The 3rd Workshop on Reactive Metal Processing

AN ENVIROMENTALLY-SOUND PROCESS FOR RECYCLING Ti SCRAP COMBINING WITH CHLORIDE WASTES

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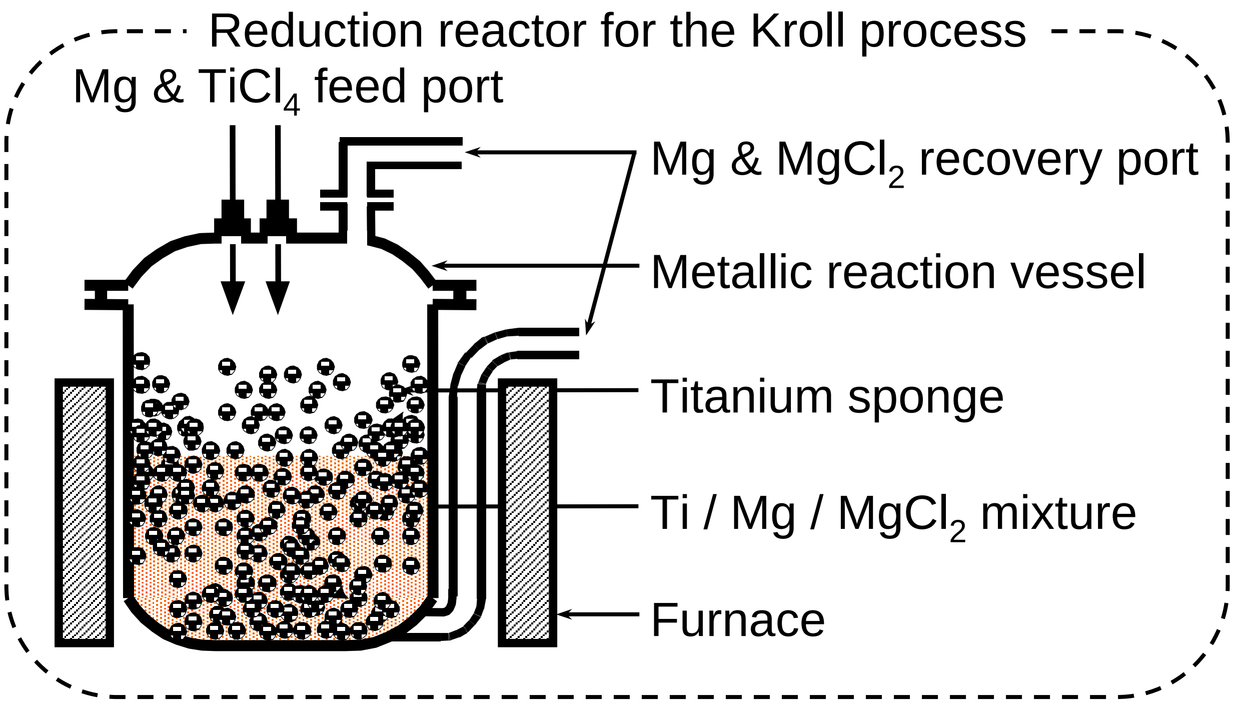
The Kroll process

Chlorination: Ti ore (s) + C (s) + 2 Cl_2 (g) → $TiCl_4$ (l) + MCl_x (s, g) + CO_2 (g)

M: Impurity element in the ore

Reduction: $TiCl_4$ (l) + 2 Mg (s) → Ti (s) + 2 $MgCl_2$ (l)

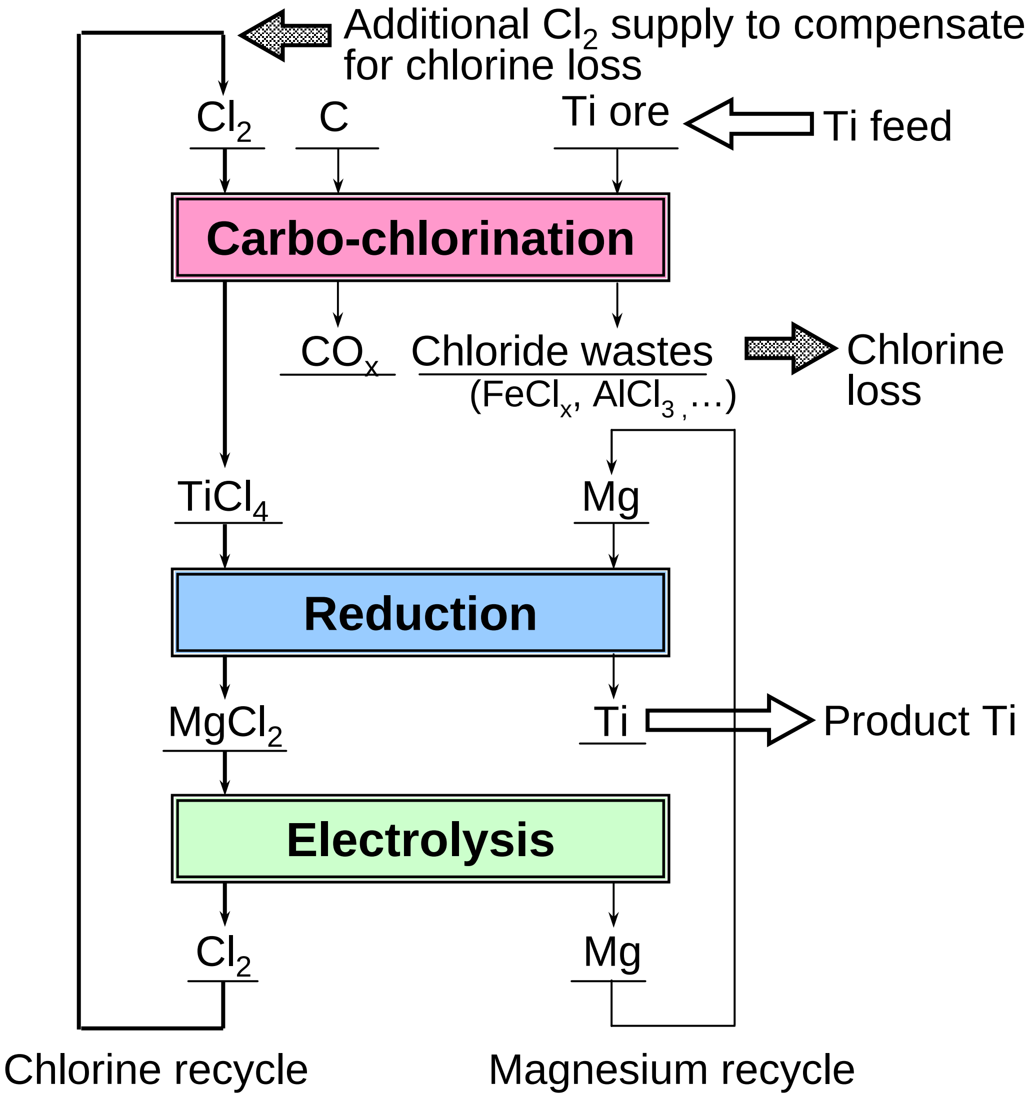
Electrolysis: $MgCl_2$ (l) → Mg (s) + Cl_2 (g)



