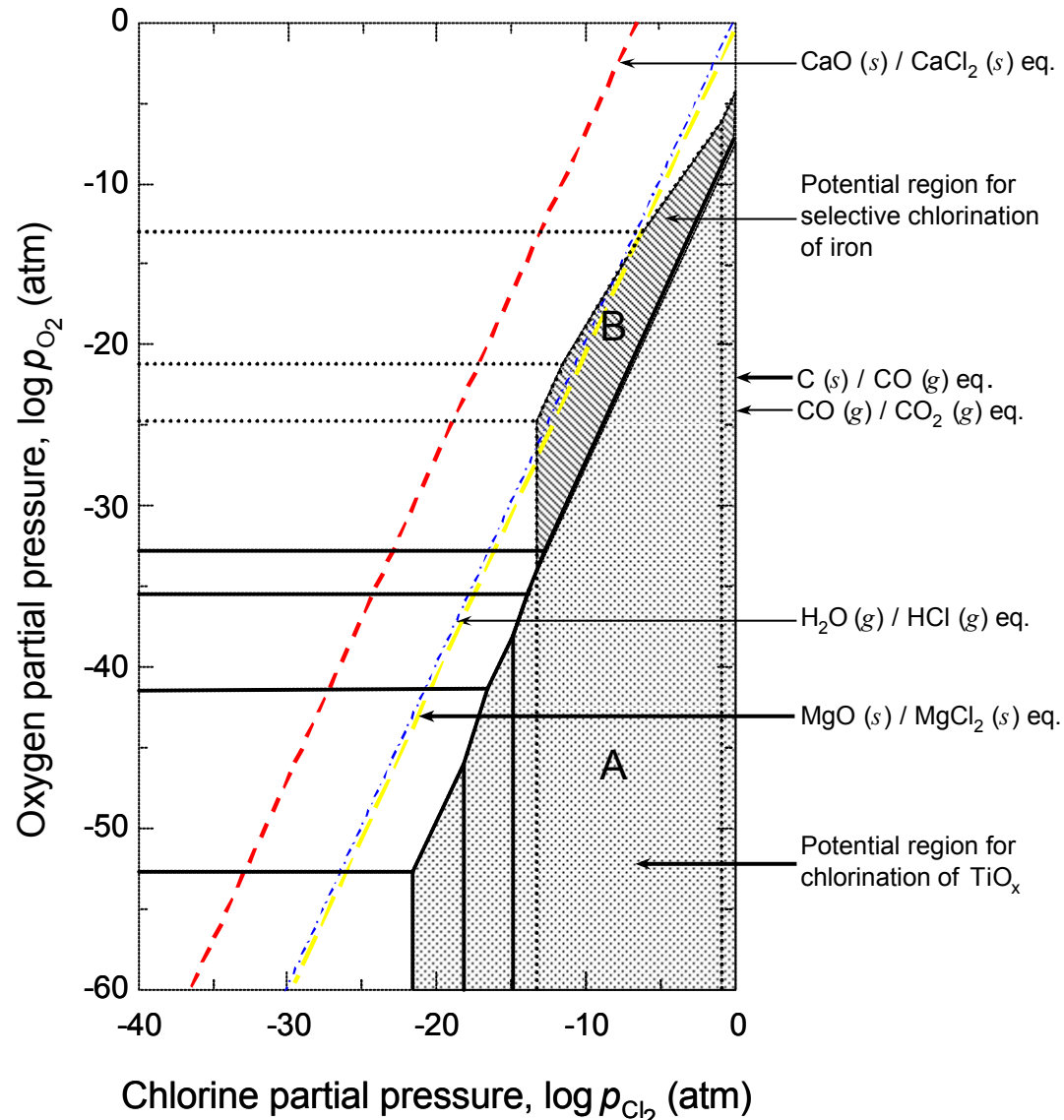
Combined chemical potential diagram of the Fe-Cl-O system
(dotted line) and Ti-Cl-O system (solid line) at 900 K.
