Iron Removal from Titanium Ore using Selective Chlorination and Effective Utilization of Chloride Wastes

Ryosuke Matsuoka[1] and Toru H. Okabe[2]

[1] Graduate School of Engineering,
The University of Tokyo

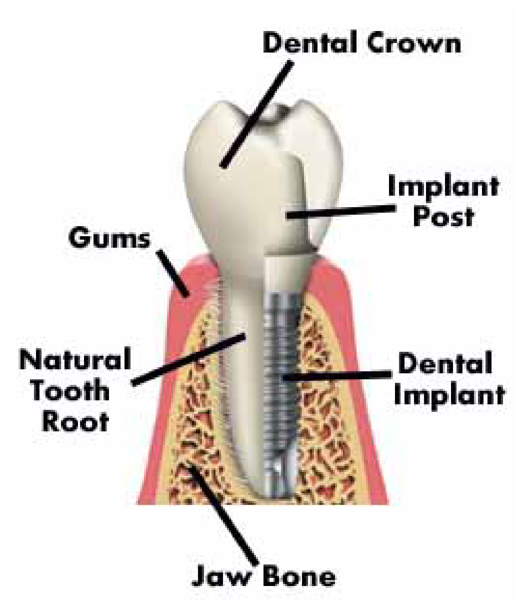
[2] International Research Center for Sustainable Materials,
Institute of Industrial Science,
The University of Tokyo

Titanium ?

Feature of Titanium

1. Light and high-strength
2. Corrosion resistance
3. Biocompatibility
4. Some titanium alloy:
   shape memory alloy
   super elasticity

Japan Aerospace Exploration Agency



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The Kroll process

Kroll process : Ti production process

Chlorination・・・Chlorination of Ti ore

TiO_2 (+ FeO_x) + C + 2 Cl_2 → $TiCl_4$ (+ $FeCl_x$) +CO_2

Reduction・・・Reduction of $TiCl_4$ using Mg

$TiCl_4$ + 2 Mg → Ti + 2 $MgCl_2$

Electrolysis ・・・Electrolysis of $MgCl_2$

$MgCl_2$ → Mg + Cl_2

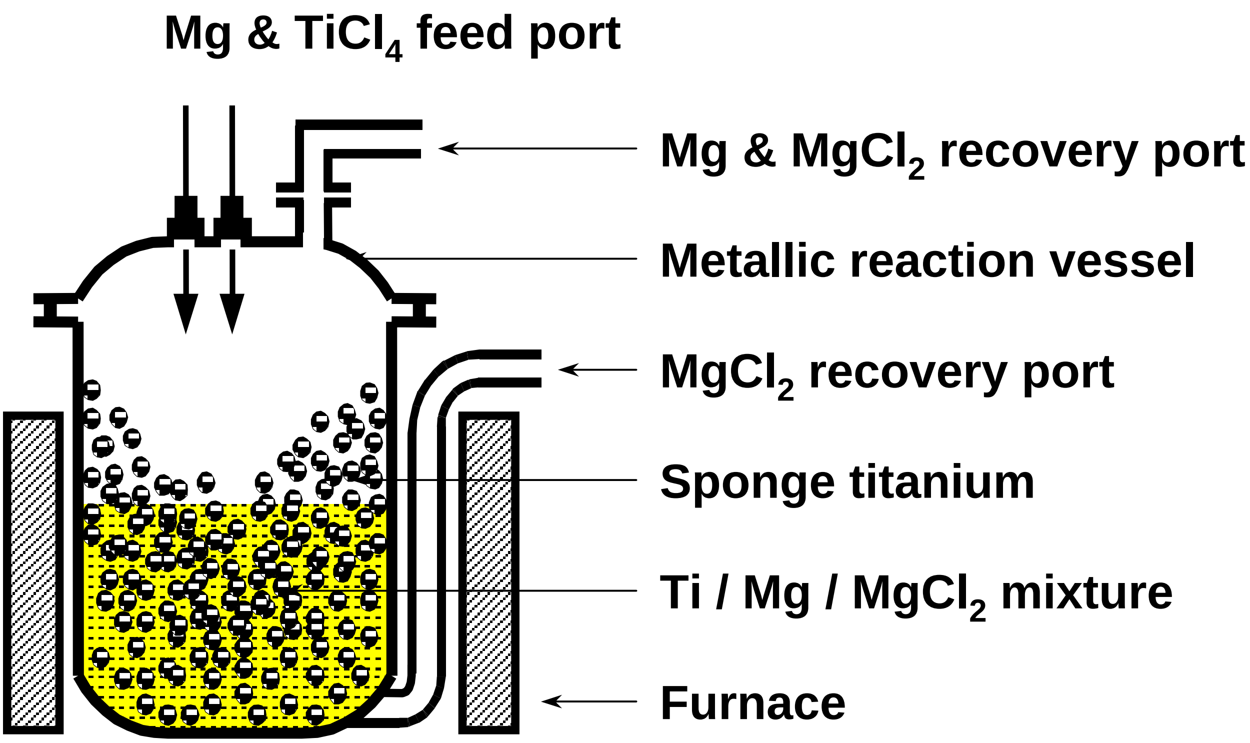
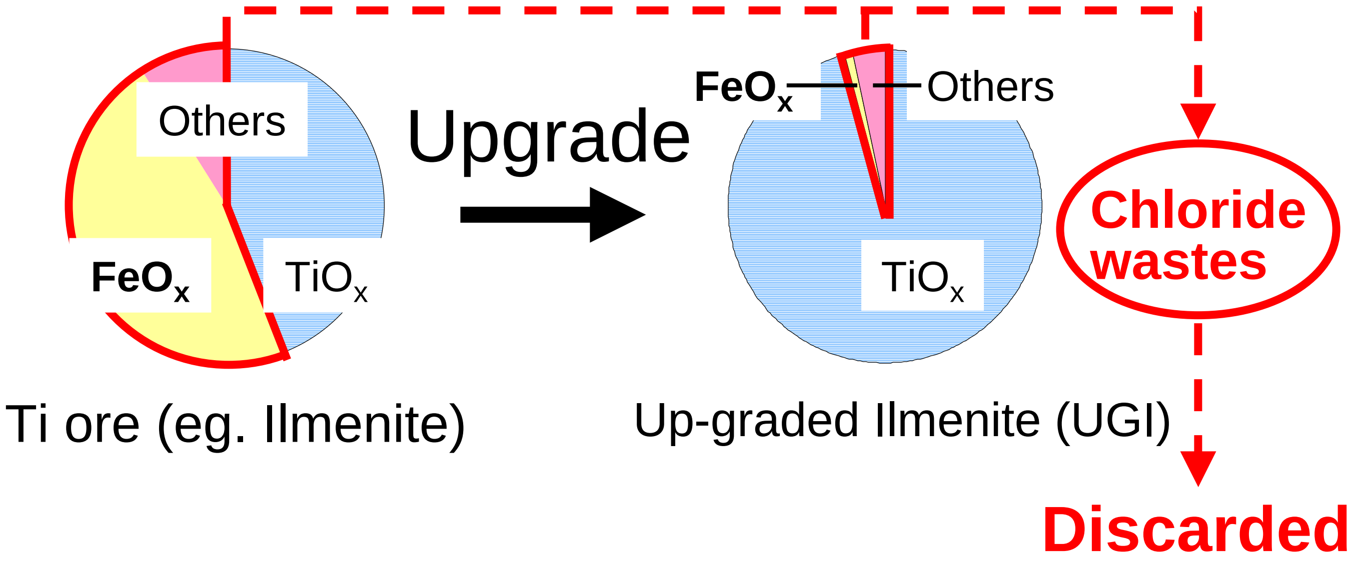


Fig. Reactor for reducing titanium by the Kroll process.