The essential advantage: High-purity Ti available

The critical disadvantage: Low productivity

Chlorine cycle in the Kroll process



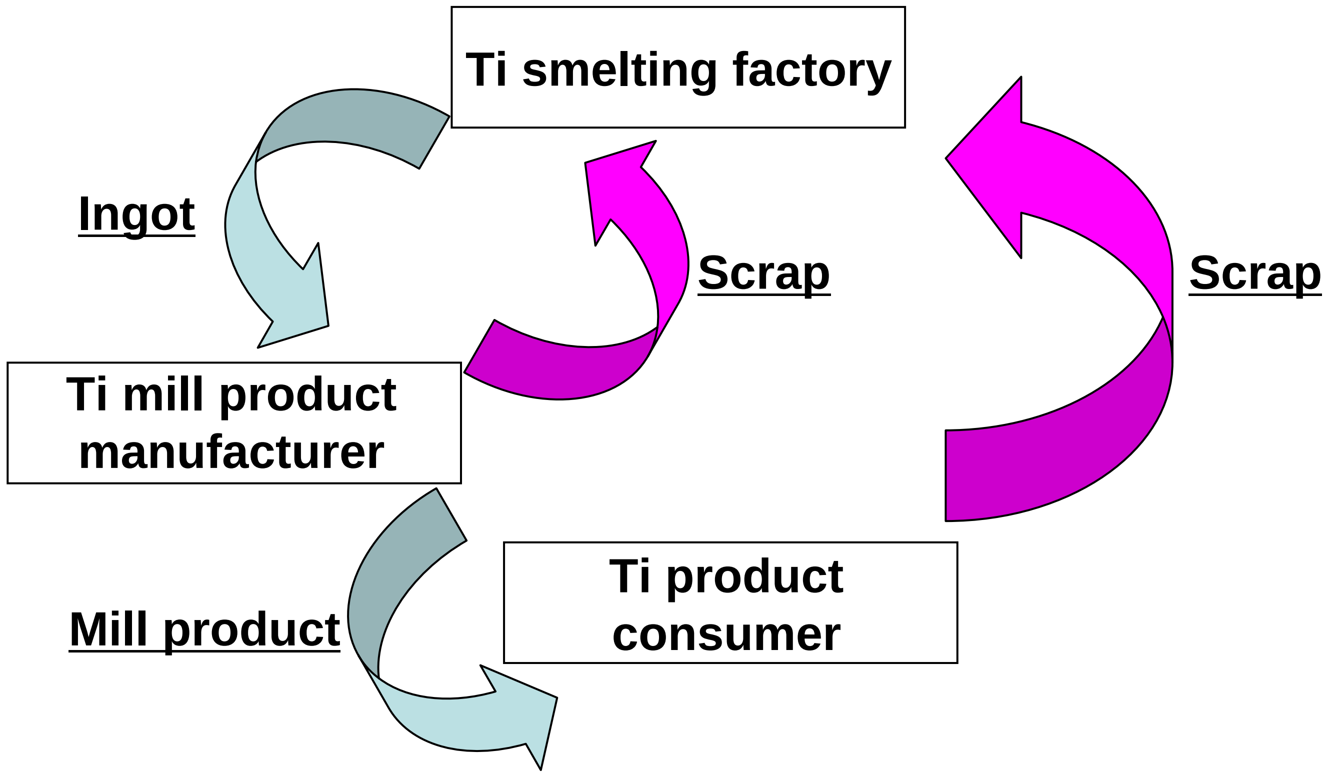
Although major portion of chlorine in the Kroll process is recycled, chloride wastes are generated in the Kroll process.

The generation of chloride wastes causes not only chlorine loss but also environmental problems.