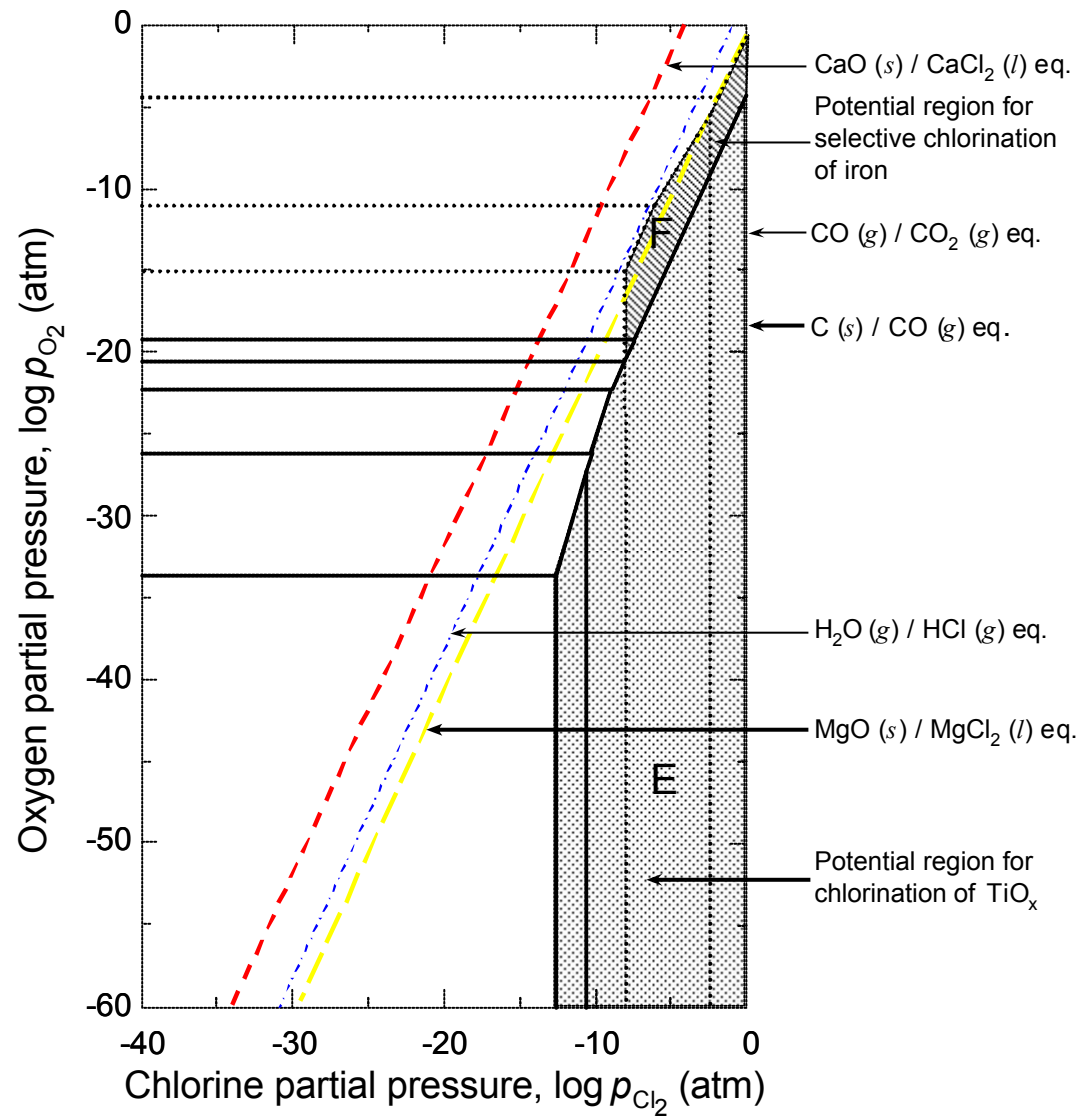
Combined chemical potential diagram of the Fe-Cl-O system (dotted line) and Ti-Cl-O system (solid line) at 1300 K.