Upgrading Ti ore for minimizing chloride wastes



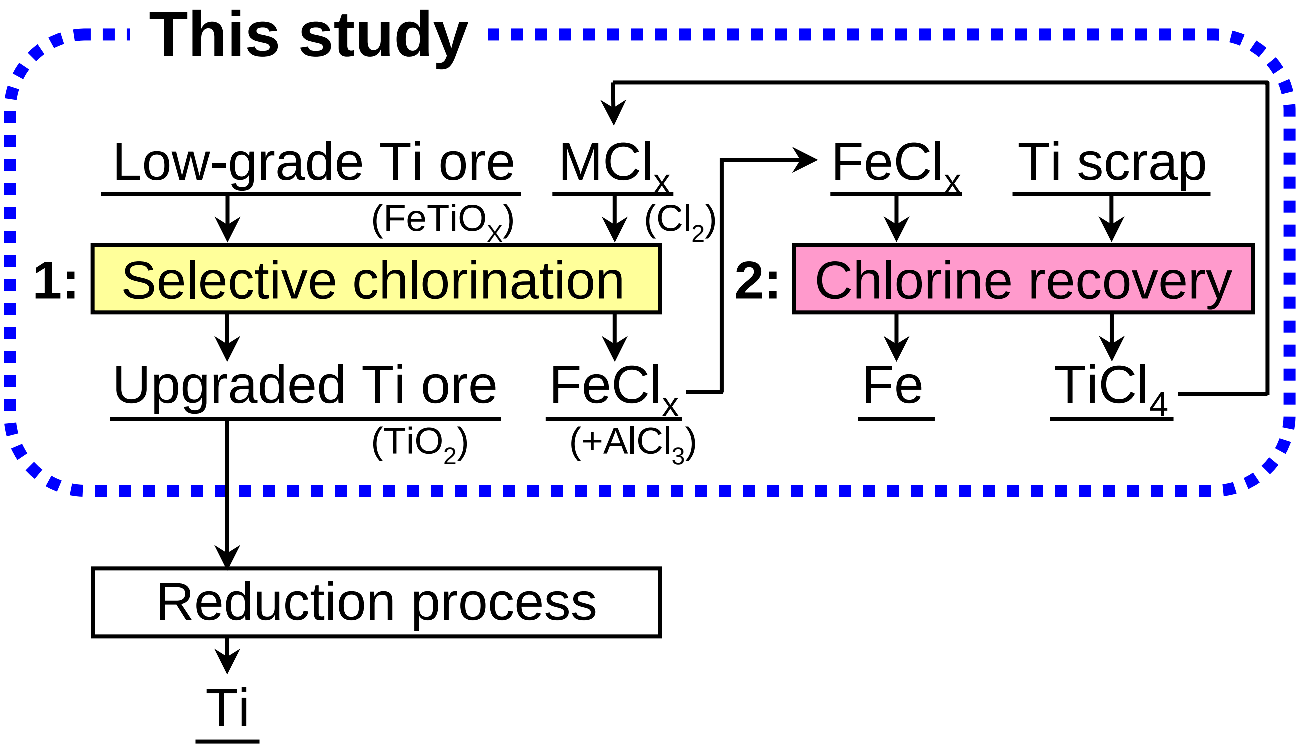
1. A large amount of chloride wastes (e.g., $FeCl_x$) are produced in the Kroll process.

2. Chloride waste treatment is costly, and it causes chlorine loss in the Kroll process.

Importance

1. Reduction of disposal cost of chloride wastes
2. Minimizing chlorine loss in the Kroll process
3. Improvement of environmental burden
4. Reduction of raw material cost

Refining process using $FeCl_x$



Advantages:

1. Utilizing chloride wastes from the Kroll process
2. Low cost Ti chlorination
3. Using low-grade Ti ore in the Kroll process

Effective utilization of chloride wastes

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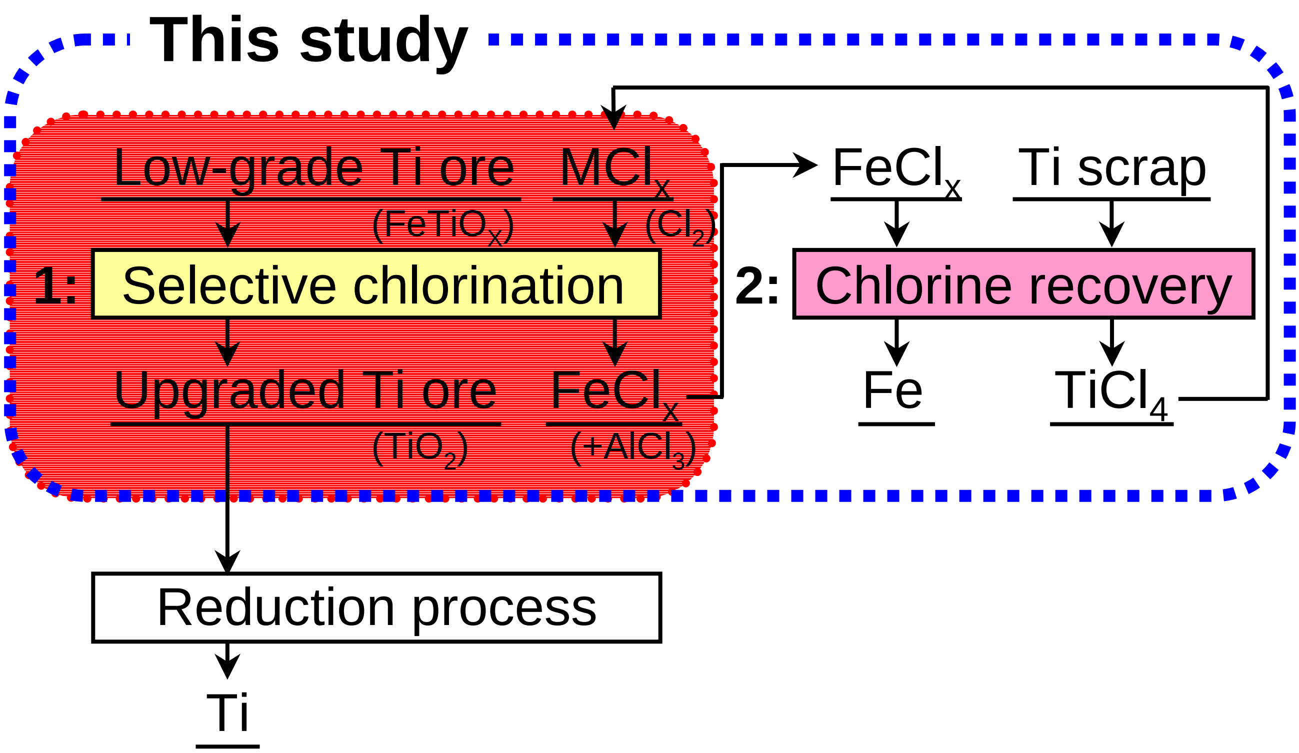
Development of a new environmentally sound chloride metallurgy

1. Selective chlorination



Thermodynamic analysis (FeO_x chlorination)

Ti ore : mixture of TiO_x and FeO_x.