Current Ti scrap recycle

1) **Ti scrap is used for producing ferro-alloys for steel making.**

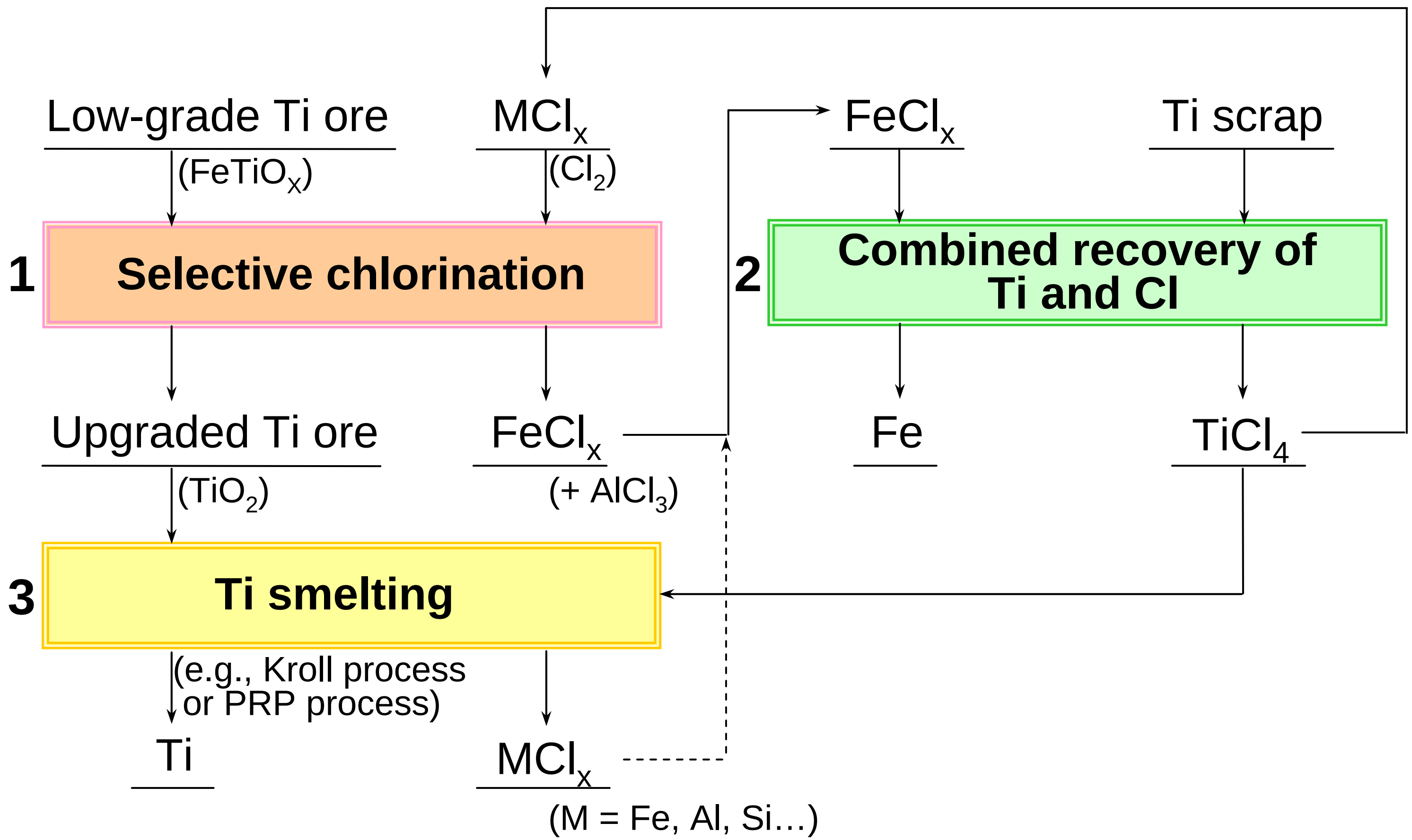
2)



**In the future, amount of low-purity Ti scrap will increase,
and a new recycling process of Ti scrap is required.**

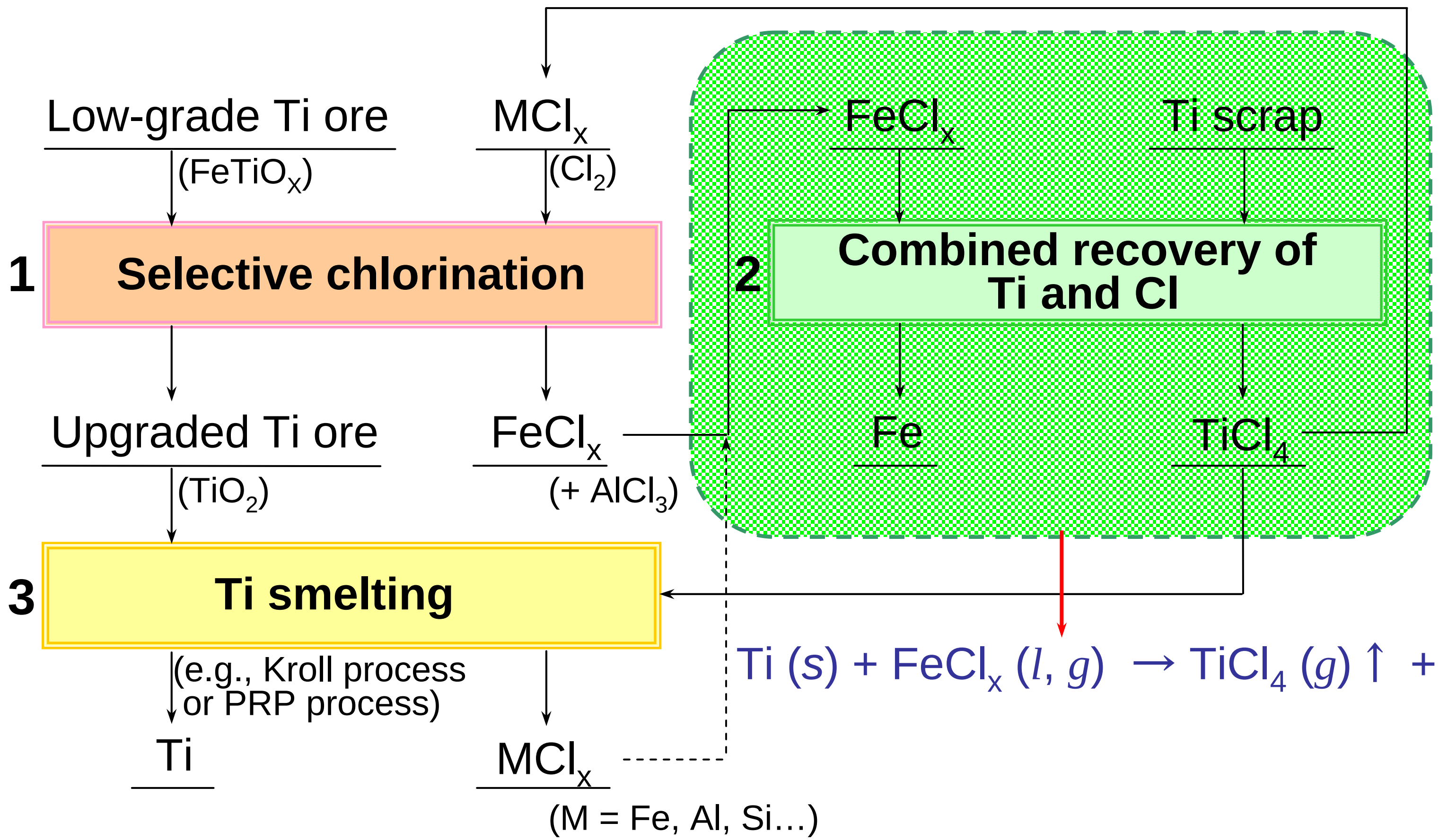
http://www.toho-titanium.co.jp/jp/index.html