Ti-Cl-O system, T = 1100 K

Isothermal chemical potential diagram for the Ti-Cl-O system at 1100 K.
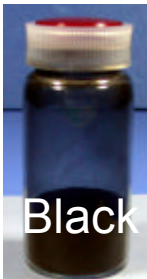
The chlorination of TiO_2 proceeds when $FeCl_3$ is reacted with TiO_2 in the presence of C (s) or CO (g).

The chlorination of TiO_2 by $FeCl_2$ is difficult even at oxygen partial pressure under C (s)/CO (g) equilibrium.
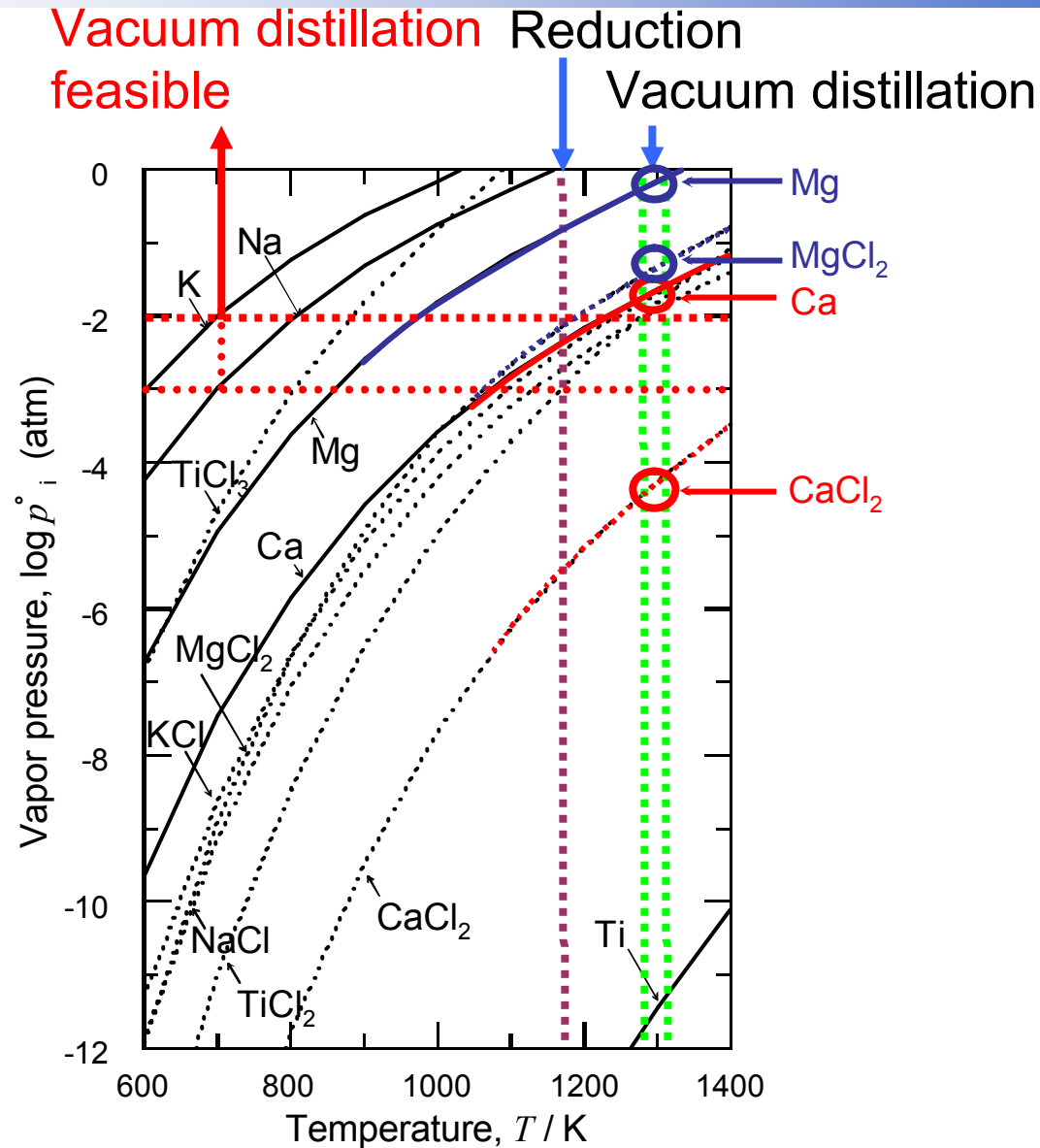
Vapor pressure of several chemical species.
[Ref. I. Barin, Thermochemical Data of Pure Substances, VCH Verlagsgesellschaft, Weinheim, (1989).]