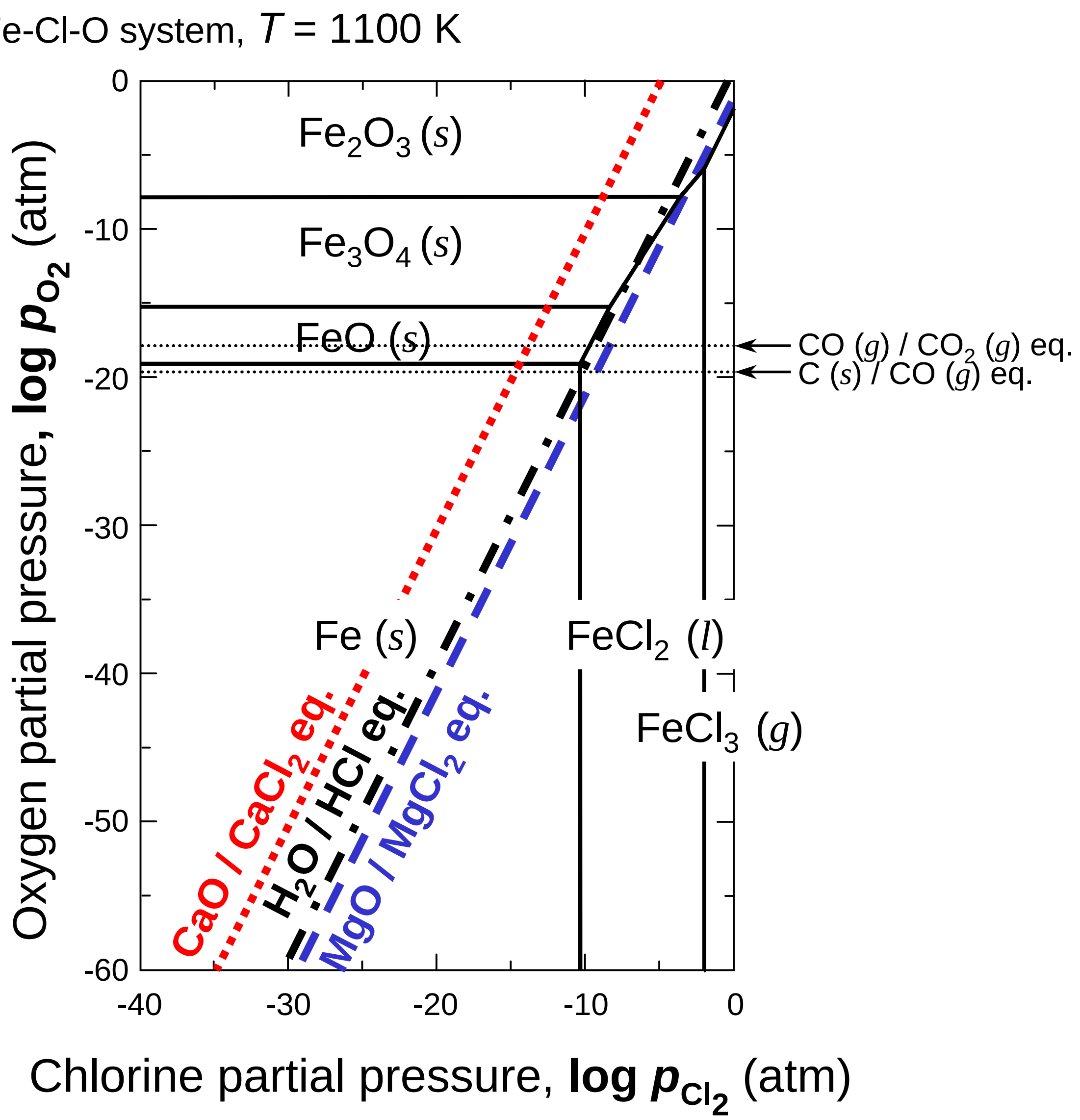


Fig. Chemical potential diagram of the Fe-Cl-O system at 1100 K.

FeO_x is chlorinated using $MgCl_2$ or $CaCl_2$ + H_2O, and high-purity $FeCl_x$ can be obtained by controlling deposition temperature.

Thermodynamic analysis (TiO_x chlorination)

Ti ore : mixture of TiO_x and FeO_x.