The purpose of this study



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

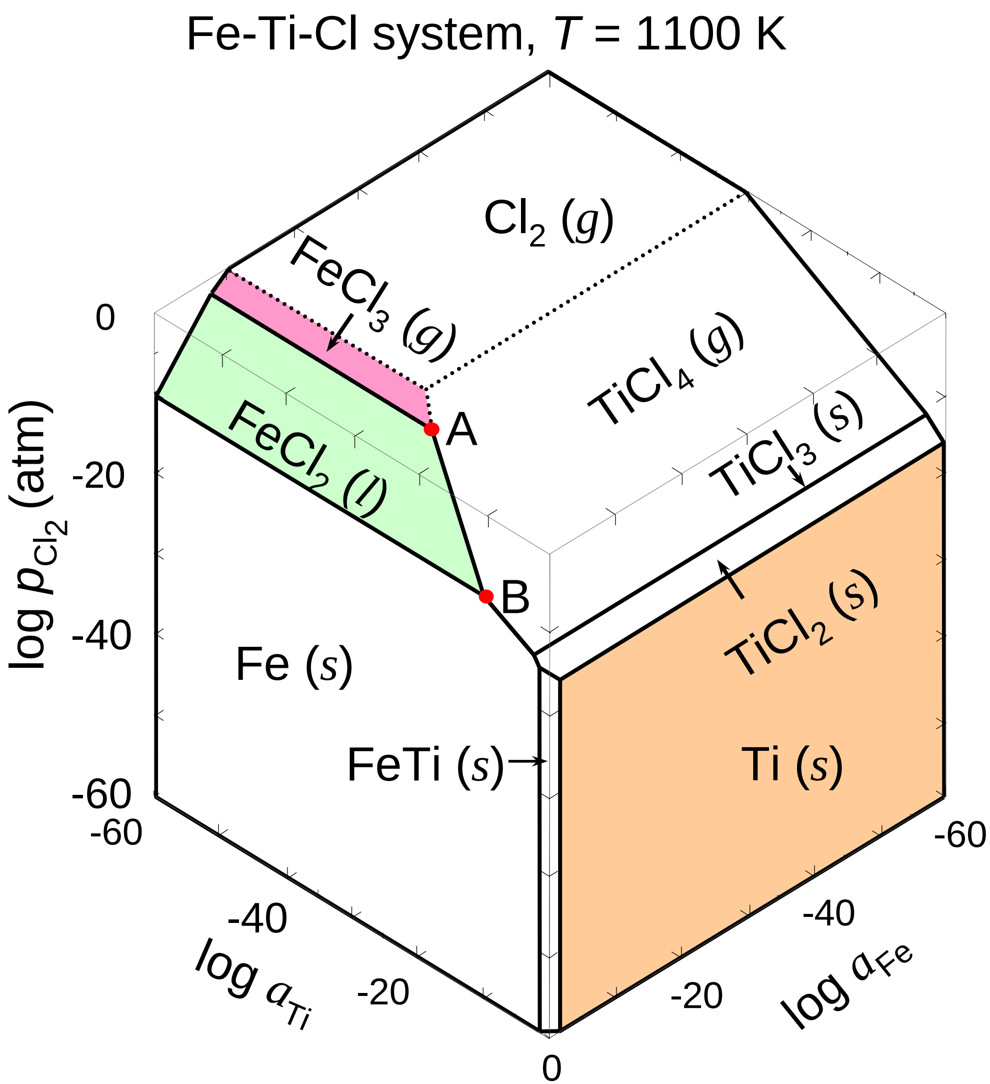
Today's topic



$$Ti\ (s) + FeCl_x\ (l, g) \rightarrow TiCl_4\ (g)\uparrow + Fe\ (s)$$

- **Ti metal scrap can be recycled.**
- **Chlorine in the chloride wastes can be efficiently recovered.**
  → Low-grade Ti ore can be used as the feed material.
  → Cost of waste treatment can re reduced.