Properties of TiCl$_x$

	TiCl$_4$	TiCl$_3$	TiCl$_2$
Appearance			
Color	Clear	Red	Black
Molecular weight (g/mol)	189.7	154.2	118.8
Density (g/cm^3)	1.70	No data	3.13
Melting point (°C)	−24.1	425	1035
Boiling point (°C)	136.5	–	–
Sublimation point (°C)	–	830	1307
$DG°_f$ at 800°C (kJ/mol Cl$_2$)	−317	−327	−344
$DG'°_f$ at 800°C (kJ/mol Ti)	−637	−491	−344
Vapor pressure at 800°C (atm)	–	0.74	1.2×10^{-4}

Recent research works (PRP)

(Metallothermic reduction process)

Preform Reduction Process

— Feed preform

— Reductant vapor

— Reductant (R = Ca, Mg)

$$TiO_2\ (s) + Ca\ (g) \quad Ti\ (s) + CaO\ (s)$$
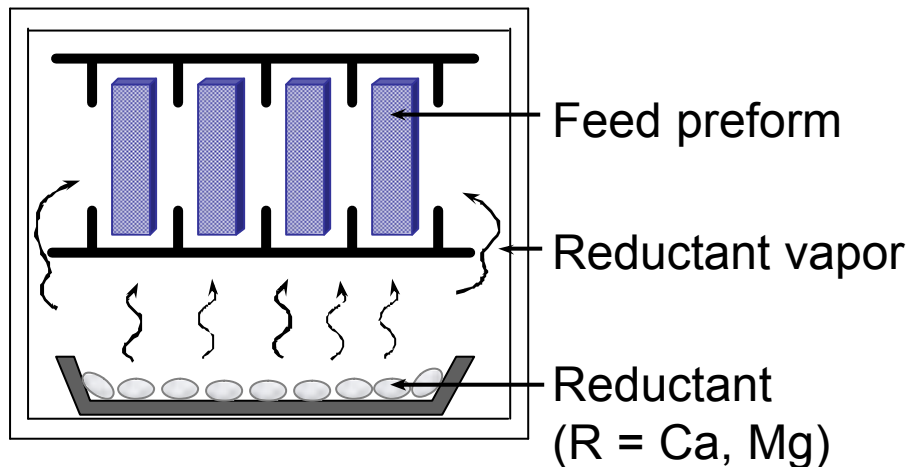
Features of PRP

Merit:

Suitable for uniform reduction

Flexible scalability

Possible to control the morphology of powder by   varying the flux content in the preform

Possible to prevent the contamination from reaction container and control purity

Simple and low cost process

Minimizing amount of waste solution

Demerit:

Leaching required

× Calcium production and control of calcium vapor
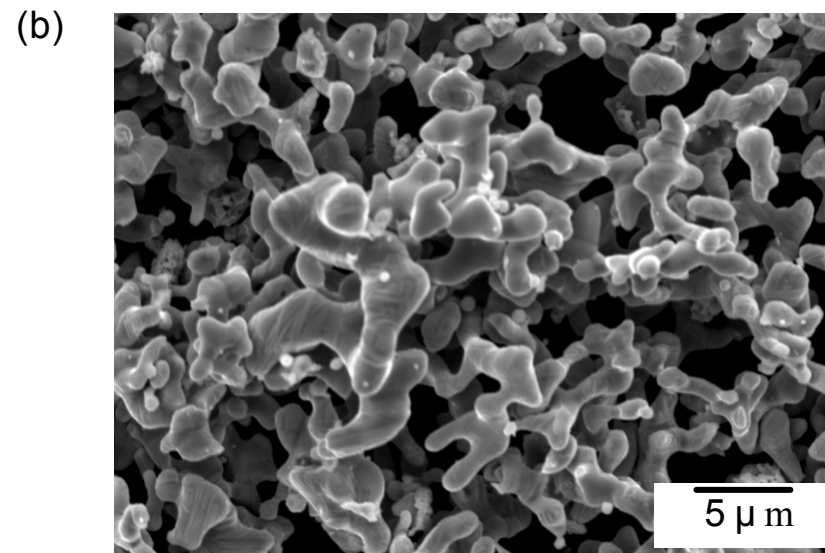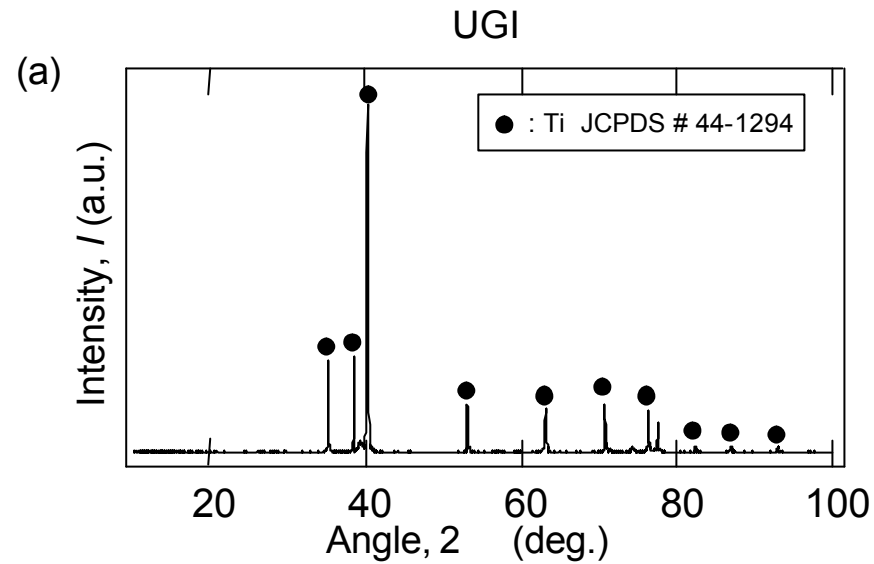
Preform Reduction Process