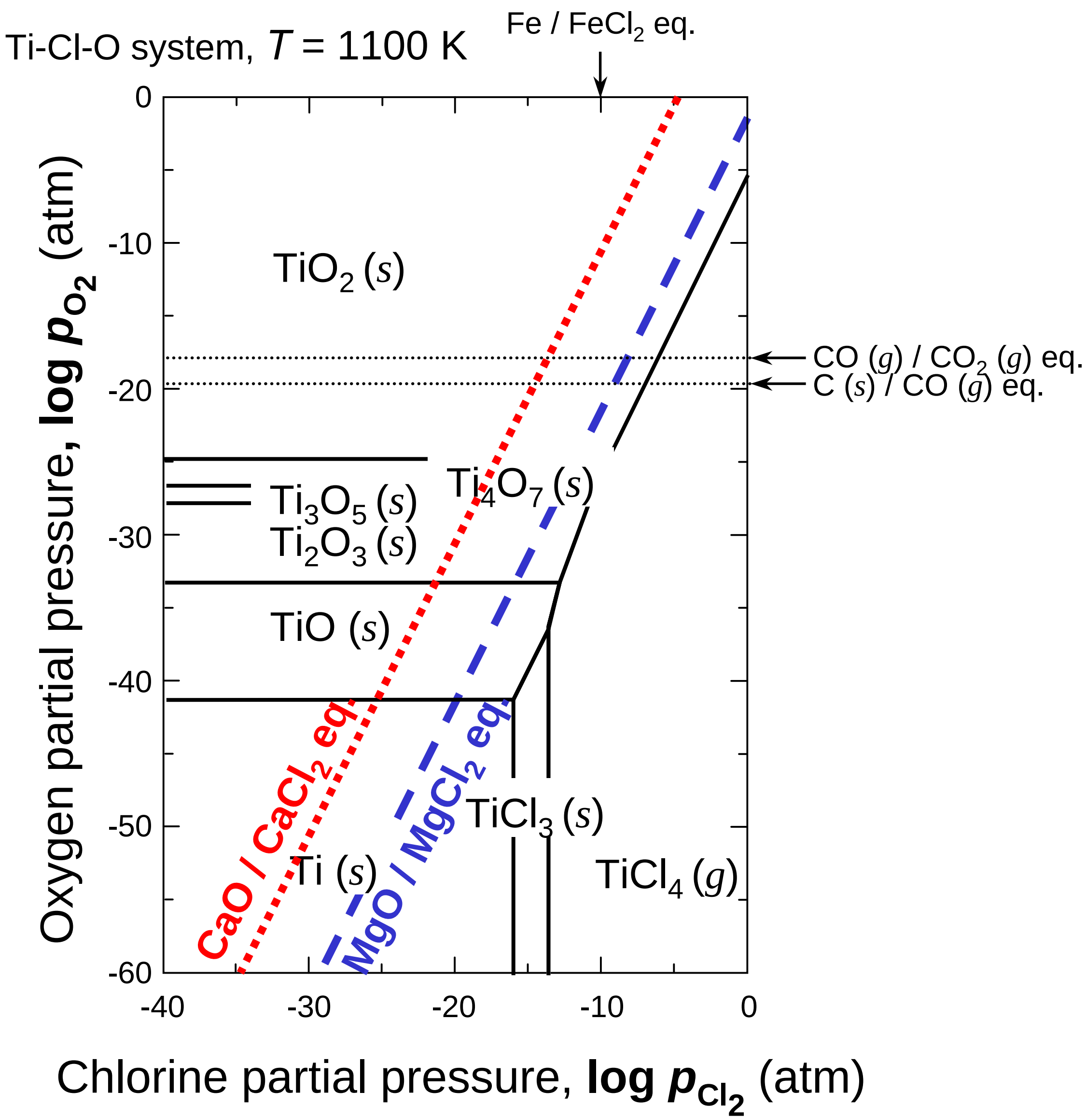


Fig. Chemical potential diagram of the Ti-Cl-O system at 1100 K.

TiO_x is not chlorinated using $CaCl_2$, $MgCl_2$, nor $CaCl_2$ + H_2O.

Thermodynamic analysis (Ti ore chlorination)

Ti ore : mixture of TiO_x and FeO_x.

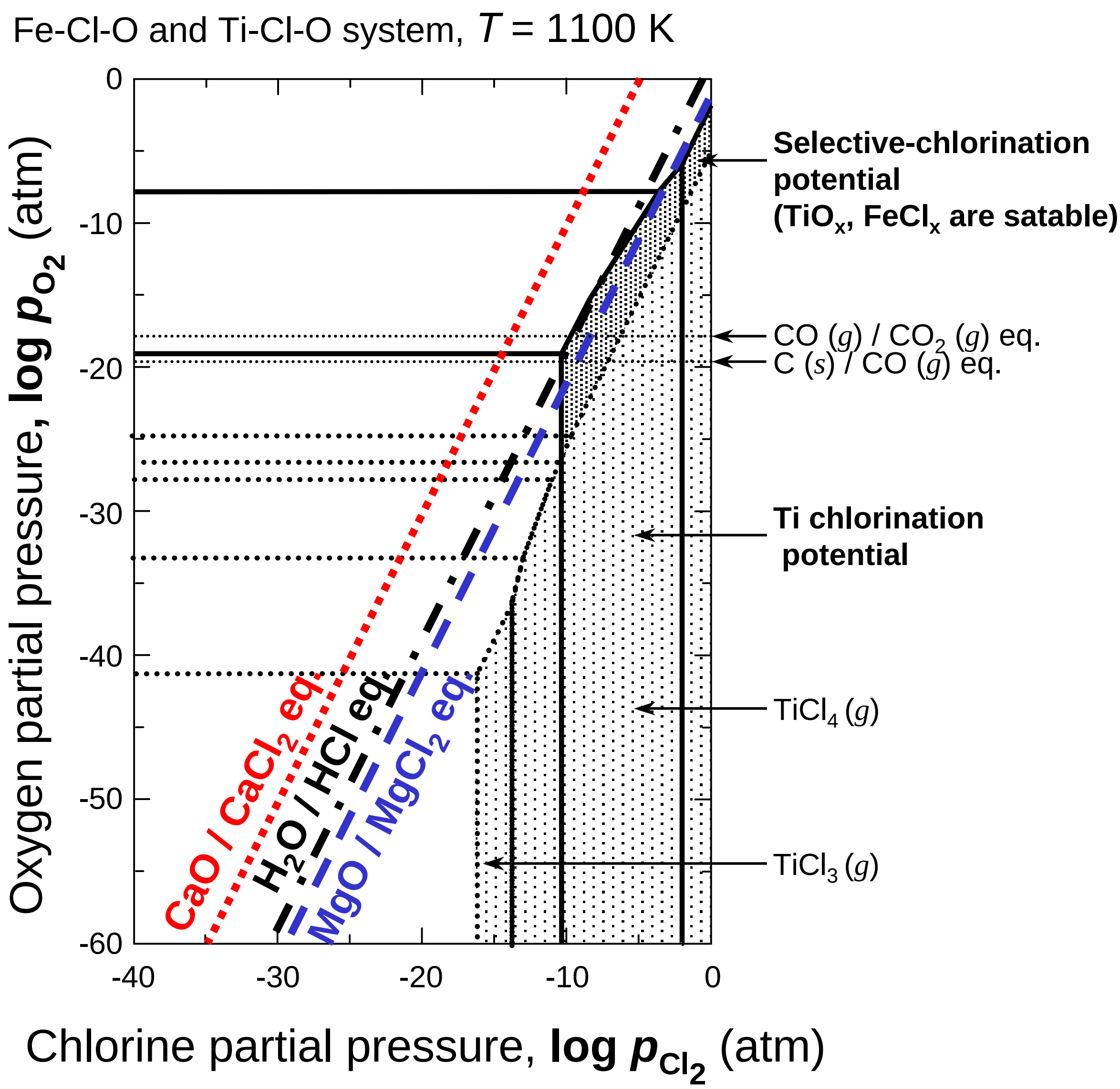


Fig. Combined chemical potential diagram of the Fe-Cl-O and Ti-Cl-O system at 1100 K.

The selective-chlorination of Ti ore using $MgCl_2$ or $CaCl_2$ + H_2O can proceed.

Selective chlorination experiment

$$FeO_x\ (s) + MgCl_2\ (l) = FeCl_x\ (l) + MgO\ (s)$$
$$FeO_x\ (s) + CaCl_2\ (l) = FeCl_x\ (l) + CaO\ (s)$$