Chemical potential diagram for the Fe-Ti-Cl system



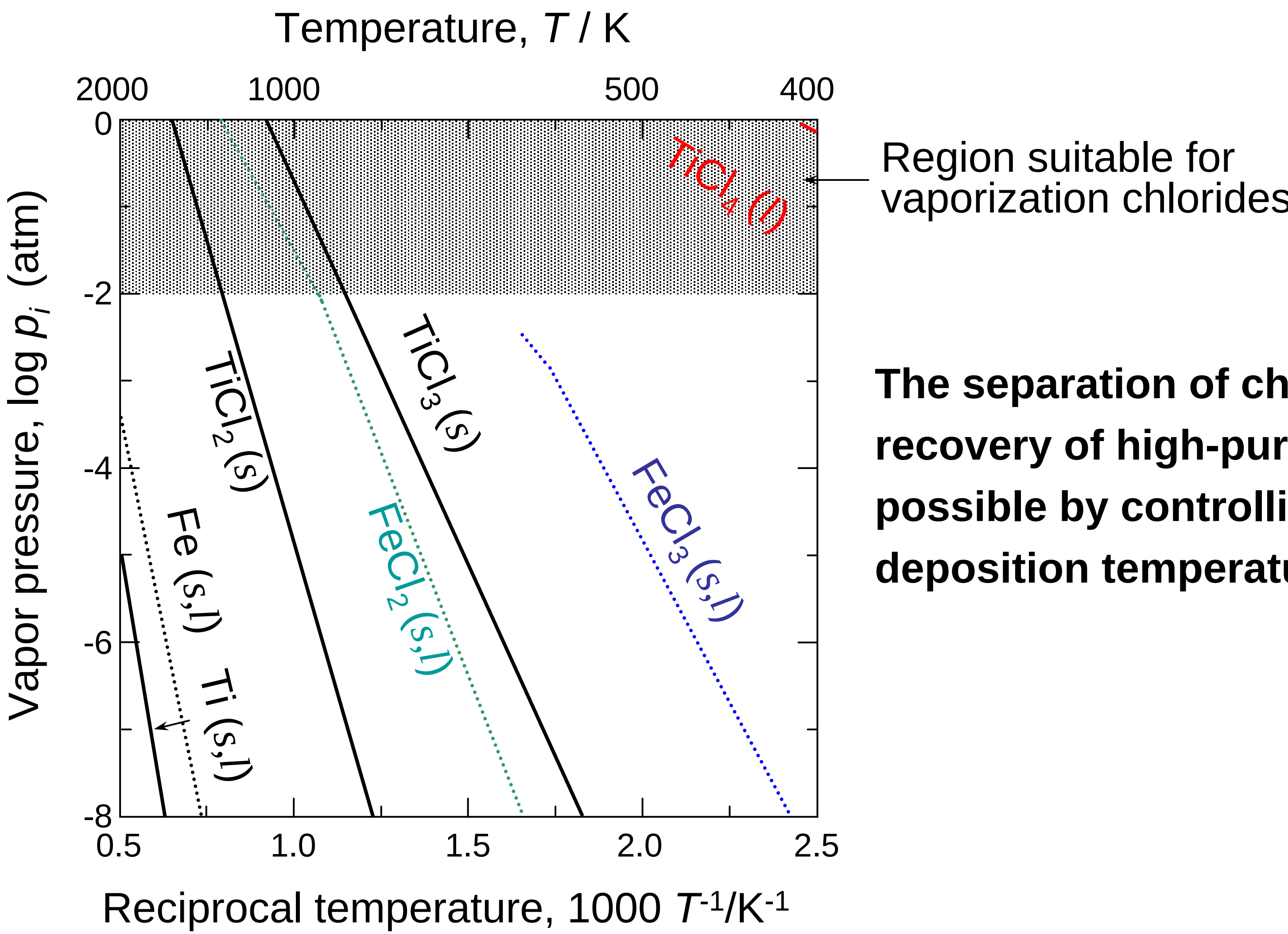
Ti (s) + $FeCl_x$ (l, g) → $TiCl_4$ (g) ↑ + Fe (or FeTi, s)

Ti present in the Ti scrap can be extracted by iron chlorides.

or

$TiCl_4$ can be obtained by reacting Ti scraps with chloride wastes.

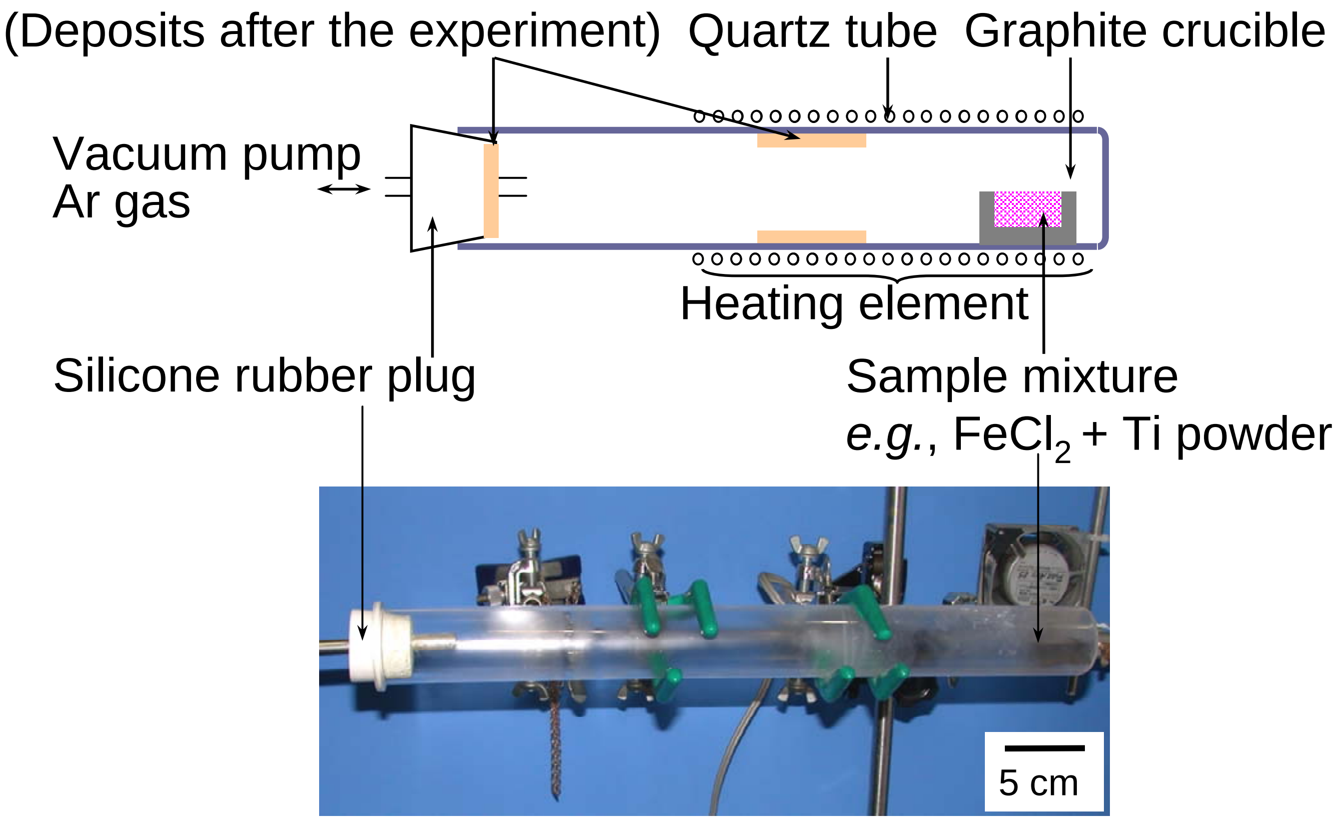
Vapor pressure of some selected chlorides and metals



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

The separation of chlorides and recovery of high-purity $TiCl_4$ are possible by controlling the deposition temperature.