Feed preform

Reductant vapor
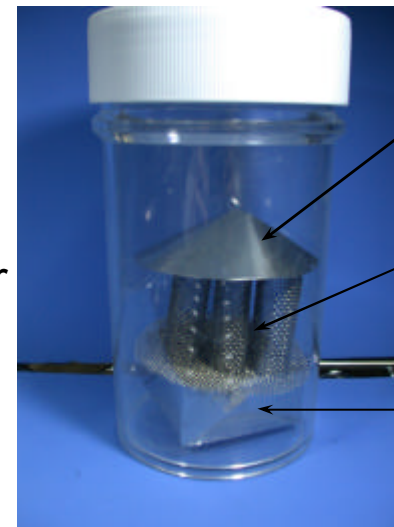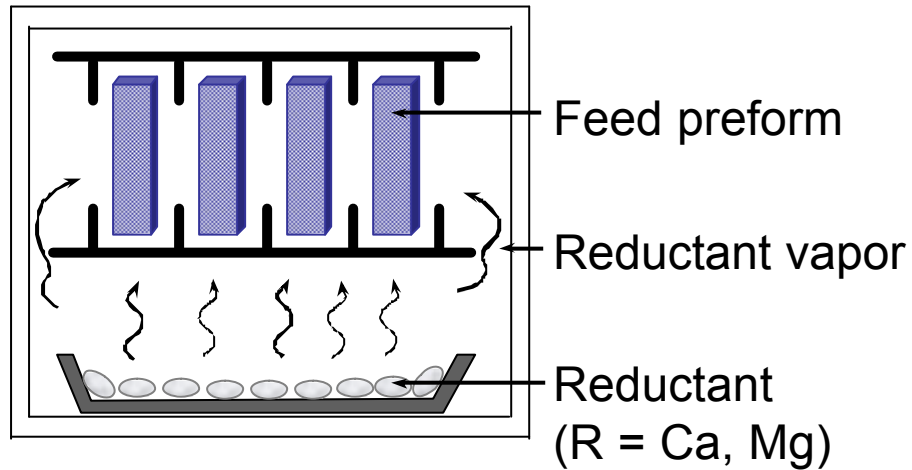
Reductant (R = Ca, Mg)

Stainless steel cover

Stainless steel net holder for preform feed

Stainless steel holder for reductant (Ca, Mg…)

$$TiO_2 + Ca \longrightarrow Ti + 2\,CaO$$

Preform Reduction Process

Ti ore   Flux   Binder

Ti ore: Rutile
Flux: $CaCl_2$
Binder: Collodion

Mixing

↓

Slurry

↓

Preform fabrication

Room temperature, 6h

Feed preform ·········

Calcination/iron removal → $FeCl_X$

1273 K, Alumina Crucible, 1h

Sintered feed preform ·········

Calcium vapor → **Reduction**

1273 K, Airtight SUS Reactor, 6h

Reduced preform ·········

50% CH_3COOH aq.,
20% HC aq.,
Distilled water,
Isopropanol,
Acetone → **Leaching** → Waste solution

↓

Vacuum drying

↓

Powder ·········

Flowchart of preform reduction process (PRP).

UGI

(a)

(b)

(a) XRD pattern of titanium powder obtained by preform reduction process.
(b) Scanning electron microscopic (SEM) image.(Exp. # A-2)
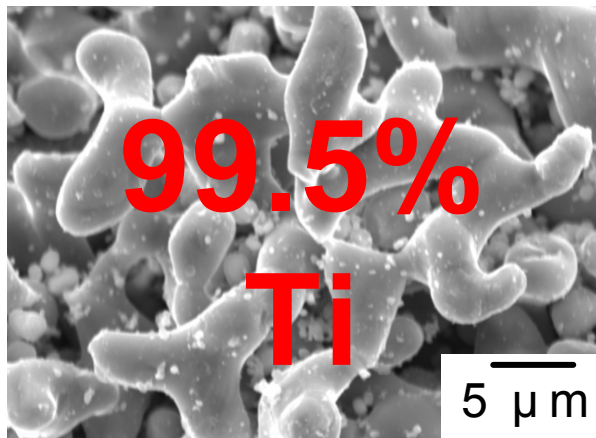
Summary of Ti ore reduction by PRP

Ti ore → **Ti metal powder**

Experiment condition : Reduction temp. $\quad: T$ = 1273 K

Reduction time $\qquad: t'$ = 6 hr

Flux $\qquad\qquad\qquad:$ CaCl$_2$

Cationic molar ratio: $X_{\text{Cat. / T i}}$= 0.3

SEM image

99.5% Ti

5 μm

EDS analysis (mass %)

Ti	Ca	Al	Fe	O
99.5	0.01	0.14	**0.01**	(0.00)

Welcome to Institute of Industrial Science, the University of Tokyo