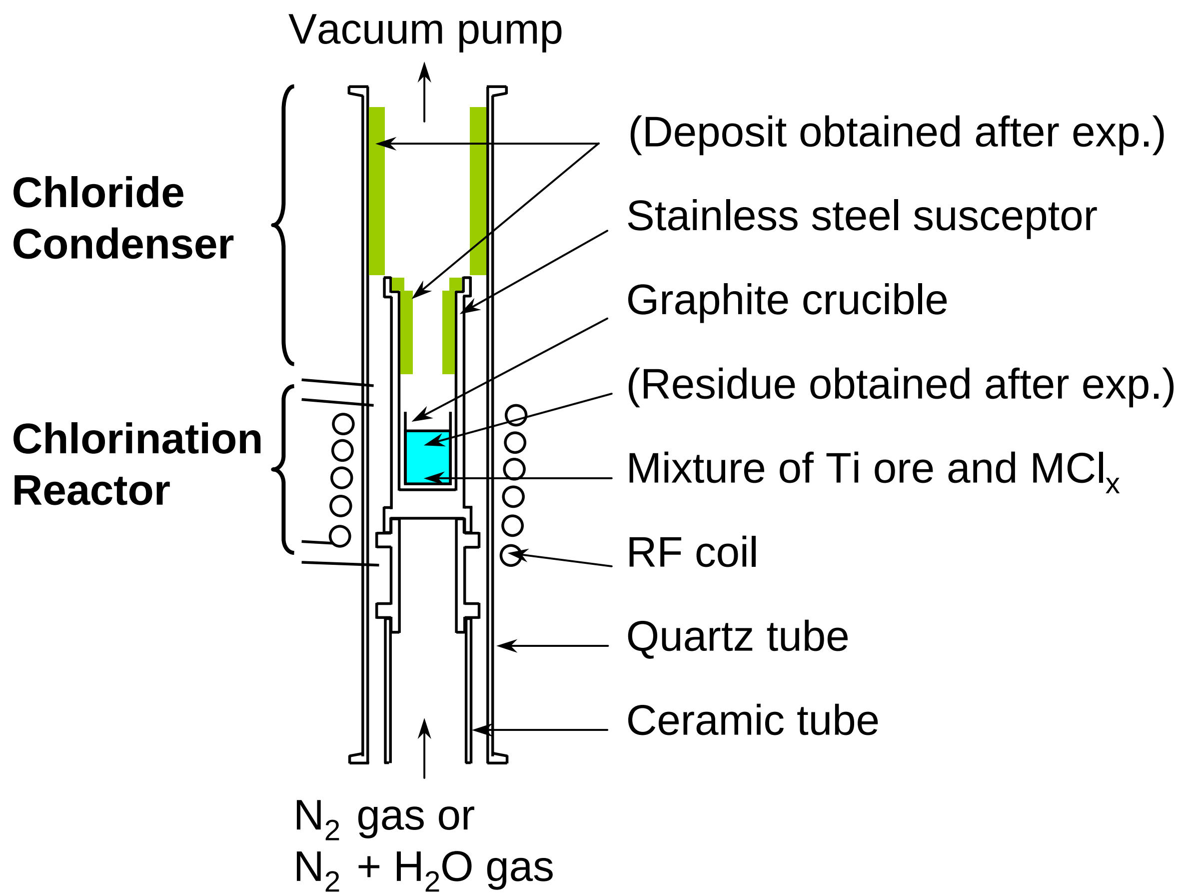


Fig. Experimental apparatus for selective-chlorination of titanium ore.

Experimental condition

T = 1100 K, t' = 1 h, Atmosphere : N_2, UGI : 4 g, $MgCl_2$: 2 g

T = 1100 K, t' = 6 h, Atmosphere : Ar + H_2O, Low-grade ore : 3 g, $CaCl_2$: 2 g

Results (chlorine source: $MgCl_2$)

$$FeO_x\ (s) + MgCl_2\ (l) = FeCl_2\ (l, g) + MgO\ (s)$$

XRD analysis

Deposit obtained after selective-chlorination.
→ $FeCl_2$ was generated.

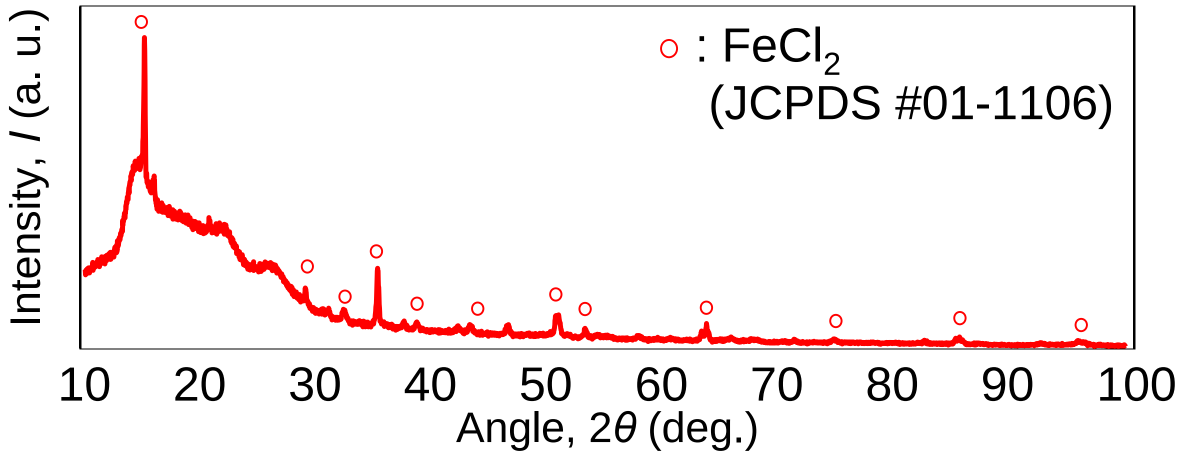


Fig. XRD pattern of the deposit in the cooling zone.
The sample powder was sealed in Kapton film before analysis.

XRF analysis

Residue after selective-chlorination.
→ Fe was selective chlorinated.

Table Analytical results of titanium ore, the residue after selective chlorination, and the sample after reduction. These values are determined by XRF analysis.

	Concentration of element i, C_i (mass%)				
	Ti	Fe	Si	Al	V
Ti ore (UGI)	96.38	**2.32**	0.42	0.12	0.76
	↓	↓	↓	↓	↓
After heating residue	97.24	**0.43**	0.44	0.37	1.51

Results (chlorine source: $CaCl_2$ +H_2O)

$$H_2O\ (g) + CaCl_2\ (l) = 2\ HCl\ (g) + CaO\ (s)$$
$$FeO_x\ (s) + HCl\ (g) = FeCl_2\ (l, g) + H_2O\ (g)$$

XRD analysis

Deposit obtained after selective-chlorination.
→ $FeCl_2$ was generated.