Experiment apparatus (1)

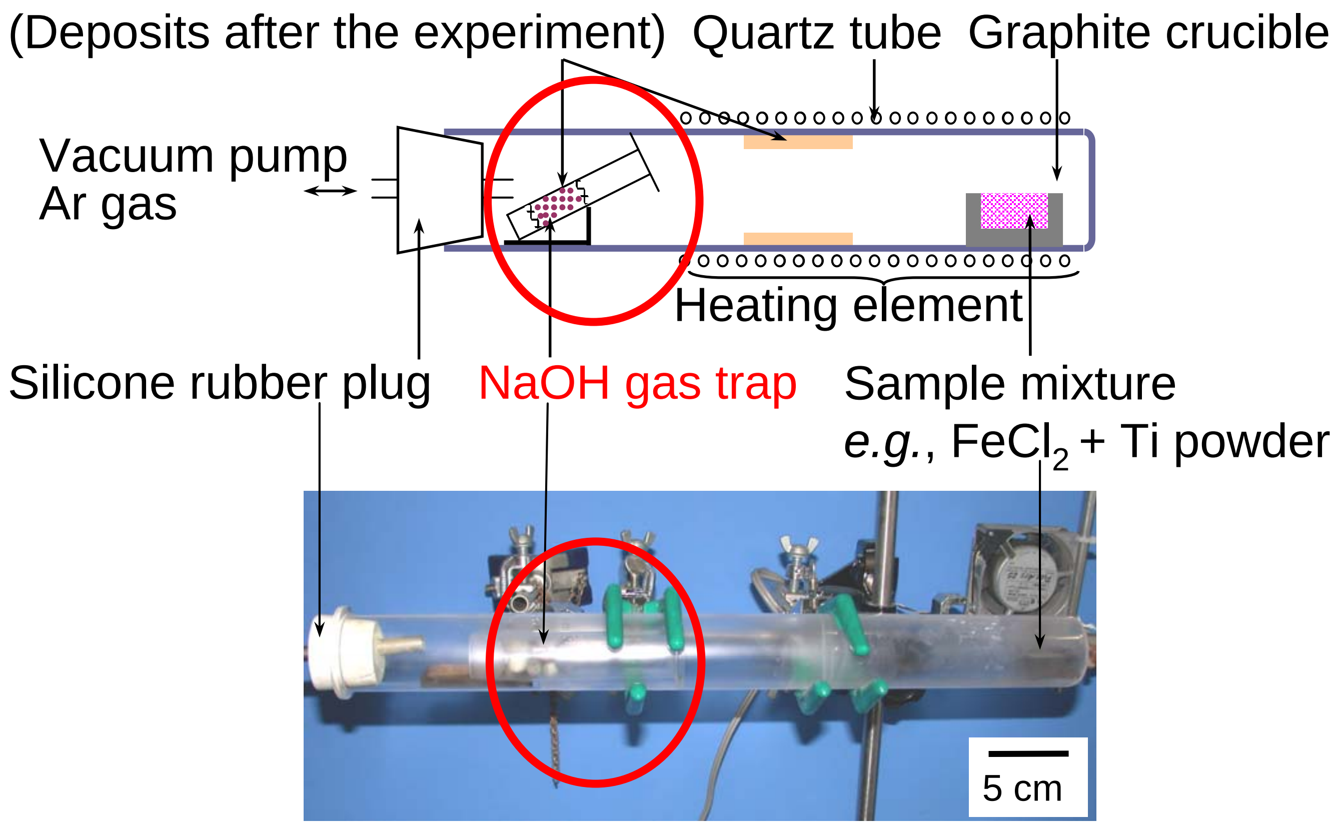


T **= 1100 K;** ***t'*** **= 1h or 3h; Ar atmosphere**

Ti (*s*) + $FeCl_2$ (*l*, *g*) → $TiCl_4$ (*g*) ↑ + Fe (*s*)

Exp. # CC

Experiment apparatus (2)



NaOH (*s*) + MCl_x (*g*) → NaCl (*s*) + $M(OH)_x$ (*s*)

Experiment conditions

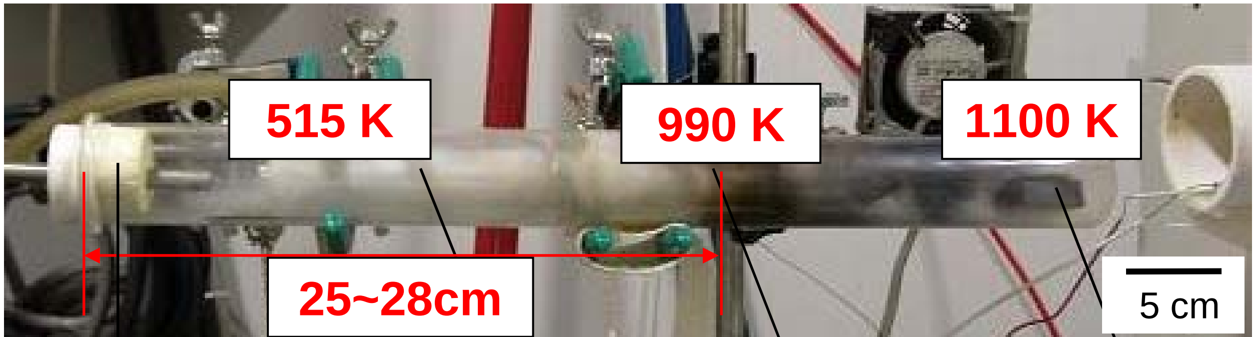
Exp. No.	Mass of feed materials, w_i / g			Mass Ratio w_{Ti} / w_{FeCl_2}	Reaction temp., T / K	Reaction time, t' / h	Atmosphere*
	Ti scraps	$FeCl_2$ (Powder)	NaOH				
CA[a]	0.33	1.90	5.27	5.79	1100	1	Ar
CB[a]	0.30	1.75	3.18	5.79	1100	1	Ar
CC[a]	0.32	1.72	-	5.36	1100	1	Ar
CD[b]	0.49	2.76	3.25	5.63	1100	3	Ar
CE[b]	0.51	2.86	5.47	5.61	1100	3	Ar
CF[c]	0.50	3.17	5.38	6.39	1100	3	Ar

a: Ti powder was used in this experiment.
b. Ti shot was used in this experiment.
c: Ti turning was used in this experiment.
*: Reduced atmosphere (0.2 atm at room temperature).

Ti (s) + 2 $FeCl_2$ (l, g) = $TiCl_4$ (g) + 2 Fe (s)
Stoichiometric amount of Ti to $FeCl_2$ is 1:5.29.

Observation

Assembled quartz tube after experiment.



The image of the obtained residue and deposit after experiment.

5 cm	5 cm	2 cm	1 cm
Silicone plug after experiment	Deposit on the surface of the NaOH gas trap	Deposit inside the quartz tube	Residue in the graphite crucible

Melting point of $FeCl_2$: 950 K @ 1 atm
Melting point of $TiCl_4$: 408 K @ 1 atm

Ti powder without NaOH gas trap: Composition

Analytical results of the samples before and after heating, and the deposits obtained on the surface of silicone plug and inside the quartz tube after heating.

Exp. CC	Concentration of element *i*, C_i (mass%)		
	Ti	Fe	Cl
Initial sample before heating	15.7[a]	37.2[a]	47.2[a]
Residue in the graphite crucible	8.95[b]	91.1[b]	-
Deposit inside the quartz tube	0.33[c]	56.2[c]	43.4[c]
Deposit on the surface of silicone plug	(16.7[b])	(2.22[b])	(81.1[d])

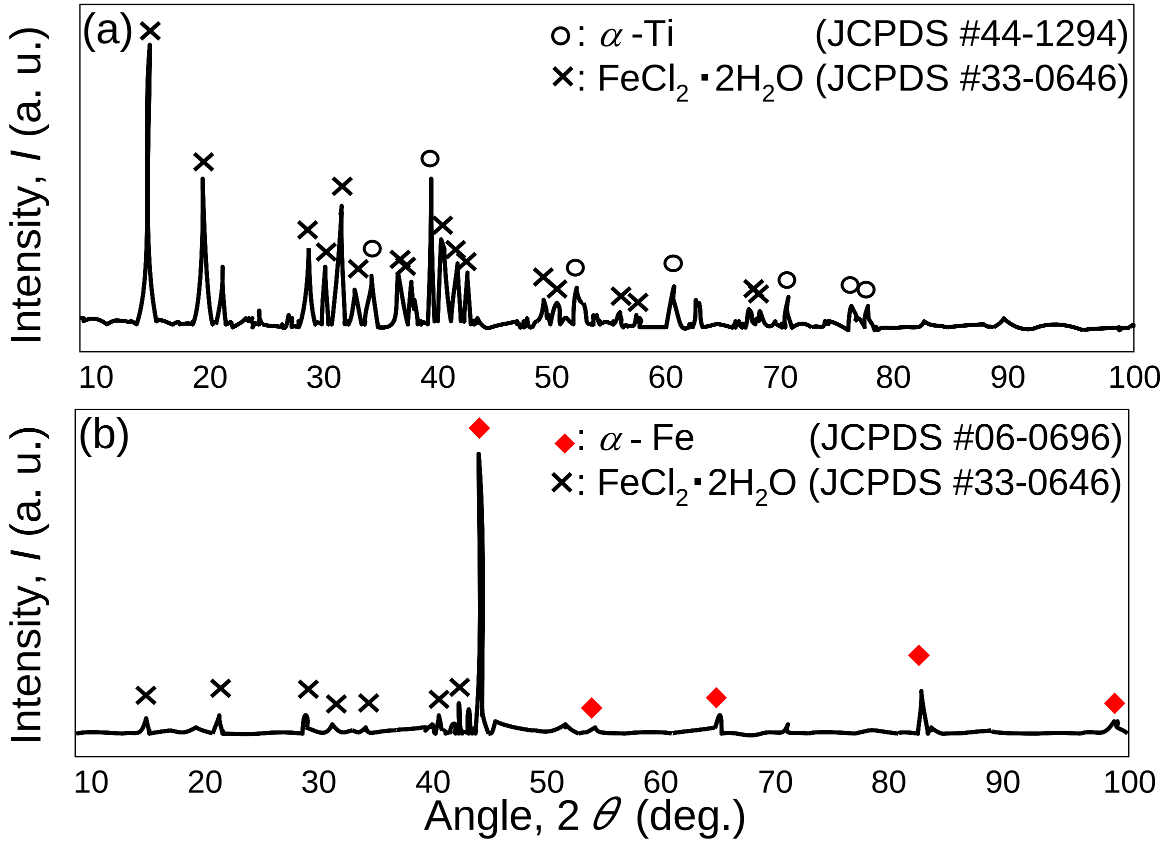
The value excludes carbon and gasous elements except Cl.
a: Calculated.
b: Determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES).
c: Determined by X-ray fluorescence analysis (XRF).
d: Determined by potentiometric titration method.

C_{Ti}: 15.7% → 8.95%.
C_{Fe}: 37.2% → 91.1%.
$TiCl_x$ ($TiCl_4$) obtained.
The silicone plug was damaged due to the reaction with $TiCl_4$.