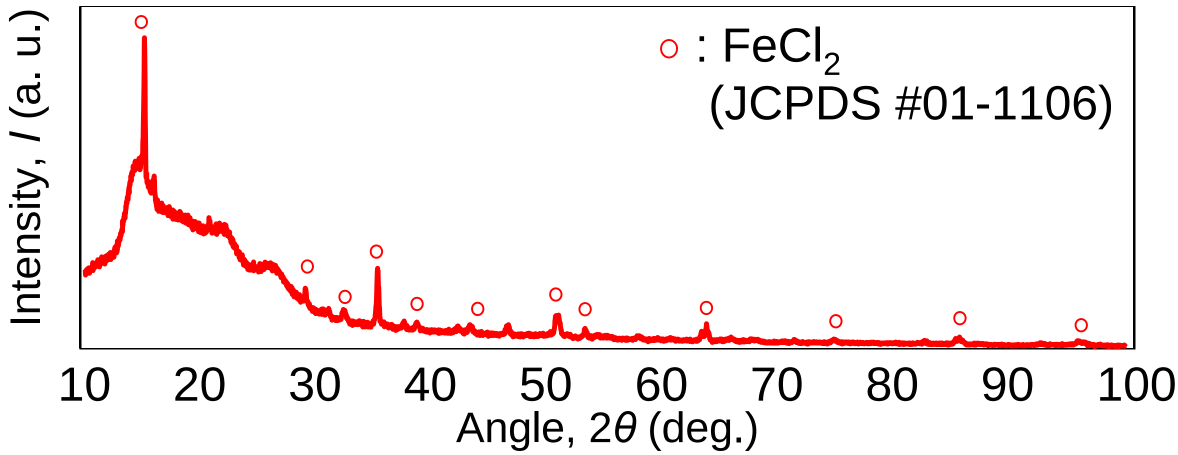


Fig. XRD pattern of the deposit in the cooling zone.
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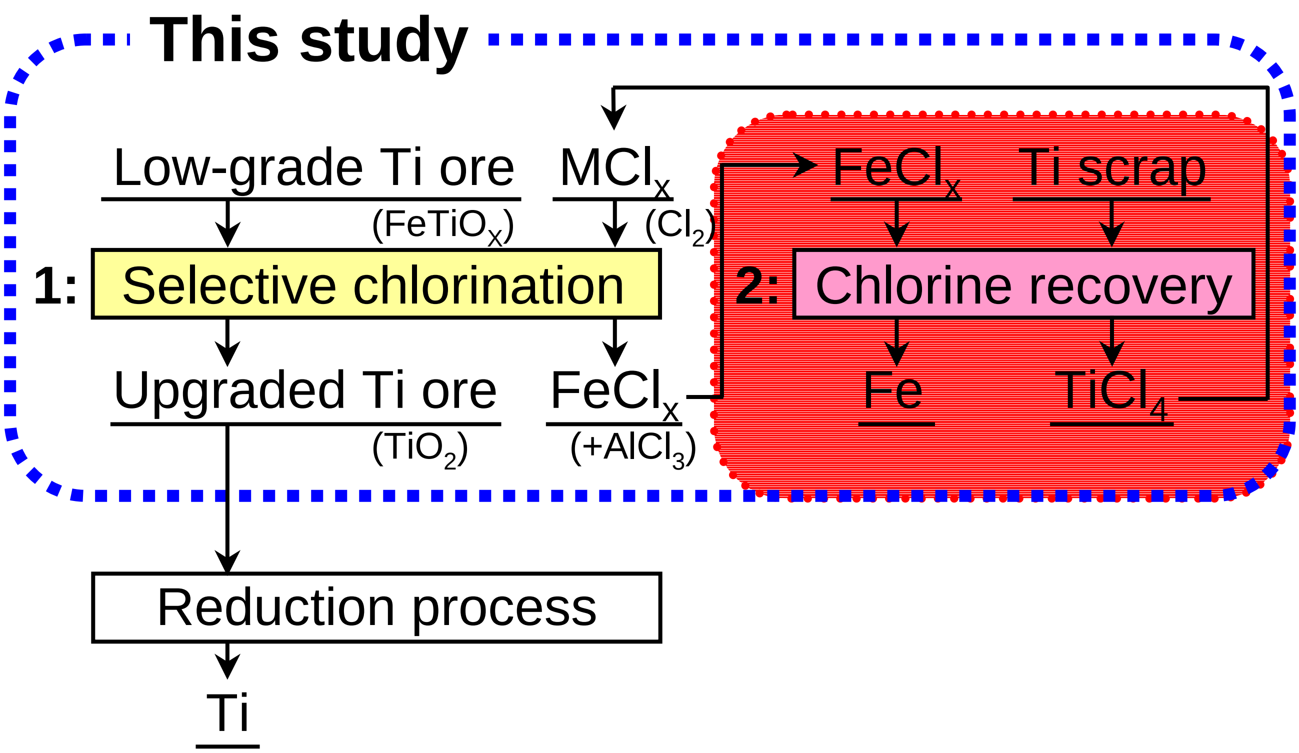
XRF analysis

Residue after selective-chlorination.
→ Fe was selective chlorinated.

Table Analytical results of titanium ore, the residue after selective chlorination, and the sample after reduction. These values are determined by XRF analysis.

	Concentration of element *i*, C_i (mass%)				
	Ti	Fe	Si	Al	V
Ti ore (low-grade ore)	46.38 ↓	**49.65** ↓	2.33 ↓	1.00 ↓	0.63 ↓
After heating residue	98.50	**0.31**	0.23	n.d.	0.96

2. Chlorine Recovery



Chlorination of Ti

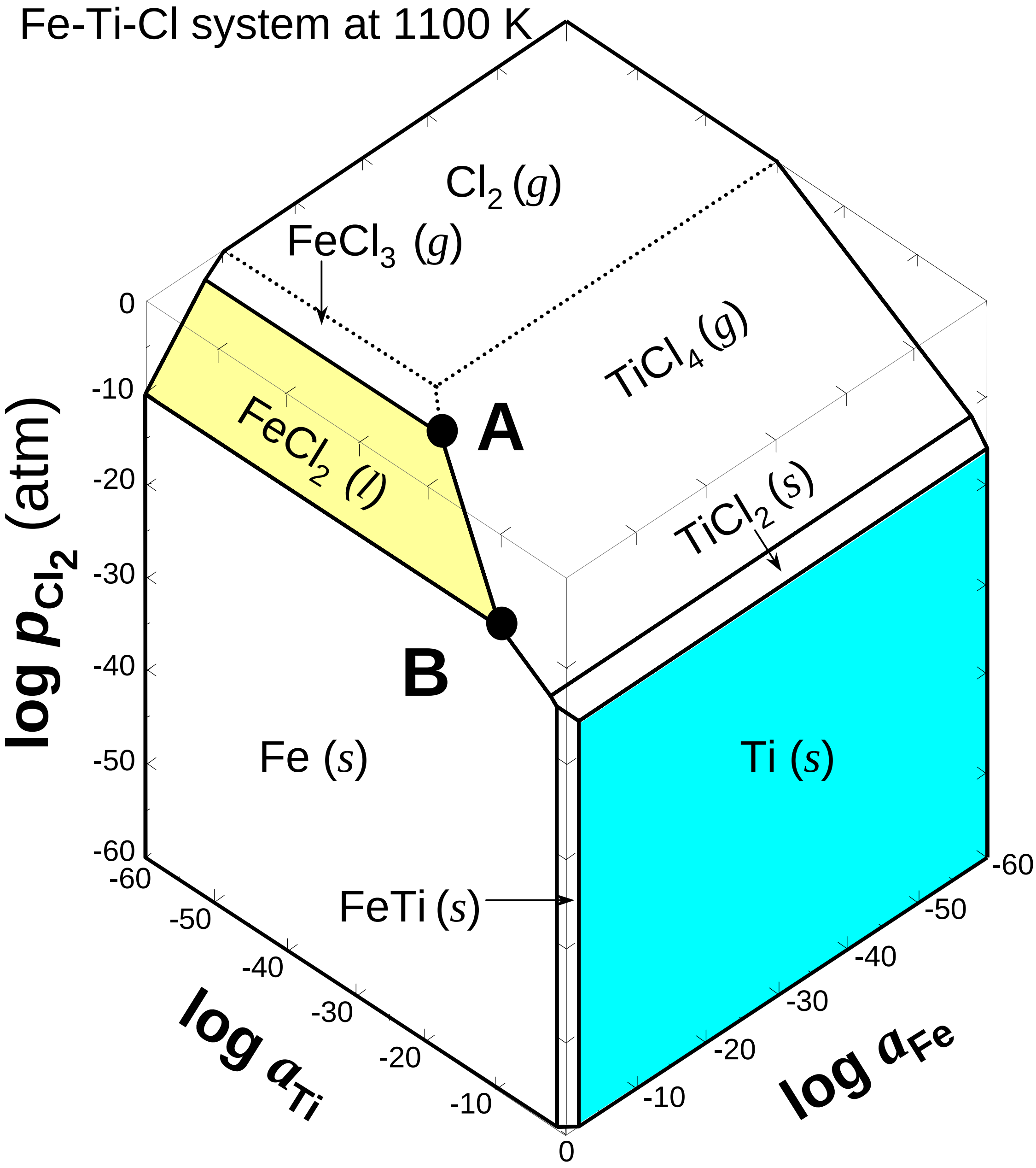


Fig. Chemical potential diagram of the Fe-Ti-Cl system at 1100 K.

$TiCl_4$ can be generated by reacting Ti and $FeCl_x$.

Thermodynamic analysis (vapor pressure)

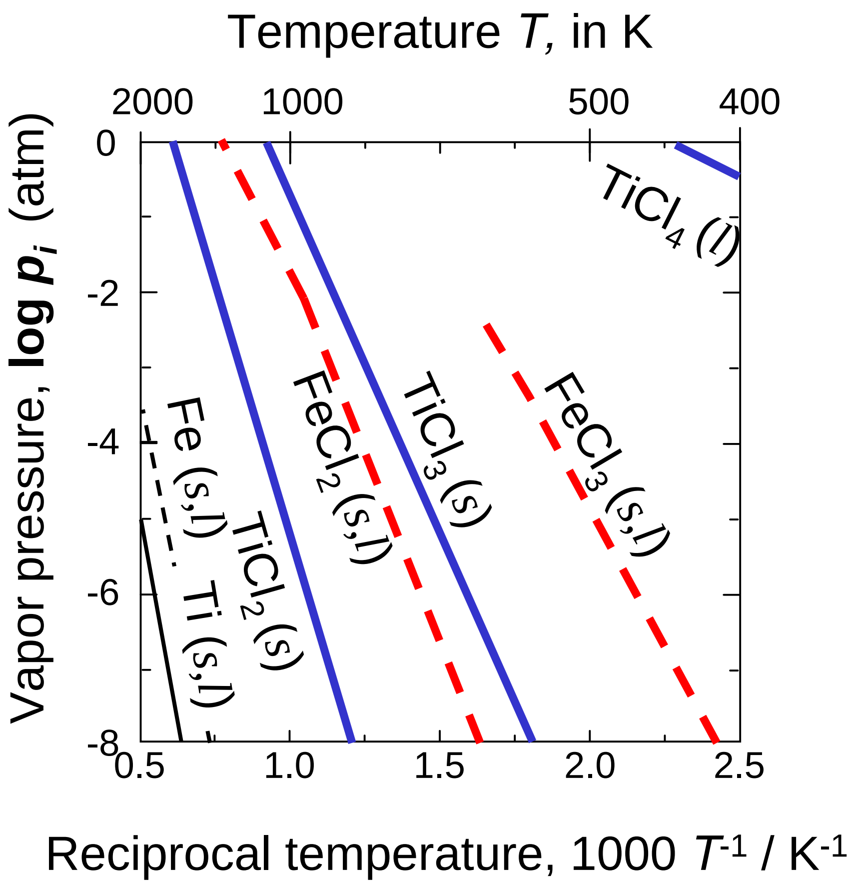


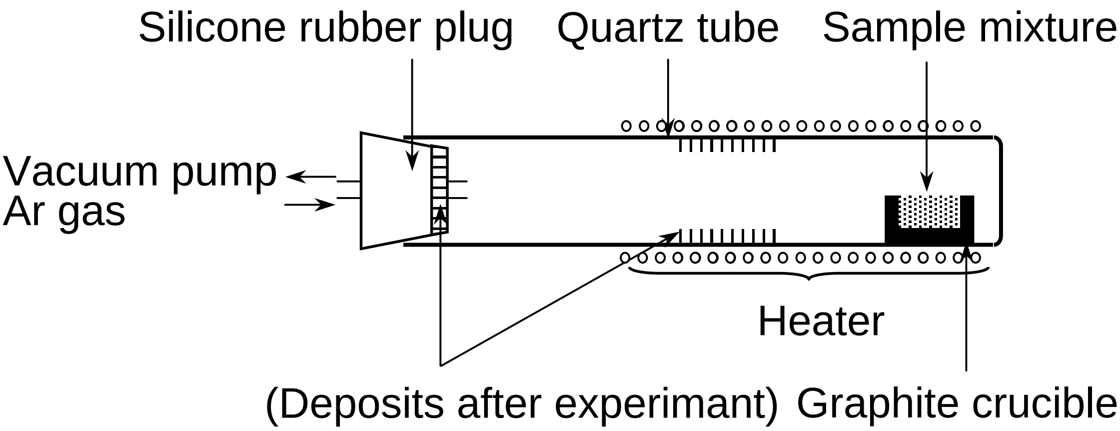
Fig. Vapor pressure of iron and titanium chlorides as a function of reciprocal temperature.

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

Chlorine recovery of $FeCl_2$ using Ti

Ti (*s*) + 2 $FeCl_2$ (*s*, *l*) = $TiCl_4$ (*g*) + 2 Fe (*s*)

(a)



(b)

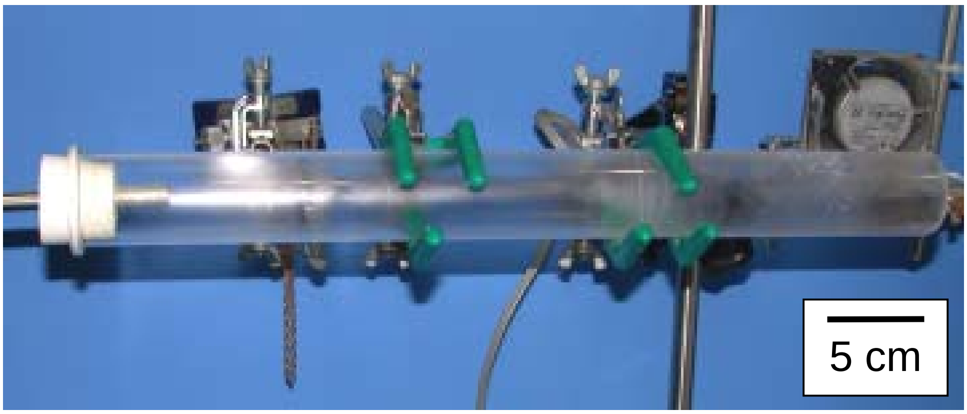


Fig. Experimental apparatus for chlorine recovery of $FeCl_2$ using Ti.