Ti powder without NaOH gas trap: XRD

Before experiment

After experiment



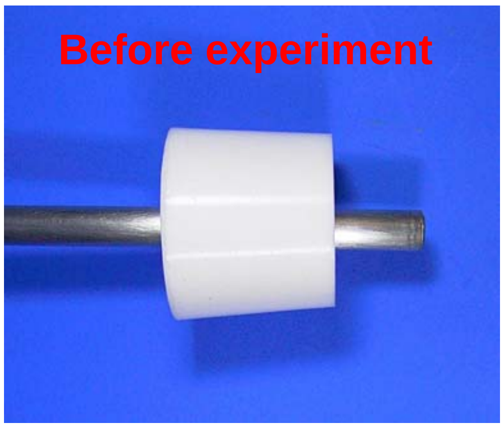
XRD patterns of the sample before experiment (a) and the residue after experiment (b) (Exp. CC)

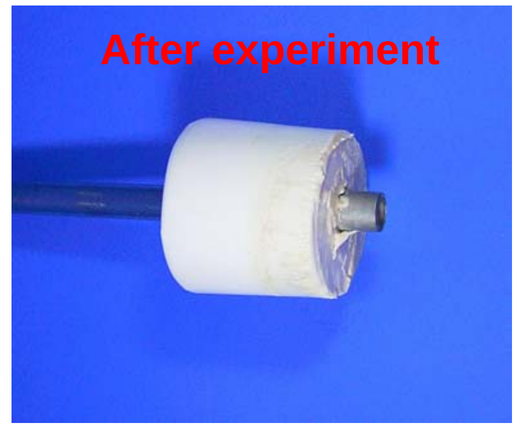
Fe was generated at heating zone.

$$\textbf{Ti}\ (s) + \textbf{FeCl}_2\ (l, g) \rightarrow \textbf{TiCl}_4\ (g)\uparrow + \textbf{Fe}\ (s)$$

Discussion

Ti in Ti scraps was recovered by $FeCl_2$ as the form of $TiCl_4$, but the silicone plug was damaged due to the reaction with the $TiCl_4$.





NaOH was introduced as a gas trap for recovering $TiCl_4$.

Ti powder: Composition

Analytical results of the samples before and after heating, and the deposits obtained on the surface of the NaOH gas trap and inside the quartz tube after heating.

Exp. CB	Concentration of element *i*, C_i (mass%)[a]		
	Ti	Fe	Cl
Initial sample before heating	14.6[a]	37.5[a]	47.8[a]
Residue in the graphite crucible	4.90[b]	95.1[b]	-
Deposit inside the quartz tube	2.71[c]	54.6[c]	42.7[c]
Deposit on the surface of the NaOH gas trap	(16.7[b])	(0.85[b])	(87.9[d])

The value excludes carbon and gasous elements (except Cl).
a: Calculated.
b: Determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES).
c: Determined by X-ray fluorescence analysis (XRF).
d: Determined by potentiometric titration method.

C_{Ti}: 14.6% → 4.90%.
C_{Fe}: 37.5% → 95.1%.
There was no damage on the silicone plug.
→ The obtained $TiCl_4$ was recovered by NaOH successfully.

Ti granule and turning: Composition

Exp. CD (Feed mateirial: **Ti granule**)	Concentration of element i, C_i (mass%)		
	Ti	Fe	Cl
Initial sample before heating	15.1[a]	37.4[a]	47.5[a]
Residue in the graphite crucible	62.8[b]	37.2[b]	-
Deposit inside the quartz tube	0.10[b]	49.7[b]	50.2[c]
Deposit on the surface of NaOH gas trap	0.15[b]	0.38[b]	99.5[c]

Exp. CF (Feed material: **Ti turning**)	Concentration of element i, C_i (mass%)[a]		
	Ti	Fe	Cl
Initial sample before heating	13.6[a]	38.1[a]	48.3[a]
Residue in the graphite crucible	29.1[d]	64.7[d]	6.18[d]
Deposit inside the quartz tube	0.06[d]	50.3[d]	49.6[d]
Deposit on the surface of the NaOH gas trap	(0.04[d])	(1.29[d])	(98.7[d])

The value excludes carbon and gasous elements (except Cl).
a: Calculated.
b: Determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES).
c: Determined by the potentiometric titration method.
d: Determined by X-ray fluorescence analysis (XRF).

Black coat was formed on the surface of the residue.
The residue was magnetic material.

Fe element presents in the residue after heating.

Mass balance

Exp. #	Form of Ti scraps	Mass of feed materials, w_i / g		Mass of the obtained sample, w / g	Concentration of Ti (mass%)	Recovery Ratio of Ti, R (%)
		Ti scraps	$FeCl_2$ (Powder)			
CA[b]	Powder	0.33	1.90	0.56	1.89	97
CB[b]	Powder	0.30	1.75	0.72	4.90	88
CC[b]	Powder	0.32	1.72	0.66	8.95	82
CD[c]	Granule	0.49	2.76	0.73	62.8	6.8
CE[c]	Granule	0.51	2.86	0.62	45.3	45
CF[d]	Turning	0.50	3.17	0.62	29.1	64

a: Experiment date.
b: Ti powder was used in this experiment.
c: Ti granules was used in this experiment.
d: Ti turing was used in this experiment.

When Ti powder was used as the feed material, recovery ratio of Ti was obviously higher than those when Ti granule or turning was used.

↓

The reaction speed was affected by the morphology of the Ti scraps.

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Summary

1. Ti in Ti scraps was extracted by chloride wastes as the form of $TiCl_4$.

2. Fe was generated at heating zone.

3. The obtained experimental results are in good agreement with the thermodynamic analysis:

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

4. The recovery ratio of Ti and Cl as well as the reaction speed were largely dependent on the morphology of the Ti scraps: Ti scraps in the form of powder is easier to be recycled by $FeCl_2$ than Ti granule or Ti turning.