Experimental condition

***T* = 1100 K, *t'* = 6 h, Atmosphere : Ar,**
Ti: 0.3 g, $FeCl_2$: 2 g

Results (residue)

Ti (*s*) + $FeCl_2$ (*s*, *l*) = $TiCl_x$ (*g*) + Fe (*s*)

XRD analysis

Residue after chlorination.
→ Fe generated at heating zone.

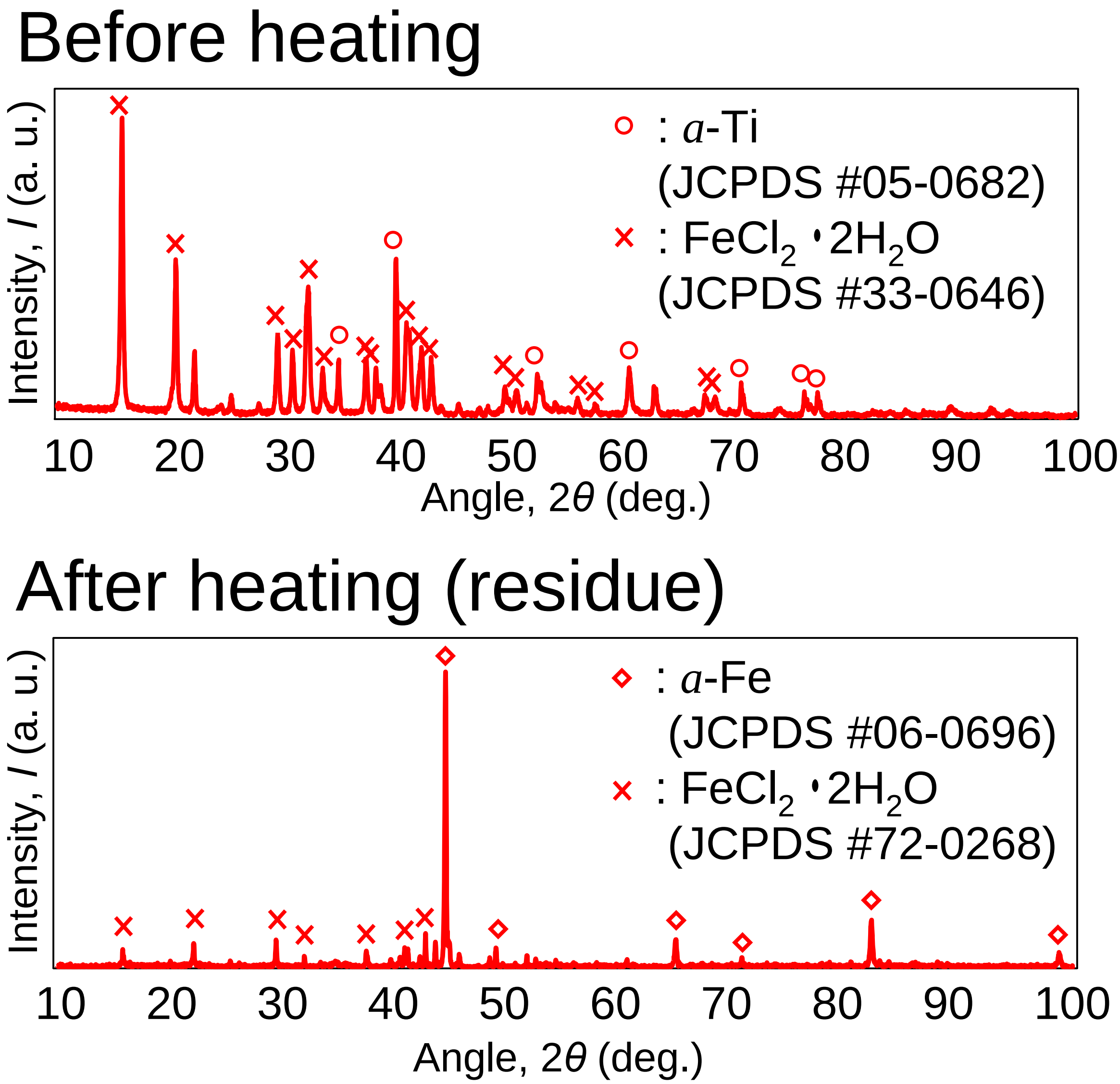


Fig. XRD patterns of the sample before heating and residue at the heating zone.

Results (deposit)

Ti (s) + $FeCl_2$ (s, l) = $TiCl_x$ (g) + Fe (s)

XRD analysis

Deposit on quartz tube
→ Unreacted $FeCl_2$ was deposited.

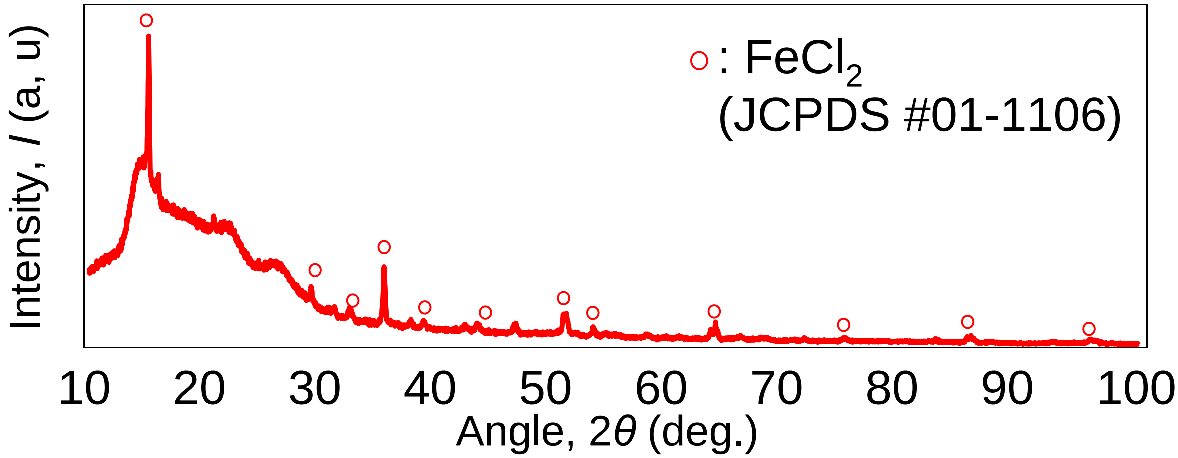


Fig. XRD pattern of the deposit in the quartz tube.
The sample was sealed in Kapton film before analysis.

XRF analysis

Table Analytical results of the samples before and after heating and the sample deposited on quartz tube and Si rubber. These values are determined by XRF analysis.

	Concentration of element i, C_i (mass %)		
	Ti	Fe	Cl
Dep. on Si rubber after heating	**64.9**	**0.9**	**34.1**
Dep. on quartz tube after heating	3.5	50.4	46.1
Residue before heating	18.4	45.3	36.2
Residue after heating	↓ 9.8	↓ 80.1	↓ 9.0

Conclusions

1. Selective chlorination of titanium ore using $MgCl_2$ or $CaCl_2 + H_2O$ was demonstrated, and Ti ore with low Fe content was produced.

2. Chlorine recovery of $FeCl_2$ using Ti was demonstrated, and Fe-free $TiCl_x$ was produced.